Manual on Water

C. E. Hamilton, editor

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MANUAL ON WATER

(Fourth Edition)

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Foreword

ASTM Committee D-19 on Water had long believed that something more than standard methods of testing are needed by those who look to the Society for aid and technical guidance. It was felt that general discussions of the nature and uses of water should illuminate these prescribed procedures and specifications. Hence, the *ASTM Manual on Water*.

Preparation of the first edition of the manual was begun in 1946. The first manual task group consisted of R. C. Adams, chairman and editor, A. A. Berk, T. H. Daugherty, O. M. Elliot, J. A. Holmes,[1] C. E. Imhoff,[1] A. K. Light, F. U. Neat,[1] F. R. Owens, and A. H. Reynolds.[1] Each member drafted an assigned portion of the manual with the assistance from his associates and other members of Committee D-19. These drafts were modified, critiqued, correlated, and assembled by the entire task group so that the resulting manual was a group product rather than a compilation of individual authorships. Many persons not in the task group also contributed to the first edition. Particular acknowledgment should be made for the individual contributions of Max Hecht,[1] L. K. Herndon, E. O. Patridge,[1] and C. K. Rice.

The second edition task group consisted of R. D. Hoak,[1] chairman and editor, F. N. Alquist,[1] R. A. Baker, G. D. Beal, F. E. Clarke, E. F. Davidson, B. W. Dickerson, D. K. French,[1] A. S. Goldin, J. E. Kinney, W. W. Leathen, S. K. Love, W. A. Moore, F. R. Owens, J. K. Rice, C. C. Ruchhoft,[1] R. K. Scott,[1] J. M. Seamon, J. B. Smith, F. N. Speller,[1] and R. F. Weston. Substantial contributions were also made by C. K. Rice, D-19 Standards Advisor.

The third edition task group consisted of J. F. Wilkes, chairman and editor, R. A. Baker, F. E. Clarke, E. F. Davidson, R. D. Hoak,[1] C. E. Imhoff,[1] R. S. Ingols, J. K. Jacobsen, Pratt Johnson, Bernd Kahn, F. N. Kemmer, R. A. Larrick, S. K. Love, J. A. Martucci, W. L. Neiland, E. P. Partridge,[1] J. H. Phillips, E. A. Savelli, J. S. Speer, and S. L. Williams. Again, many of those named had worked on the previous edition. Preparation of the manual was a collaborative effort, involving the entire group plus many other D-19 members not assigned to the group. The major decision to remove the standard methods of analysis of water from the manual was made. These methods and specifications are published annually as the *Annual Book of ASTM Standards*, Part 31. Each year all newly accepted methods and revised methods are incorporated into the reissued book.

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[1] Deceased.

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Contents

Introduction

This manual is intended as brief reference source of information on water. It will not replace an adequate library on the subject, but it does provide basic information for routine use and cites references to the technical literature, thus serving as a point of departure for more specific and detailed studies.

For executives and administrators, it offers information on the influence of water on industries in which it is used as a raw material or in conjunction with manufacturing operations. The influence of water on various industries ranges from that in the paper industry, where large volumes of water of good quality are used, to industries where only incidental quantities and qualities of water are needed. The manual should serve as a guide to the nature of water planning required at the executive and investment levels of management. At no level, however, can the quantity and quality of available water be disregarded as it relates to the requirements of each process or manufacturing operation for today and for the foreseeable future.

Operations personnel will find the manual to be a guide to the significance of the treatment being applied. Combined with the general discussion of the problems arising from water use are the specific details of control procedures and instructions for such critical operations as sampling water under the various conditions and in the several forms in which it is used. The manual may be useful as a text for plant operator training and for the indoctrination of technologists from other fields. Chemists and other technologists who have special knowledge of water can use the manual as a reference for specific information not published elsewhere.

The manual may be useful as a text or reference resource in technical schools, universities, and continuing education short courses or seminars. While this was not the prime purpose for its preparation, the material presented should be suitable for classroom use. Despite the extensive use that can be made of the manual, it should not be expected to replace competent and well-trained technologists. It will present general information to some and detailed information to others, but the design and efficient application of the treatments and techniques discussed require experience that no books can supply.

This edition of the manual represents a substantial expansion of the previous editions. It has been developed to satisfy the growing need for dependable information about the characteristics of water and the problems its use and reuse entail. New chapters have been added to highlight problem areas and to suggest new approaches for their identification and solution.

The five new chapters are: Production and Preservation of Ultrapure Water, Chapter 3, which discusses this problem area and the need for the definition of solutions thereof; Chapter 15, Sediments in Streams and Other Water Bodies, describes the state of the art in this newly developing field; Nuclear Water Technology, Chapter 17, pulls together information and experience in this relatively new water field; and Chapter 18 deals with practices for the measurement of radioactivity.

Water Quality Monitoring, Chapter 10, while not all new material, has been expanded extensively with the addition of sections on surveillance and sample conditioning. The other thirteen chapters have been updated and revised to a lesser extent over the previous edition. The Appendix has also been revised but still contains much useful information for the water analyst or engineer.

A new task group is now being organized to consider further new material, revisions, and updating of the current edition. If you have comments or suggestions of material which you think would be helpful to you or to other users of the manual, please contact the ASTM D-19 Committee on Water.

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Chapter 1—Water Sources and Supply

Water is one of the most important engineering materials used by industry. Without an adequate supply of water of acceptable quality, virtually no industry can exist. In a very real sense, man's industrial progress can be traced by charting his utilization of the water resources of the earth. Our future industrial progress will depend in large measure on our rational use of water.

A reliable water supply is a basic consideration in the selection of a site for any industrial plant. This chapter will discuss the sources and distribution of water available for industrial use in the United States.

For the purpose of discussion, the total water supply may be subdivided into precipitation, runoff, groundwater, and saline water.

Precipitation—The Basic Source

Precipitation on conterminous United States averages about 76 cm/year (30 in./year). This totals about 1.66×10^{10} m^3/day [4400 U. S. billion gal/day (Bgd)]. Of the 76 cm (30 in.), 55 cm (21½ in.) is evaporated (including evapotranspiration). The remaining 21 cm (8½ in.) is our manageable water supply, about 4.7×10^9 m^3/day (1250 Bgd). Of this 21 cm (8½ in.) we used in 1960 a little less than 5 cm (2 in.), of which about 1.25 cm (½ in.) eventually evaporated. The remainder (3.75 cm) (1½ in.) joined the unused flow to make a total of 20 cm (8 in.) that flowed into the oceans, about 4.4×10^9 m^3/day (1165 Bgd).

The distribution of rainfall is very uneven. In the humid East it ranges from about 76 to 152 cm (30 to 60 in./year) and in the semiarid West from about 25 to 50 cm (10 to 20 in.). Extremes range from 380 cm (150 in.) or more in the Olympic Peninsula in Washington to less than 2.7 cm (5 in.) in Death Valley, California. If we include the State of Hawaii we find the maximum reported rainfall is over 1143 cm/year (450 in./year) on the island of Kauai.

Runoff—Source of Surface Supplies

As would be expected from the wide variability in precipitation, the 4.4×10^9 m^3/day (1165 Bgd) runoff also is distributed unevenly. For example, in the North Atlantic Slope area, runoff averages about 5.1×10^2 m^3/day (136 Bgd); in the Mississippi River basin the average is about 1.5×10^9 m^3/day (400 Bgd); in the Colorado River basin it is about 5.7×10^7 m^3day (15 Bgd); and in the Columbia River basin, about 8.4×10^8 m^3/day (223 Bgd).

In 1960 the national average runoff was equivalent to about 25 000 litres per capita per day (lcd) (6500 gal per capita per day) (gcd). Based on population growth projections, this figure would be about 18 000 lcd (4800 gcd) in 1980 and 13 000 lcd (3500 gcd) in the year 2000. If the total runoff to the oceans could be apportioned equally to each person, there would be enough water from this source on a national basis for the foreseeable future. But based on actual current and anticipated future distribution of population and available water resources, the per capita figure may range from as little as 11 000 litres/day (3000 gal/day) (gpd) to as much as 110 000 litres/day (30 000 gpd).

Groundwater—Invisible Source

In the discussion on runoff, the figures given for runoff to the oceans include groundwater. The water falling as precipitation to the ground follows three courses. Some runs off directly to streams and rivers, some infiltrates to the ground water reservoirs, and the rest evaporates or transpires through vegetation.

The water in the ground may be thought of as a temporary natural reservoir. It is invisible and consequently to many people is shrouded in mystery. Nearly all groundwater is in constant though slow motion toward streams or other surface water bodies. In fact, in dry periods streams maintain their flow because of groundwater discharge. Thus the water discharging through streams to the oceans includes most of the runoff from the groundwater reservoir. The remainder discharges by underground routes.

Groundwater reservoirs store far more water than is or conceivably could be stored in surface reservoirs. The available and accessible supply of groundwater in the United States is estimated to be in excess of 2.2×10^{14} m^3 (59 000 000 billion gallons) [*1*].[1] However, when large quantities are being sought it usually is more difficult and expensive to locate, to study and evaluate, to develop, and to manage groundwater than surface water. Furthermore, the management of groundwater is complicated by deficiencies and incorrect concepts of groundwater hydrology and by much of existing water law. Development of groundwater as a phase of coordinated multiple-purpose water management can be achieved on a large scale only if adequate hydrologic information is available [*2*].

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

Saline Water—Prospective Future Source

Natural saline water (usually seawater or mixtures of seawater and freshwater) is used by industry only where adequate supplies of freshwater are unavailable. Nearly all industrial use of saline water is for cooling at or near the seacoast. The quantity of seawater is unlimited. Converted saline water may become an important new source of freshwater when and where the cost of conversion including conveyance to the point of use becomes competitive with sources of freshwater. Desalination of brackish water in arid regions also is practiced.

Beginning in 1952 the Federal Government began a program of research in converting saline water into freshwater. This effort has resulted in the construction of five demonstration plants. The location, process of conversion, and capacity of these plants are given in Table 1.

TABLE 1 *Saline water demonstration plants.*

Location	Source of Water	Conversion Process	Plant Capacity, gpd[b]
Freeport. Tex.	Gulf of Mexico	multiple-effect distillation. falling film	1 000 000
San Diego. Calif.[a]	Pacific Ocean	multistage distillation. flash	1 000 000
Webster. S. Dak.	wells	electrodialysis (membrane process)	250 000
Roswell. N. Mex.	wells	distillation. vapor compression	1 000 000
Wrightsville Beach. N.C.	Atlantic Ocean	freezing	250 000

[a] Relocated. 1964. at U. S. Naval Base. Guantánamo Bay. Cuba.

[b] Metric conversion factor: 1 gpd = 0.003784 m^3/day.

The cost of converting saline water has been reduced substantially during the past 20 years. Cost at the conversion plant ranges from about $0.60 to $1.50 per thousand gallons depending on the process used, the salinity of the raw water, the capacity of the plant, and other factors. Distribution cost would have to be added.

In areas where adequate quantities of freshwater are not available, certain kinds of industries and domestic uses probably can justify the cost of converted saline water. Reuse of fresh or converted water will keep cost of industrial water to a minimum.

Water Demands

Demands for water for all purposes are constantly increasing. Estimates of present and future demands will suggest how the available water resources should be utilized.

Water Withdrawals

Many estimates have been made about the quantities of water that are withdrawn from our surface and underground sources for useful purposes. Among those frequently quoted are estimates compiled by the U. S. Senate Select Committee. The total water withdrawn in 1954 for all uses, excluding hydropower, was about 3.4×10^8 m^3 (300 Bgd), which was equivalent to about 6800 lcd (1800 gcd). Of this amount 58 percent was used for irrigation, 36 percent for industry, and 6 percent for public supplies, rural and other purposes. A projection by the Select Committee [*3*] to the year 2000 anticipates total water use of about 3.1×10^9 m^3 (900 Bgd), of which over 70 percent will be used by industry. However, only about one fifth of the water withdrawn would be consumed and most of this by agriculture.

In another estimate [*4*] the total water withdrawn in 1960 was 1.0×10^9 m^3 (270 Bgd), of which 51 percent was for industry, 40 percent for irrigation, 6 percent for public supplies, and 1 percent for rural use.

From 90 to 95 percent of industrial water is used for cooling. After cooling is accomplished, the water is returned to the water system for reuse. The heat removed in cooling processes is transferred from the industrial equipment to the water as it reenters the hydrologic system. The higher temperature tends to upset the delicate balance established by living plants and animals indigenous to the receiving streams. The heated water also reduces oxygen solubility and increases the biochemical oxygen demand, thus producing an oxygen sag in the streams. In extreme cases, other pronounced and complex quality changes will occur as a result of the temperature change. As larger quantities of water are employed for cooling, some of the other uses of water will be affected to some degree.

Consumptive Use

Consumptive use of water has been defined as ". . . the quantity of water discharged to the atmosphere (evaporated) or incorporated in the products of the process in connection with vegetative growth, food processing, or incidental to an industrial process" [*5*].

Industry consumes only about 2 percent of the water it uses. This is divided principally between water evaporated and water incorporated in products of manufacturing. The heaviest consumption is in connection with irrigation, where 60 percent or more of the water withdrawn is lost to the water system through evaporation and transpiration. About 17 percent of water used for public supplies is consumed.

Storage

Water is stored in reservoirs to control floods, develop power, provide water supplies for municipalities, industries, and irrigation, dilute wastes, stimulate recreation, and for other beneficial uses. In 1954 [*6*] a total of

3.4×10^{11} m^3 (278 000 000 acre-ft) (91 000 billion U. S. gal) was stored in conterminous United States having usable capacities of 6.2×10^6 m^3 (5000 acre-ft) (1.6 billion U. S. gal) or more.

The distribution of these storage capacities by states is given in Table 2.

TABLE 2—*Summary of reservoirs showing usable storage.*

	Usable Storage	
State	Acre-Feet[a]	U. S. Billion Gallons[b]
Alabama	2 522 900	822
Arizona	33 246 800	10 834
Arkansas	9 561 800	3 116
California	17 700 900	5 768
Colorado	3 826 700	1 247
Connecticut	413 500	135
Delaware	6 800	2.2
Florida	2 752 300	897
Georgia	4 792 300	1 562
Idaho	9 530 100	3 105
Illinois	203 700	66.4
Indiana	236 000	76.9
Iowa	458 000	149
Kansas	4 008 700	1 306
Kentucky	8 451 000	2 754
Louisiana	1 307 600	426
Maine	5 180 500	1 688
Maryland	472 600	154
Massachusetts	1 791 200	584
Michigan	521 900	170
Minnesota	3 822 500	1 246
Mississippi	3 825 900	1 247
Missouri	5 744 500	1 872
Montana	23 888 100	7 784
Nebraska	3 842 400	1 252
Nevada	673 300	219
New Hampshire	1 069 900	348
New Jersey	216 100	70.4
New Mexico	3 530 700	1 150
New York	4 383 600	1 428
North Carolina	3 112 600	1 014
North Dakota	18 786 100	6 121
Ohio	3 089 200	1 007
Oklahoma	10 248 400	3 339
Oregon	3 747 000	1 221
Pennsylvania	1 739 500	567
Rhode Island	117 700	38.4

(*Continued*)

TABLE 2—*Continued.*

State	Usable Storage Acre-Feet [a]	U. S. Billion Gallons [b]
South Carolina	3 759 800	1 225
South Dakota	22 476 600	7 324
Tennessee	10 053 700	3 276
Texas	18 852 900	6 143
Utah	2 053 200	669
Vermont	351 700	115
Virginia	2 440 800	795
Washington	11 364 600	3 703
West Virginia	932 800	304
Wisconsin	2 156 500	703
Wyoming	4 855 800	1 582
Total	278 121 200	90 626

[a] Metric conversion factor: 1 acre-foot = 1233.49 m^3.
[b] Metric conversion factor: 1 gal (U. S.) = 0.003785412 m^3.

Reusable Supplies

Most of the water withdrawn is not consumed but is returned to a downstream or underground source. Thus the total supply is depleted by only a portion of the entire amount withdrawn. For this reason the water returned augments the original supply and is available for reuse. Were it not for reuse, some areas would have run out of water. It must be kept in mind, however, that each use of water (except for generation of hydropower) will degrade its quality to some extent. Impoundment of water for hydropower or other uses can cause significant changes in water quality.

Quality Considerations in Industrial Supplies

Water is relatively pure when formed in clouds, but it absorbs gases from the air, mainly oxygen, carbon dioxide, SO_2 and NO_x, during its fall as rain or snow. Upon reaching the earth, water dissolves materials with which it comes in contact. The amount of dissolution depends upon the solubility of the soil or rocks in the area and the length of time that the water and the earth-environment are in contact. Water also becomes polluted with industrial, municipal, and agricultural wastes.

General Quality Factors

Both the total concentration of dissolved solids and the concentration of the more important constituents determine the suitability of water for specific industrial applications. Hardness also is an important factor.

Surface waters in general are softer and less concentrated than groundwaters. However, hardness and dissolved solids in surface waters vary considerably over the period of a year and in many streams from day to day. Surface waters are frequently turbid, some excessively so, and with few exceptions must be filtered before use for public supplies or by industry.

In a given stream, hardness and concentration of dissolved solids generally vary inversely with the volume of water discharged. This is because the proportion of groundwater, which usually is more concentrated than surface water, is much smaller during high water than during low water periods. During periods of low flow, groundwater discharge to a stream channel may account for the total water in a stream.

The average concentration of dissolved solids in major rivers of the nation ranges from about 60 to 700 mg/litre (ppm). The lower concentrations are found in streams in the Atlantic and eastern Gulf Coasts, in the Pacific Northwest, and in the Great Lakes. Higher concentrations are found in the western Gulf, Midcontinent, and Southwestern streams.

Groundwaters are characterized by essentially constant composition and temperature and ordinarily can be used without filtration. They normally are harder and contain more dissolved minerals than surface waters and thus are less desirable for certain industrial purposes.

The varying quality characteristics of surface and groundwaters are illustrated by the analyses given in Table 3. These analyses represent the raw water used for public supplies of eight of the larger cities in the United States. Analyses 1 through 4 are for surface waters and 5 through 8 are for groundwaters. A more extensive tabulation is given in the Appendix.

Hardness

Because of the importance of the hardness characteristic of industrial waters, this topic will be discussed in greater detail. For many industries, the hardness of the intake water is the principal basis for classifying water. Hardness is defined in accordance with the ASTM Definitions of Terms Relating to Industrial Water and Industrial Waste Water (D 1129) [7], as a characteristic of water generally accepted as representing the total concentration of calcium and magnesium. Although other constituents, such as iron, manganese, and other polyvalent cations cause hardness, they usually are present in such small concentrations that they do not materially affect the hardness of industrial water. Only calcium and magnesium are included in the term hardness as used in this discussion.

Hardness may be divided into two types, carbonate and noncarbonate. Carbonate hardness includes that portion of the hardness which is equivalent to the carbonate and bicarbonate present in the water. Any hardness in excess of this amount is called noncarbonate. Carbonate hardness generally is not objectionable in industrial use of water. Where it is excessive, however, it can be reduced or removed rather simply and inexpensively. Noncar-

TABLE 3—*Analyses of typical surface and groundwaters in the United States.* [*From* U. S. Geological Survey Water Supply Paper 1812 (*milligrams per litre*).]

Analysis number[a] Date of collection	1 8/22/61	2 9/1/61	3 10/19/61	4 1961	5 8/9/61	6 9/15/61	7 8/23/61	8 7/25/61
Silica (SiO_2)	5.9	2.1	5.5	8.7	25	8.3	9.1	21
Iron (Fe)	0.00	0.17	0.40	. . .	0.03	0.72	0.10	0.01
Manganese (Mn)	0.00	0.14	0.00	. . .	. . .	0.01	0.06	0.00
Calcium (Ca)	8.5	28	37	84	65	12	57	26
Magnesium (Mg)	2.6	7.0	8.9	28	23	6.1	32	6.2
Sodium (Na)	3.6	4.1	17	92	14	7.5	3.4	86
Potassium (K)	1.5	0.9	5.1	4.0	1.8	0.7	1.7	1.9
Bicarbonate (HCO_3)	25	92	128	140	179	78	332	254
Carbonate (CO_3)	0	0	0	1	0	0	0	0
Sulfate (SO_4)	9.0	18	48	285	112	3.8	12	11
Chloride (Cl)	5.5	8.0	10	83	18	3.0	3.5	40
Fluoride (F)	0.1	0.0	0.4	0.4	0.8	0.4	0.1	0.7
Nitrate (NO_3)	4.7	0.5	3.2	1.4	0.2	1.2	0.2	0.0
Dissolved solids	59	129	222	657	410	87	284	318
Hardness as $CaCO_3$	32	99	129	323	256	55	274	90
Noncarbonate hardness as $CaCO_3$	11	24	24	206	110	0	2	0
Specific conductance (micromhos at 25°C)	91	213	324	1040	535	137	498	533
pH	6.4	7.6	7.7	8.4	7.9	6.8	7.6	7.2
Color	5	3	5	. . .	5	5	1	0

[a] Analyses numbers are identified as follows:

1. Baltimore, Md., North Branch Patapsco River (raw).
2. Detroit, Mich., Detroit River (raw).
3. St. Louis, Mo., Mississippi River (raw).
4. Los Angeles, Calif., Colorado River (raw).
5. Jacksonville, Fla., Composite of several wells (raw).
6. Memphis, Tenn., Allen Well Field. Composite of several wells 122 to 183 m (400 to 600 ft) deep (raw).
7. Rockford, Ill., Well No. 15, 413 m (1355 ft) deep (raw).
8. Houston, Tex., Southwest Well Field. Composite of 12 wells 149 to 610 m (490 to 2000 ft) deep (raw).

bonate hardness, on the other hand, especially where sulfate is the predominant anion, may result in formation of hard, adherent scale in boilers and other heat-exchange equipment. This type of hardness is more difficult and more costly to remove.

Any descriptive or numerical classification of hardness of water is arbitrary. A water that is termed hard in some areas may be considered soft in other areas. The U. S. Geological Survey uses the following classification:

Range of Hardness mg/litre (ppm)	Descriptive Classification
1 to 60	soft
61 to 120	moderately hard
121 to 180	hard
Above 180	very hard

Figure 1 shows the hardness in the foregoing ranges for the finished public supplies of the 100 largest cities in the United States in 1962. The numbers in the map identify the cities listed in Table 4. The tables also gives, in figures, the approximate average hardness in these cities.

Other Quality Parameters

Other quality parameters also have a bearing on the suitability of water for particular uses.

Silica in water ranges in concentrations from less than 1 to over 75

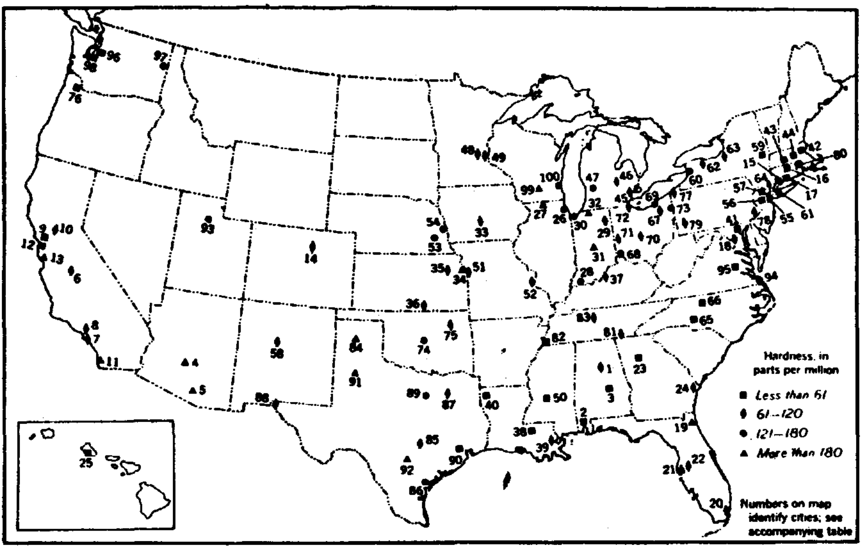

FIG. 1—*Hardness of treated public water supplies of the 100 largest cities in the United States, 1962 (average weighted by population served).*

TABLE 4—*Hardness of finished water supplies of 100 largest cities in the United States, 1962.* [*From* U. S. Geological Survey Water-Supply Paper 1812 (*hardness in milligrams per litre of calcium carbonate*).]

State	Number on map (Fig. 1)	City	Average Hardness
Alabama	1	Birmingham	88
	2	Mobile	35
	3	Montgomery	42
Arizona	4	Phoenix	250
	5	Tucson	185
California	6	Fresno	82
	7	Long Beach	110
	8	Los Angeles	110
	9	Oakland	58
	10	Sacramento	65
	11	San Diego	235
	12	San Francisco	35
	13	San José	205
Colorado	14	Denver	78
Connecticut	15	Bridgeport	31
	16	Hartford	28
	17	New Haven	42
District of Columbia	18	Washington	115
Florida	19	Jacksonville	280
	20	Miami	61
	21	St. Petersburg	92
	22	Tampa	115
Georgia	23	Atlanta	23
	24	Savannah	105
Hawaii	25	Honolulu	60
Illinois	26	Chicago	140
	27	Rockford	280
Indiana	28	Evansville	155
	29	Fort Wayne	85
	30	Gary	140
	31	Indianapolis	285
	32	South Bend	350
Iowa	33	Des Moines	95
Kansas	34	Kansas City	250
	35	Topeka	105
	36	Wichita	105
Kentucky	37	Louisville	110

(*Continued*)

TABLE 4—*Continued.*

State	Number on map (Fig. 1)	City	Average Hardness
Louisiana	38	Baton Rouge	5
	39	New Orleans	91
	40	Shreveport	60
Maryland	41	Baltimore	55
Massachusetts	42	Boston	13
	43	Springfield	12
	44	Worcester	15
Michigan	45	Detroit	100
	46	Flint	85
	47	Grand Rapids	140
Minnesota	48	Minneapolis	65
	49	St. Paul	90
Mississippi	50	Jackson	50
Missouri	51	Kansas City	85
	52	St. Louis	105
Nebraska	53	Lincoln	180
	54	Omaha	150
New Jersey	55	Jersey City	40
	56	Newark	35
	57	Paterson	55
New Mexico	58	Albuquerque	99
New York	59	Albany	52
	60	Buffalo	135
	61	New York City	36
	62	Rochester	86
	63	Syracuse	110
	64	Yonkers	78
North Carolina	65	Charlotte	24
	66	Greensboro	47
Ohio	67	Akron	130
	68	Cincinnati	160
	69	Cleveland	125
	70	Columbus	100
	71	Dayton	105
	72	Toledo	70
	73	Youngstown	85
Oklahoma	74	Oklahoma City	130
	75	Tulsa	93
Oregon	76	Portland	7

(*Continued*)

TABLE 4—*Continued.*

State	Number on map (Fig. 1)	City	Average Hardness
Pennsylvania	77	Erie	120
	78	Philadelphia	105
	79	Pittsburgh	110
Rhode Island	80	Providence	28
Tennessee	81	Chattanooga	87
	82	Memphis	40
	83	Nashville	92
Texas	84	Amarillo	215
	85	Austin	88
	86	Corpus Christi	135
	87	Dallas	90
	88	El Paso	97
	89	Fort Worth	145
	90	Houston	60
	91	Lubbock	310
	92	San Antonio	230
Utah	93	Salt Lake City	180
Virginia	94	Norfolk	77
	95	Richmond	60
Washington	96	Seattle	20
	97	Spokane	150
	98	Tacoma	15
Wisconsin	99	Madison	290
	100	Milwaukee	130

mg/litre and averages from 5 to 15 mg/litre. Under certain conditions, silica forms hard scale in boilers and on turbine blades.

Iron, manganese, and aluminum in surface waters usually range from 0.01 to 0.5 mg/litre. Organic matter can form complexes with these metals, thus permitting higher concentrations to occur. These metals frequently are present in groundwater in substantially higher concentrations than in surface water. Values from one to several milligrams per litre (parts per million) in groundwater are not uncommon. Iron and manganese are especially objectionable in many industrial processes primarily because they impart undesirable colors and stains to manufactured products.

Other minor elements occur in small concentrations commonly in the micrograms per litre (parts per billion) (parts per 1000 million) range.

Sodium and potassium are not important industrially in low concentrations. The sodium content of water varies over a wide range from below 5 mg/litre in freshwater to many thousands of milligrams per litre (parts per million) in brines. Seawater contains about 10 700 mg/litre of sodium.

Potassium is ordinarily present in freshwater in low concentrations, seldom in excess of 10 mg/litre.

Alkalinity in water supplies usually represents the bicarbonate ion, HCO_3^-, although it also includes carbonate, CO_3^{--}, and in water receiving certain alkali wastes, hydroxide, OH^-. Alkalinity customarily is expressed as calcium carbonate, $CaCO_3$. Practically all natural waters have alkalinity unless neutralized by acid from industrial effluents or from mine drainage. The alkalinity is related to the buffer capacity of the water, that is, the capacity of the water to receive acid without substantially lowering the pH. It also is troublesome in certain industrial processes.

Sulfate concentrations range widely in natural waters. Sulfate may be derived from leaching of gypsum, anhydrite, and shale deposits, or from oxidation of sulfides. Waters in arid or semiarid regions, such as Southwestern United States, may contain relatively large quantities of sulfate. Sulfate, when combined with calcium, forms troublesome scale in industrial heat exchangers and is difficult to remove.

Chloride is found in all natural waters, and occurs over a wide range of concentrations. Streams along the Atlantic Coast, eastern Gulf Coast, and in the Pacific Northwest normally contain less than 25 mg/litre of chloride, except in tidal reaches or where polluted. Streams in arid or semiarid regions may contain several hundred milligrams per litre of chloride. Seawater contains about 19 000 mg/litre of chloride, and other brines may contain much higher concentrations.

Chloride in concentrations less than 50 mg/litre has no detrimental effects on most industrial uses, and water supplies with higher concentrations are used rather widely. High-chloride waters promote corrosion of metal surfaces.

Dissolved gases, including carbon dioxide (CO_2), oxygen (O_2), hydrogen sulfide (H_2S), or ammonia (NH_3), frequently are important, depending on the final use of the water. While some of these gases may be combined as ions, they are usually considered as dissolved gases because they may be separated as gases by heat or agitation, and they leave no residue on evaporation. Gases must be removed from water for certain industrial uses, especially where steam is generated in boilers.

Carbon dioxide is a respiration product of aquatic plants and animals and is one of the by-products of aerobic and anaerobic decomposition of organic matter. Acids from natural sources or pollution liberate carbon dioxide from bicarbonate. Most of the carbon dioxide in water is derived from these sources. Air contains only about 0.04 percent carbon dioxide, and the concentration in water in equilibrium with air will approach 0.7 mg/litre. Streams normally contain low concentrations of carbon dioxide, but some groundwaters contain 20 mg/litre or more in their natural environment.

Dissolved oxygen ranges between about 3 and 12 mg/litre in surface waters and there is little or none in most groundwaters. Polluted surface waters may contain less than 3 mg/litre, even zero in extreme situations.

Hydrogen sulfide may range from 0.0 to several mg/litre in groundwaters but usually does not exceed 1 or 2 mg/litre. It is seldom found in surface waters unless they are polluted. As little as 0.1 mg/litre in water causes perceptible odor.

Ammonia ranges between 0.0 and about 4 mg/litre and occurs naturally in both surface and groundwaters. Ammonia also results from the presence of sewage or industrial wastes.

Hydrogen ion concentration, or pH (which is a measure of the hydrogen ion activity), is related to the acidity or alkalinity of a water. The pH of most surface waters ranges between 6 and 8. Waters containing free mineral acids from mine drainage or other industrial wastes may have pH values below 4, depending on the buffering capacity of the receiving water. Some groundwaters have pH values above 8 and some below 5, but most are in the 6 to 8 range. The pH values of waters have a very definite bearing on the utility of supplies for many industrial purposes.

Turbidity is a characteristic of most surface waters. It is caused by particulate matter in suspension and results from erosion of land surfaces. Turbidity may also result from inadequately stabilized or filtered treated water. Groundwaters usually are not turbid. However, some groundwaters that are chemically unstable may develop turbidity on exposure to the atmosphere.

Color usually results from the presence of organic matter; it may come from decayed vegetation or from municipal or industrial wastes.

Microorganisms are present in nearly all surface waters, and they are commonly a problem. They may be classified as bacteria, fungi, and algae. They are part of natural life processes of the hydrologic, geologic, and ecologic environments. Microorganisms also are influenced by man-made activities and may increase or decrease in population in response to waste materials discharged into the streams.

Other properties of importance to industry are taste, corrosiveness, and radioactivity. All of these quality parameters and their effects on industrial processes will be discussed at greater length in succeeding chapters.

Summary

The country is not likely to run out of water in the foreseeable future. The total water supply is essentially the same now as in the past and will be in the future. The distribution of water, however is highly variable as to time and place. In addition, the needs for water on a countrywide basis cannot be correlated with its availability.

Industrial water requirements must be carefully assessed in terms of the quantity and quality of water that can be obtained at the plant site. If the available supply is not of suitable quality, the cost of conditioning must be weighed against the costs of making available other water sources or other plant locations.

Reuse of water is being practiced widely in industry. The practice will undoubtedly increase as industry uses an increasingly large share of the available supply.

Converted brackish and saline water is an additional source of water. Although the cost of desalted water is greater than that of available freshwater, increasing demands in water-short areas may justify its use.

Industry is expected to make maximum efficient use of the available sources of water supply and to return the used water to the hydrologic system with as little impairment in quality as possible.

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Chapter 2—Uses of Industrial Water

Since earliest times, men have settled along the shores of rivers and lakes to avail themselves of freshwater for their homes and industries. The American colonists built their mills along streams which could furnish power and supply the quality of water necessary for the manufacture of such goods as textiles and paper.

In modern times, public awareness of the importance of water is mounting as headlines warn of a growing problem of water quality and availability. The expanding industry must carefully examine the limitations which water may impose on it: How much raw water will be available ten years hence? Can a portion of the plant's usage be reduced by recycle? What quality water might be required by new uses? How can this quality be achieved economically while impurity levels in the raw water supply continue to rise? What degree of waste treatment is required to preserve the stream water quality?

To help bring these problems into perspective, this chapter on the uses of industrial water outlines general principles and practices rather than specific details of water usage by individual industries.

There are few, if any, significant uses of water which are peculiar to a single industry. The major uses—steam generation, cooling, and processing—are common to all industries. Of the various categories of process uses of water, such as conveying and washing, many appear in a variety of plants unrelated in any other way.

These general principles and practices are presented to orient the engineer toward good water management in his own industry. The examples illustrating water use in several specific plants were selected for their universal appeal. In them, engineers in all branches of industry will find practices related to their own operations.

Some Thermodynamic Properties of Water

The polar nature of the water molecule makes water a unique material for the transfer of heat from one system to another. The heat capacity of water is so great that when 0.45 kg (1 lb) of water absorbs 1055J (1 Btu) of heat from a system which it is employed to cool, its temperature rises only 1 deg F. By comparison, if oil or alcohol were used for the same cooling service, the temperature rise would be twice as great or twice the volume would be needed to keep within the same temperature limits. If air were used, almost 3000 volumes of air would be needed to replace a volume of water at the same temperature rise.

Because water molecules tend to "adhere" to one another by the process known as "hydrogen bonding," considerable energy is required to convert water to steam. But once in the form of steam, water vapor can convey large quantities of heat from one system, such as a steam boiler, to another, such as a steam-heated cooking vessel. When the steam gives up its heat to the material in the vessel, each pound liberates about 1023 kJ (970 Btu).

Since this quantity of heat, the heat of vaporization, is associated with a change in state from liquid or vapor, the evaporation of a stream of water sprayed into the air cools the water-jet as it gives up energy to the water vapor escaping into the air. Thus, evaporation can be used either to supply heat, as steam is produced, or to cool water for extraction of heat. A third property of water related to heat transfer is its heat of fusion, about 337 kJ/kg (144 Btu/lb). This is considerably greater than the heat released by solidification of other common liquids, another consequence of the unique structure of the water molecule.

Basic Water Uses

Of the many services which water can perform for our society, those which may be defined basic to industry are heat transfer, power generation, and process uses.

Heat Transfer

Industry capitalizes on the large heat capacities of water for economical heating or cooling of process units.

The most common method of supplying heat to various areas of an industrial complex is by steam generation. The steam is produced from fuel at a central generating station and distributed at relatively high pressure and velocity throughout the plant. Temperature at each unit is easily controlled by regulating flow or pressure.

In addition to the steam generated by direct firing of a boiler with coal, oil, or gas, additional steam may be produced by firing waste products or by recovering heat from a high-temperature process stream. Some typical process heat boilers (sometimes called "waste-heat boilers") are described in Table 1.

Although steam historically has been the major conveyance of industrial heat because of high heat capacity and heat-transfer coefficients, hot water is replacing it in some of the newer plants. This is due to the lower installation

TABLE 1—*Some industrial process heat boilers.*

Type of Plant	Description of Heat Source
Cement lime	hot gases leaving kiln
Sulfuric acid	hot SO_2 from sulfur burners
Ammonia	synthesis gas after exothermic reaction
Sugar	burning bagasse (pressed cane stalks)
Wood pulp	burning bark; burning black liquor
Steel	burning blast furnace gas; hot gases leaving open hearths or basic oxygen furnace
Oil refining	burning CO from cat-cracker; hot catalyst from cat-cracker

cost of modern circulating hot-water systems. However, many factors are involved in the choice between these two systems, a major one being the possibility of on-site generation of power from steam which may then be used a second time at lower pressure for heating.

Circulating water has been used for cooling process equipment for many years. Early industry, with a plentiful supply of water, simply pumped cool water from a nearby stream or lake through the plant and discharged the heated water in any convenient manner. Even today there are areas where this practice is still the most practical means of moving heat. This is particularly suited to coastal locations, with plants designed to withstand the corrosive attack of seawater.

The volume of water which must be withdrawn from a freshwater source for cooling can be tremendously reduced by adding an evaporative cooling tower or pond to the system. For example, if a plant withdraws and uses 1.26 m^3/s (20 000 gal/min) of freshwater, heating this water 6 deg C in cooling its process equipment on a once-through system, a reduction in withdrawal to about 0.015 m^3/s (250 gal/min) freshwater may be practical by recirculation of 1.26 m^3/s (20 000 gal/min) over a cooling tower. This is due to the high heat of vaporization of water, which cools the recirculated water about 6 deg C for each 1 percent evaporated.

The temperature to which the recirculated water can be reduced by this process is limited by the wet-bulb temperature of the air used to induce evaporation. This temperature of recirculated water will usually be higher than that of the fresh makeup source. If further temperature reduction is needed, individual refrigeration may be added to those units in the plant needing the additional cooling.

In the chemical industry, hot hydrocarbon gas streams are often passed through a spray of water which serves the combined purpose of quenching the high-temperature vapor, condensing heavy fractions, and washing unwanted material from the stream.

A method of cooling that is not widespread but sometimes practical is the introduction to ice into a system. This method is used to quench the heat of certain organic chemical reactions.

Power Generation

By far the greatest share of our total power generation comes from steam plants. The public utilities today produce over 9 x 10^{12} kJ/day (2.5 billion kWh/day) of electricity by this route. Most of these plants recover the steam with condensers, so that the water makeup is usually extremely low—less than 1 percent. However, some of these utility plants have been located adjacent to industrial plants to whom they supply both electricity and steam. This steam is often consumed or contaminated, so that such plants may require as much as 50 percent makeup. A typical arrangement of this kind involves a utility station adjoining a refinery. The refinery supplies the utility water from its private source and fuel, and the utility supplies its neighbor electricity and low-pressure steam.

The industrial plant generating steam for power differs from the utility station in the relatively greater extent of water loss, with higher makeup, in the variation and degree of condensate contamination, and in the temperature of the returned condensate.

A major reason for the relatively larger makeup rate in industrial plants is the unfavorable cost of installing piping to return condensate from a large, complex plant. A typical case is the petroleum refinery where some of the steam is sent to the outlying tank farm to heat heavy, viscous oils and keep them pumpable. Not only is it costly to run douple piping to return condensate, but, in this case, recovery is unattractive because of the likelihood of oil contamination. It is certain that the future will bring greater pressure to reclaim a large share of industrial condensate which until now has appeared not worth recovering.

The relatively high temperature of industrial process condensate is due to the steam being condensed at high temperatures. In the utility station, steam is expanded through a turbine to subatmospheric pressure and finally condensed in a condenser by cooling water. The condensate returned to the system is only a few degrees warmer than the discharged cooling water. In the industrial plant, the condenser is the process equipment, and it usually operates at pressures above atmospheric. Therefore, the industrial plant typically returns condensate at 65 to 121°C (150 to 250°F) as compared to 38 to 49°C (100 to 120°F) utility condensate.

The industrial steam plant may use steam to drive machinery, to generate electricity, or both. The paper mill is a good example of this. A typical mill will produce steam at 6205 kPa (900 psi). This may be used through a number of turbines to drive pumps, generators, compressors, paper machines, and auxiliary equipment. Some of the steam will exhaust to an 862-kPa (125-psi) steam line, used to heat the large drier rolls over which the paper passes. Other drier rolls may operate at 413 kPa (60 psi). This steam will also go to cooking the wood chips in a digester to make pulp. Some of the turbines in the power plant may expand the high-pressure steam all the way down to vacuum, as a utility operation, to obtain maximum thermal efficiency. A typical paper mill system is shown in Figure 1.

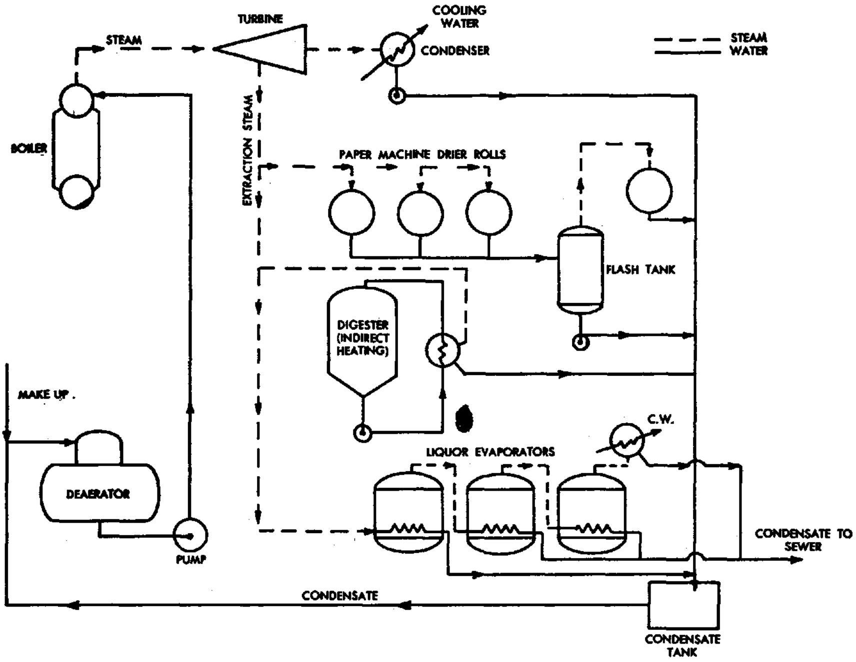

FIG. 1—*Paper mill steam system.*

In some geographical areas, the electrical energy cost may be so low that the industrial plant cannot afford to generate electricity even though the steam is available. Such is the case, for example, with a paper mill in the area served by Tennessee Valley Authority. All turbines discharge steam at 413 kPa (60 psi) or above, none operate with condensers, and only mechanical power is produced from the steam.

Even the tax structure plays an important part in the decision as to the best use to make of steam in an industrial plant. Corporate tax rates tend to favor higher operating costs as against extra capital costs which could lower operating costs. As a result, industry tends to depreciate capital equipment at a more rapid rate than do the utilities. Because of this, industry has not been encouraged to install the higher-pressure (over 8274 kPa) (1200 psi) steam generating plants which utilities are finding so economical to operate.

The generation of mechanical power from water flowing through hydraulic turbines recalls the early days of the industrial revolution and the use of the water wheel to mill grains. A number of industrial plants today continue to use natural hydraulic power for mechanical jobs or for generation of electricity. In some parts of Canada, the excess of hydroelectric power and its low cost is such that at times of the year it is actually cheaper to generate steam in electric boilers than in fuel-fired boilers.

In addition to making use of natural hydraulic power, industry also uses artificially generated hydraulic power for special applications. The most common of these involves high-pressure water-jets used to focus a high concentration of kinetic energy on a small area. Steel mills blast mill scale from steel sheet in this manner. Lumber mills strip the bark from gigantic redwood logs rotating on a lathe with water jetting from a nozzle at 17 237 kPa (2500 psi). The mining industry has employed jets for many years to fragment ore lodes and separate the desirable minerals from the surrounding burden of soil.

Role of Water in Industrial Processes

In process applications, water has valuable duties to perform in conveying other materials, in various washing procedures, as a raw material itself, and in numerous other uses which may be peculiar to only one industry or even to a single plant.

Conveying—Just as our watercourses convey a natural burden of suspended matter, water streams constrained by piping or flumes in a plant can be put to work transporting materials from one area to another. The pulp and paper industry is one of the largest users of water for this purpose.

An integrated mill of 900 t/day (1000 tons/day) capacity producing a variety of grades of paperboard, for example, may withdraw 7.57 to 11.36 × 10^4 m^3/day [20 to 30 million gal/day (Mgd)] of water, of which 80 to 90 percent will be required for process uses. After the pulp is produced, it may be screened to remove oversize material and debris at a "consistence" of 6 to 8 percent, or about 92 to 94 percent water. It will then be dewatered to reduce volume for storage at about 12 percent consistency. It is then diluted again to about 8 percent for pumping to the paper mill area. After refining and further processing, the pulp may finally be diluted to a consistency of perhaps 0.5 to 1.5 percent (98.5 to 99.5 percent water) as it is fed onto the Fourdrinier wire.

Water is then removed on passage over the paper machine by drainage, pressing, and heating, each succeeding step requiring more elaborate machinery and costing considerably more per pound of water removed. The finished sheet may contain only 2 to 3 percent water. Water removed at the machine by drainage is recovered and returned for another cycle of dilution and conveying. A typical flow diagram is shown in Fig. 2.

A number of mining processes use water to dissolve or melt underground mineral deposits and convey the material to the surface for further processing. Trona is brought up from depths of thousands of feet below the surface in Wyoming by pumping water down one pipe and concentrated sodium bicarbonate liquor up another. Salt deposits are also mined in this fashion.

The Frasch process for mining sulfur is somewhat more complex in that the water must be heated to 177°C (350°F) to melt the surfur below ground.

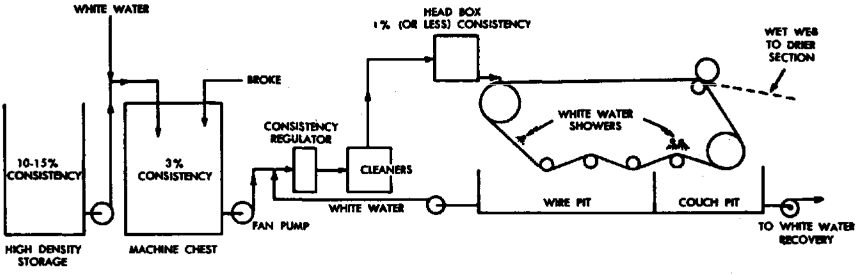

FIG. 2—*Flow diagram for paper mill processes.*

Air must then be used to help lift the water-sulfur mixture to the surface, since the sulfur is insoluble in water.

The mounting cost of oil exploration and oil well development has led to secondary and tertiary recovery of remnant oil from older fields by water and steam flooding. Specially treated water, brine, or water-steam mixture is pumped underground to displace oil from zones where it had escaped capture by primary methods. Water must be treated for this purpose by rather sophisticated means to avoid plugging the underground formation with debris.

Other examples of water's job as a conveyor can be found in such diverse industries as food, where water carries vegetables in canning plants and beets in the beet sugar mills, and coal, where pulverized coal is transported long distances by pipeline as a water slurry.

To some extent, almost every industry uses water as a conveyor and diluent for wastes, just as man does in his own society through sewerage systems.

Even in the vapor phase, water is an effective conveyor. In steam distillation processes, the bubbling of steam in a vessel containing an organic liquid causes a mixture of water vapor and hydrocarbon to be discharged in a molecular ratio equal to the ratio of the individual vapor pressures of the two materials. Steam is also used for the evacuation of other gases from an enclosure. An example is the use of steam jet eductors on turbine condensers to continually remove noncondensible gases from the condenser shell to prevent gas-binding the heat-transfer surfaces.

Water for Washing—Water is convenient and economical to use for general cleanup of industrial equipment. Aside from the aesthetic view, washup of equipment is important from such practical considerations as safety (personal injury may result from slipping on debris accumulated on the operating floor), quality (trash may find its way into the products), and production (equipment may be damaged by dirt). The nuclear industry probably has the most elaborate procedures of any industry for washup. Equipment exposed to accumulations of radioactive particles is throughly cleansed with detergents and rinsed copiously with water.

Washing of production materials takes a variety of forms, each suited to a particular type of operation. These may be generally categorized as washing by dilution, displacement, or extraction.

The electroplating industry provides a unique example of washing by dilution, since the items being plated pass through many chemical solution tanks, and carryover from one to the next must be avoided by intermediate rinsing. Figure 3 shows a typical plant of this type. Modern plating plants are equipped with carefully designed countercurrent rinse tanks to provide a thorough washing with a minimum loss of water or production of waste water. The washing effect is accomplished in the rinse tank by dilution of the surface film of chemical from the previous reaction tank. Diffusion, of course, plays a part, too, in an effective rinsing operation.

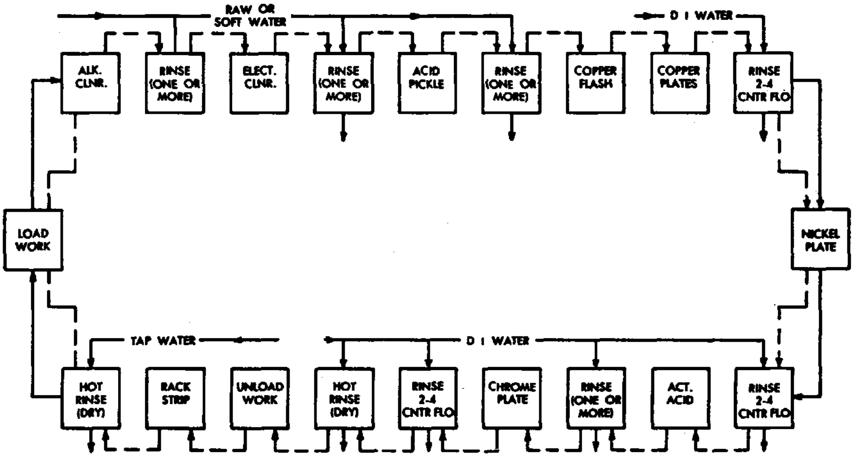

FIG. 3—*Electroplating plant rinse system.*

The microelectronic industry requires water of extremely high quality. The washing of the miniature parts must be done with water that is ion free and contains no suspended matter because the residue from a drop of evaporated water on a miniature part would make it defective. The production of this high-quality water requires the use of extensive filtration and demineralization techniques.

The paper industry provides an example of washing by displacement in the removal of residual cooking liquor from pulp on brown stock washers. These units are essentially vacuum filters, with the filter drum rotation partly submerged in a vat of digested pulp at about 15 percent consistency. The pulp forms a mat on the drum as the liquor flows through the screen covering the drum to a collection pipe inside. When the revolution of the drum has carried the wet mat out of the vat, upward, and toward the opposite side, flat sprays of water wash the pulp and displace the remaining liquor through the mat to the collection pipe for recovery and reuse.

A similar displacement process is used to remove and recover caustic soda from mercerized cotton fabric. The recovered caustic is then freed of cellulosic material by washing it in a dialyser. In this apparatus, caustic on one side of a membrane is extracted by water on the other side, leaving the large carbohydrate molecules behind.

Washing by extraction is practiced in many industries. It is used in most domestic oil refineries to remove salt from crude oil so that the salt will not foul distillation columns. Water is pumped into the crude oil, amounting to about 4 percent of the oil flow, and thoroughly mixed for maximum salt extraction. Emulsion breaking chemicals may then be added, just before the oil passes into a vessel having electrodes to break the water out of the oil and cause it to separate by gravity.

Refined sugar is also washed by water extraction during centrifuging. The wash water removes the film of molasses from the crystals of sugar so that the final product will be white and free-flowing.

The widespread growth of air conditioning has led to the use of water for washing debris from air. Often the temperature of the wash water will be closely controlled to provide the correct humidity in the cleaned air. This has become increasingly important in the aerospace industry, where entire assembly rooms must be completely dust-free to avoid any dirt accumulation on machined surfaces or control devices.

Hydraulic classification may be considered as a special form of water-washing. Water acts as a medium for separation of a desired material from its contaminants, as in the separation of slate from coal and in froth flotation in the mining industry.

Water as a Raw Material—Many a schoolboy has been startled by the demonstration in his chemistry class of the sputtering reaction of sodium metal with water, evolving caustic soda and hydrogen. Mercury cell caustic soda is manufactured in much the same way, the sodium in the amalgam reacting thus:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

This is one of many industrial chemical reactions in which water participates as a raw material.

In some processes, the reactions take place in the vapor phase. This is illustrated by the first reaction in the chain of events leading to the manufacture of ammonia, in which steam is reacted with methane in natural gas to produce the needed hydrogen:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

In this reaction, oxygen is split from the water molecule. Coal also reacts with steam in this way in gas producers to manufacture illuminating gas.

Water of high quality becomes the bulk of the finished product in the beverage industry. Each beverage has its own quality standards, ranging from an exceptionally clear water for carbonated beverages (even traces of suspended matter greatly reduce the degree of carbonation) to a fully demineralized water for deproofing of alcoholic beverages.

Water is similarly an important raw material for the drug industry. It becomes a part of many liquid formulas, including parenteral solutions.

Water may be considered as a convenient vehicle for many chemicals. Many acids are aqueous solutions of acidic gases in water, such as hydrogen chloride (HCl), sulfur trioxide (SO_3), and phosphoric anpydride (P_2O_5). Household ammonia is a solution of ammonia gas in water. Caustic soda, which was described earlier as manufactured by reacting sodium with water, is kept in an excess of water and handled entirely as a solution by a number of plants. This saves the cost of evaporation necessary to produce solid sodium hydroxide.

Miscellaneous Uses—Water is such an inexpensive and convenient material that industry has put it to work in countless odd jobs. It is widely used as a barrier material, such as sealing liquid on the glands of centrifugal pumps and on gas holders.

Used in large hydraulic clutches, it can be injected and withdrawn from the system to start and stop a driven load or to adjust its speed. The heat developed in this service must be dissipated to avoid deposit formations, and the water must be treated for both scale and corrosion control.

Water is a neutron moderator, making it a valuable shield in the nuclear industry for protection of personnel from radiation. Radioactive elements are cut or fabricated in a pool of water by special machines, observed by an underwater television camera which transmits the picture to the operator. The operator manipulates the controls at the operating floor, shielded by perhaps 6 to 9 m (20 to 30 ft) of water from the radioactive object on the floor of the pool. The water must be of extremely high clarity.

Summary

Water is essential to most industries. Its value is earning increased recognition. Each plant is becoming cognizant of the need to be alert to its use of water and to the quality required of each use. A water balance sheet should be prepared and kept up to date by every water-using industry both for its own protection and as a part of its obligation as a good neighbor.

The aspects of water sources, quality standards, use, and reuse are explored in other chapters of this manual. Of one thing we may be certain: There will be no end to discovering new jobs for water to perform for industry, nor will its importance in existing jobs diminish.

Chapter 3—Production and Preservation of Ultrapure Water

The word water probably has as many meanings as there are people discussing the term. This chapter attempts to define and limit a particular type of water called "ultrapure" water so that the reader will be in a better position to draw up his own definition within the scope of his own use of the material.

History and Background

The preparation of pure water probably ranks among the oldest of all known chemical processes, having been noted by Aristotle (384-322 B.C.), who made mention of the fact that pure water was produced by the evaporation of seawater. Thus, distillation as a method of producing pure water appears to have been used by the early experimental scientists. Later on, Pliny the Elder (A.D. 23-79) described methods of designing a still which included the use of wool in the upper condensing section to collect various oils as well as water droplets. The Alexandrians refined this system further by adding a head to the still, enabling them to prepare larger quantities of distilled liquids, including water and turpentine.

The Arabians made further improvements on this apparatus by cooling the condenser section or head with water, which led to the production of essential oils by the distillation of plants as well as alcohol from the distillation of wine. Distilled water was also produced by this system in practical quantities for more widespread use. The development of this still design also made possible the study by the alchemist of hydrochloric, nitric, and sulfuric acids in the relatively pure state. Evidently, the production of distilled water was limited to relatively small systems until the 17th century, when the production of drinking water from seawater became somewhat of a challenge. In 1683, Fitzgerald patented a process for "the sweetening of sea water." In 1739, Hales wrote a history of the early attempts to produce quantities of pure water from seawater in his book *Philosophical Experiments*.

In the 19th century, the production of pure water by various distillation systems became quite widespread with patents having been given to Chaplin of Glasgow, Scotland; Rocher of Nantes, France; and Galle and Mazeline of Havre, France. These patents were aimed mainly at solving the drinking water problem for the different navies.

In the last half of the 19th century, distillation began to become more refined with the introduction of the Liebig condenser and the reflux condenser design invented by Kolbe and Frankland. Vacuum distillation was developed at about this time by two individuals independent of each other, Dittmar and Anschutz. Shortly thereafter, in 1855, Wurtz developed a special fractional distillation condenser, with refinements on such condensers following in 1871 by Linnemann and in 1874 Le Belle and Henninger. Although much of this development work was related to the distillation of liquids other than water, the references consistently seem to refer to the fact that the chemists were attempting to find methods of making water of higher and higher purity.

In 1878, the first company known to have a business of producing water stills among its products was founded by a William Barnstead in Boston, Massachusetts. Shortly thereafter, in 1893, Kohlrausch and Heydweiller conducted the classic experiment to determine the resistance of absolute water. They redistilled water 28 times from quartz stills and found that the resistance was 26.8 megohms at 18°C.

At the turn of the century, the interest in producing pure water increased not only because of the advances in chemistry, but also because of the emerging scientific fields of biology and medicine. In 1905, Delavierre was awarded a patent on a process for the purification of water by subjecting the water to electrolysis. In 1906, Frank Candy of Westminister, England, received a patent on the manufacture of special water filters by heating basalt scum and basaltic lava with a carbonaceous matter in a reduced atmosphere. This development was the basis of the beginning of a company which has become very large and is still in existence. That same year a man named James H. Bridge of Philadelphia was awarded a British patent on the sterilization and purification of water by the use of ozone. In 1907, another British patent was issued to an American company, the Sanitary Waterstill Company of Brooklyn, New York, for what appears to have been a still with a combination condenser and special storage container. A year later the Schmeisser compound still was developed in Germany. This was essentially a multiple-effect concentric-walled still designed to produce water with a reduced energy input.

With the exception of the development by Candy noted in the foregoing, the purification techniques to this point were limited almost entirely to various methods of distillation. In 1909, however, a Doctor Gans, working in the laboratory for soil culture at the Royal Prussian Geological Institute in Berlin, succeeded in producing artificial zeolites by melting silicates of alumina with sodium carbonate and quartz. These synthetic ion exchange materials were given the name "permutit." The development of synthetic ion exchange materials has continued from that time on, with notable progress having been made by Adams and Holmes in England in 1936 with the development of the synthetic gel-type anion resins. During the decade starting in 1940, patents were issued or applied for, or both, on most of the basic cation and anion exchange materials in use today. Similarly, applications were made on the four-bed process and the mixed-bed process of utilizing these various materials, which formerly had been employed only in single- or two-bed configurations.

In addition to distillation and ion exchange, the historical methods of producing pure water include the preparation of small quantities by burning pure oxygen and hydrogen and the use of freeze crystalization techniques. Both of these techniques will be covered briefly later under methods of preparation; however, neither was employed to produce any significant quantities of ultrapure water. Over the past 20 years, numerous other improvements have been made in the design of stills, ion exchange systems, various membrane processes, and in the chemical structure of ion exchange materials. However, with a few exceptions, references to these improvements will be omitted. The reader interested in pursuing such information is referred to *Properties of Ordinary Water Substance* by Ernest Dorsey, which is not only a very valuable source of reference information, but is the most complete compilation available of information on water properties. Also, a review by Greppin on the preparation and preservation of pure water produced by distillation and ion exchange contains over 100 references.

Uses of Ultrapure Water

Perhaps a short discussion of some of the uses of ultrapure water might help to give a proper perspective to the reader interested in an understanding of the term. The original use for distilled water was the requirement for improving drinking water from brackish and biologically contaminated raw-water supply. This was, of course, a medical use in the final analysis since it became obvious that sickness resulted from drinking certain naturally occurring waters. This medical use continued to expand as the alchemist developed remedies for the sick, compounding many of their elixirs with distilled water. As the art of surgery developed, doctors recognized that incisions or wounds which were washed with potable water oftentimes became badly infected, generally with unpleasant end results. It is not surprising that the use of boiled water for sterilization prior its use on patients soon became recognized as standard medical practice. In this connection, ultraviolet irradiation of water was discovered and practiced at about the turn of the century.

With the advent of ether as a general anaesthetic during the 1840's, more complicated general surgery became commonplace, which led to the discovery of a phenomenon which to this day remains a mystery and continues to plague hospital patients. It was noted that certain patients who had undergone surgery which included the irrigation by sterile water of an open cavity in the body suddenly developed strange symptoms of shock, including a relatively rapid increase in their body temperature. In many instances, the temperature would rise to a lethal point for reasons not at all clear to the doctors in attendance. Eventually, it was discovered that the water which was introduced into the bloodstream of the body not only had to be sterile, but also had to be distilled in such a way that the fever-producing substances were removed. Because the temperature-producing symptom was the most obvious result of the injection of these impurities, they were termed "pyrogens" and the reaction on the body became known as "pyrogen shock." It is said that two ounces of concentrated pyrogenic material properly diluted for injection would cause pyrogen shock and perhaps death to the entire population of the United States.

Since pyrogens are the by-product of bacterial metabolism, they are almost always found in the presence of biological impurities, but because their detection is more qualitative than quantitative, the mere presence of bacteria does not necessarily guarantee the presence of detectable pyrogens. Similarly, because pyrogens are not destroyed by conventional sterilization techniques, the fact that water has been distilled and sterilized does not insure freedom from pyrogens. This difficulty has led to the classic hospital procedure whereby only freshly distilled water from a special still designed to remove pyrogens may be used for intravenous injections. This observation was made by Burlage and McAllister in 1936 and has been the procedure followed by the hospital and pharmaceutical industry in the United States for the past quarter century. The attitude in Europe has been slightly different, as indicated by Bauer, who pointed out in 1957 that the use of potable water that had been boiled and filtered had been permitted for the preparation of injectables up to that time. His investigation indicated that only distilled water should be used for that purpose, which is the practice followed by most hospitals and pharmaceutical companies in the world today.

With the improvement in storage techniques involving ultraviolet irradiation and special air filters, pyrogen-free water may be stored for extended periods of time, making the sizing of distillation apparatus dependent upon daily and weekly production rather than hourly production. Other methods of preparing pyrogen-free water have also been investigated, including a method involving filtered demineralized water which has been electrolyzed using a direct current of 0.1 mA per square millimeter at 7500 V. Such a process evidently oxidizes the pyrogens. Another method developed by Smith involves caustic digestion of demineralized water followed by neutralization with acid.

The widespread use of pyrogen-free water in the preparation of solutions for intravenous injection has been one of the bases of the present remarkable improvement in medical progress which has been noted over the past 20 years. Intravenous feeding not only prevents dehydration of the patient, but also gives the physician a method of maintaining the nutrient intake which prevents much of the weakening of the patient that formerly was so debilitating following surgery. The use of the many chemotherapy methods of medication which utilize massive intravenous injections is also becoming commonplace. All of the water used for these procedures must be pyrogen-free by law and must have been produced by distillation.

Another allied use of pure water is in the preparation of media which are employed in research involving the growth of live tissue outside a living host. This entire science is referred to as tissue culture and was the basis of the development of the polio vaccine, the measles vaccine, and is presently one of the most important processes used in the study of cancer. The definition of water purity for this application cannot be stated since the impurities that prevent the development of cells under certain conditions are not even known, nor are the quantities measurable. For example, it has been demonstrated that water which has been processed through ion exchange resins prior to distillation may not be suitable for successful tissue culture experiments while raw water passed through the same still works quite well. Certain heavy metals, such as copper and silver, are extremely harmful while others are an absolute necessity. The tissue culture medium itself contains many of the elements normally found in the body tissue, such as potassium and sodium. Since silica and boron are also evidently relatively harmless, glass stills are often used as redistillers by technicians working in this field. It should be noted that impurities harmful to the growth of tissue in some cases are not ionized to the extent of the normal ionization of the water molecule and, therefore, cannot be detected by conductivity techniques.

Since the previous uses do not involve really large volumes of ultrapure water, one might think that the uses for such water are quite limited. On the contrary, one of the largest users of pure water is continually upgrading its purity requirements while at the same time increasing its use of the material. The power industry was probably the original volume user of ultrapure water and continues to maintain its reputation in this regard. Both the fossil and nuclear plants are making demands on the water purification industry for a continuous source of ultrapure water having total solids not including organic matter and volatile matter in the range of one to two parts per billion. This concept of purity was originally requested by the atomic energy industry but is now in demand by the industry in general, particularly where boilers are operating in the critical range. The seriousness of this purity problem is probably best exemplified by a 650-MW power plant of modern design which operates at a boiler feedwater rate of 292 500 kg (650 000 lb) per minute. On this basis, two parts per billion of impurity in the feedwater will amount to 3.78 t (4.2 tons) of scale or residue in the system per year.

As the various disciplines of science become more aware of the materials or the changes in the substances they are working with, the contaminants in the materials under study become more important. These disciplines include chemistry, biology, botany, bacteriology, nuclear science, physics, biochemistry, and electronics. The research conducted in this last general area has been heavily dependent upon ultrapure water for its success since essentially all semiconductor and microelectronic development and experimentation has involved the use of ultrapure water as a cleaning agent. It is conceded that molecular quantities of contaminants can ruin the yield of production runs of electronic components and make the development of others completely impossible. It has been postulated that one part of copper in 10 million billion (10^{15}) parts of water can be the difference between success and failure. The reason for this critical water requirement is based on its use as a solvent or final rinse in almost every chemical processing step used in the production of basic electronic components. The industry has developed to the point where complete electronic packages are much smaller than the head of a pin. The circuits within these packages are in the dimension range of one micrometre, which means that any particulate matter much larger than 0.2 μm can cause failure of a device.

Prior to World War II, pure water was used in the rinsing of components of electron tubes. However, it is well known that these tubes failed after a relatively short life of perhaps two or three years. Following World War II, the importance of contamination control in the production of electron tubes became obvious and relatively large water purification plants were installed to improve the reliability of tube production. This was particularly noticeable in the television tube industry since each tube produced required approximately 190 l (50 gal) of ultrapure water. During this period, it also became evident that contamination-free electron tubes could be produced which would have an estimated life of perhaps 20 years. This type of life expectancy was essential for all components being used in such systems as the repeater stations installed in the transatlantic telephone cables. It is important to recognize that, without a source of ultrapure water as a final rinse for the components of these devices, their production would have been impossible. As the industry became aware of the importance of contamination-free water in the production of electronic tubes, the semiconductor industry was developed in the late 1950's, which added to the requirements for much larger volumes of water of even higher quality. The state of the art is fast approaching the point where absolute water, free of molecular quantities of all types of impurities, will become desirable if not essential to the production of electronic components.

Description of Types of Pure Water

Industry, the various areas of science, and medical and pharmaceutical investigators have been defining pure water since the writing of definitions and standards began. As noted previously, the definition of pure water in most cases is a very subjective one since the investigator using the water is often particularly interested in the absence of only certain classifications of impurities or perhaps individual substances rather than in the general absence of all matter. Traces of sodium chloride in water being prepared for intravenous injection would not be of serious consequence whereas traces of biologicals and pyrogens would be of the utmost importance. Similarly, traces of organic matter would be of minimal concern to the chemist running inorganic analyses. Rather than attempt to define ultrapure water in terms of resistance or parts per trillion of impurity, it is more logical to refer the reader to the *Annual Book of ASTM Standards*, Part 31, Method D-1193, Specification for Reagent Water, and to the *U. S. Pharmacopia*, which list several different grades of waters stipulated for certain uses. Briefly, these various standards are as follows:

Type I grade of reagent water shall be prepared by the distillation of feedwater having a maximum conductivity of 20 μmho per centimetre at 25°C (77°F) followed by polishing with a mixed bed of ion exchange materials and a 0.2 μm membrane filter.

Type II grade of reagent water shall be prepared by distillation using a still designed to produce a distillate having a conductivity of less than 1.0 μmho per centimetre at 25°C (77°F). This may be accomplished by double distillation or the use of a still incorporating special baffling and degasing features.

Type III grade of reagent water shall be prepared by distillation, ion exchange, or reverse osmosis followed by polishing with a 0.45 -μm membrane filter. Such water shall have a conductivity of less than 1.0 μmho per centimetre at 25°C (77°F).

Type IV reagent grade water may be prepared by distillation, ion exchange, reverse osmosis, or electrodialysis and shall have a conductivity of less than 5.0 μmho per centimetre at 25°C (77°F).

The *U. S. Pharmacopia* definitions are as follows:

Purified water is obtained either by distillation or by ion exchange treatment. It cannot contain more than 10 ppm total solids and must meet the United States Public Health Service regulations for potable water with respect to bacteriological purity.

Water for injection is water purified by distillation which meets the test requirements for Purified Water plus the Pyrogen Test.

Sterile water for injection is water for injection that is sterilized and suitably packaged.

Future definitions of ultrapure water will undoubtedly depend upon the development of test procedures as well as various combinations of systems of preparation. Since the contamination of water by molecular quantities of impurity is becoming of significant interest to certain users, it is likely that ultrapure water of molecular purity may be defined based upon tests which have been promulgated by the user himself. These special test procedures may be based upon the use of the water in carrying out a standard procedure with known standard methods and materials in such a way that the water itself will be tested. For example, the purity of water might be defined as that water which when used in the preparation of tissue culture media would support the growth of monkey brain tissue for a period of 60 days or longer.

Water passing this specification might then be used to grow another type of tissue of a sensitive nature. The rinsing of standard semiconductor devices could also be used to detect molecular contaminants and could be the basis of a definition of molecular-free water.

Since molecular quantities of impurities may be measured by various theoretical techniques, it is quite possible that the actual number of molecules in the water may be used to define the grade of water. Another measure of the purity or type of water may depend upon the polymetric structure of the water molecule, which may vary depending upon the preparation techniques and the previous history of the water. The various isotypes of hydrogen and oxygen combined to form water molecules can also be of significance and may be another basis for a series of definitions.

Classification of Impurities

Any discussion of pure water or ultrapure water must include some parameter on the type and limit of impurity; otherwise, the entire discussion, whether on the method of purification, the method of handling, or the method of testing for impurities, will be meaningless. Ultrapure water to many, especially to those involved in central power station operations and the pharmaceutical and electronics industries, has been pretty well defined by the industry. This chapter may, therefore, seem somewhat theoretical and impractical; on the other hand, it is possible that individuals within the industries may wish to revalue their definition based upon some of the changes in the methods of preparation and preservation which are outlined. Since any investigator considering the use of ultrapure water usually has an idea about the types of impurities which cause difficulty to his experiment or process, he should govern his method of preparation and preservation in such a way as to prevent contamination from the undesirable constituents. The preparation and preservation based on the elimination of contaminants might be conducted considering those contaminants which can generally be classified as liquids, solids, or gases.

In some instances the classification may be unclear. In general, however, the physical state of the impurity can be postulated. A further breakdown of the contaminants may be made by classifying the materials as organics, which generally are all compounds containing carbon in any form, or as inorganics, which are essentially all substances which do not contain carbon in their molecular structure.

Generally speaking, liquid impurities are the most difficult of all to remove if one is attempting to produce ultrapure water, particularly if the impurities fall in the classification of miscible organic substances. Examples of this impurity might include alcohol, liquid detergents, and organic acids such as acetic or citric acid. Many of these substances that ionize may be removed by ion exchange, as would be the case with acetic acid, and might also be removed quite effectively by adsorption. Large-molecular-weight impurities including many of the naturally occurring organic liquid contaminants present in part-per-million quantities in natural waters can be removed quite effectively by reverse osmosis and ultrafiltration techniques. Fractional distillation may be considered in combination with adsorption for the removal of the liquids such as alcohol; however, if part-per-million quantities are involved, such systems for removal may be of questionable value. Under these conditions, destructive digestion using solutions of potassium permanganate and potassium hydroxide may be far more effective.

Fortunately, there are very few miscible inorganic impurities. However, hydrogen peroxide and bromine, in small quantities, are examples. Both of these materials should be removed by destruction of the molecule as such in the case of the hydrogen peroxide or by combination of the molecule with other substances in the case of bromine. Chemical decomposition or combination should always be considered as a final step in any removal technique to be considered.

The immiscible organic liquids include all of the naturally occurring oils which may be derived from contact of a person's skin with the water to be purified or from petroleum products which may contaminate naturally occurring waters in a myriad of ways. Sometimes these oils may be separated by filtration employing special adsorbents which attract hydrophobic impurities or by membrane filtration varying from the reverse-osmosis pore size materials to the membrane filters having pore sizes in the range of one micrometre. Distillation may also effectively remove these compounds, particularly if an oxidizing digestion step precedes the distillation process.

Inorganic liquids as such are not common and generally fall into the classification of low melting metals such as mercury and the synthetic silicones, which are similar in many respects to organic oils except that silica is used as the building block instead of carbon. The metallic impurities, of course, can be removed quite easily by physical separation of the elements followed by a combination of filtration, ion exchange, and distillation. If the elements concerned contaminated the water with ionized impurities, ion exchange would be quite adequate. However, generally such elements would probably impart colloidal oxide impurities which would dictate the desirability of distillation as a preferred method of removal. The oil-like silicone impurities should be removed by adsorption, distillation, digestion, and membrane filtration, as was indicated in the case of the organic oils.

Molecular solid organic impurities form one of the more troublesome classifications since they cannot readily be removed by conventional ion exchange and filtration processes. Examples of such impurities include sugars, impurities from plastics, residues from plastic containers, pyrogens, and viruses depending upon the size of the viruses involved. Molecular organic substances which may be present in small quantities in the range of one or two parts per million may be removed by digestion with strong oxidizing agents followed by distillation, as was the foregoing case with the organic matter. The development of reverse-osmosis membranes has made the use of this system practical.

Chapter 4—Effects of Composition on Industrial Use

Water is essential to practically all industrial operations, but it rarely should be used just as it is drawn from stream, lake, or well. The impurities introduced into water by either natural or man-made pollution can seriously affect both equipment and product if appropriate precautions are not taken.

Natural Contamination

Absolutely pure water is a laboratory curiosity. Even in the absence of municipal sewage and industrial wastes, raw water in nature always carries various foreign substances. The most common impurities in water are dissolved gases, such as carbon dioxide and oxygen, and soluble mineral matter, including such metal ions as calcium, magnesium, iron, and sodium in chemical balance with such anions as sulfate, bicarbonate, carbonate, hydroxyl, chloride, and others. These substances are dissolved as water flows over or percolates through the ground. In addition to dissolved substances, many surface waters carry solids ranging from sand, coarse enough to settle rapidly, to colloidally dispersed particles indefinitely stable.

Depending upon its source, raw water also carries variable amounts of disolved or dispersed organic material. Obvious examples are drainage from peat bogs and cypress swamps, runoff from farms, and decomposition products from aquatic plants and animals killed by changes in weather or environment. Most organic matter persists over relatively short distances in streams because of the purifying capacity of stream organisms that utilize organic matter as food. Some organic substances, for example, humates and tannates, are highly resistant to biochemical destruction, and color from them may persist almost indefinitely.

The natural accumulation of impurities in water is a result of the chemico-physical constitution of our world, and very little can be done to prevent it. On the other hand, pollution from the discharge of municipal and industrial wastes can be controlled.

Industrial and Municipal Pollution

Pollution of streams has been going on ever since the appearance of settled communities. People found it expedient to dispose of unwanted materials in natural watercourses because they were quickly carried away. Stream pollution did not become a problem in the United States until the Industrial Revolution and the introduction of water carriage of sewage around 1885 began to exert their effects. Pollution steadily increased as the manufacturing industry expanded and communities grew larger.

Pollution by municipal sewage and industrial wastes has come to be considered a national problem. Solution of the "national" problem requires, however, the working out of an untidy mess of local problems for each drainage basin.

While control of pollution is important to each individual as he drinks, washes, swims, fishes, boats, or merely gazes upon water, in this chapter it is pertinent to consider only the adverse effects which impurities in water may exert upon its use by industry.

Types of Pollution

A watercourse can be polluted either directly or indirectly, and the causes may be physical, chemical, biological, thermal, and radiological. Although these species of pollution can be identified, it would be an unusual case that could be classified wholly under one particular form. The only exception to this might be instances of pollution by radioactive substances.

Physical pollution can be caused by sludge deposits, floating debris, scum and foam, turbidity, color, taste, odor, and temperature, to name some of the more common kinds.

Chemical pollution can take many forms. Increases in hardness, salinity, and acidity or basicity are commonly encountered. Discharge of toxic metal ions, such as chromium, copper, lead, mercury, silver, and zinc, is not uncommon, although their value may often warrant recovery in waste treatment plants. Iron, manganese, and aluminum are present in most mine waters and various industrial wastes. Cyanides, flourides, and odorous organic compounds may be present in waste water. In fact, every chemical manufactured or used in industry may be present to some extent in streams receiving industrial waste water.

Biological pollution can be important in water for industrial operations, as well as in water for drinking. Slime organisms, for example, reduce heat transfer when they develop on the tubes of condensers and coolers, or impair the quality of paper.

Heat is regarded as a significant pollutant. Temperature increases in some streams have seriously impaired their value for cooling water, have increased their capacity for assimilating wastes beyond the reaeration capacity of the stream, and have destroyed aquatic life.

The advent and rapid expansion of uses for radioactive elements have generated an awareness of the possibility of pollution of water by radioactivity. The great potential danger of this kind of pollution was promptly recognized and the problem of waste disposal was studied in advance. As a result, no cases of serious pollution have occurred.

Effect of Pollution on Industrial Operations

A specific pollutant may be generally undesirable in many industrial operations. For example, silt resulting from erosion must usually be removed from water to be employed in process operations, in the cooling of all but direct once-through equipment, and in the generation of steam. Some other pollutant may be considered inoffensive except in some unique situations. Thus, little attention is normally paid to chloride ion up to concentrations of several hundred milligrams per litre. An extreme effort has been made, however, to exclude it from the water in nuclear reactors because of its effect in accelerating stress-corrosion cracking of stainless steel.

An exhaustive catalog of each specialized industrial system in which each possible pollutant found in water has produced an undesirable effect is beyond the scope of this chapter. For a broad look, it is possible, however, to consider separately the effect of pollutants on corrosion, on the generation of steam, on the cooling of industrial processes, on the performance of water as a constituent in a process for reacting, washing, separating, or transporting materials, and as an ingredient of a product.

Corrosion

Corrosion is probably the most ubiquitous and expensive problem in water collection and distribution systems, water treatment equipment, and water-using equipment. Its effects range from such spectacular hazards as boiler explosions to the downgrading of product quality as a result of the presence of corrosion products in process water.

The total cost of corrosion in the United States has been estimated at $50 billion annually. The ruptured boiler must be replaced, as must the leaking water pipe, but there are many other direct or indirect costs resulting from corrosion. Among these are the increased power required for pumping, the reduced product yields resulting from inefficient cooling, and the increased costs from the use of equipment with heavier walls and expensive alloys to compensate for corrosion.

Although the fundmental corrosion reactions are simple, the form and rate of corrosion are influenced by subtle and complex interactions of design, construction, and operation that make corrosion prevention and control a far from simple task. Corrosion is generally understood as the deterioration of a metal in its environment. Although nonmetallic materials such as plastics and wood also deteriorate in their environment, this deterioration is generally not considered as corrosion. More specifically, corrosion is the solution of some portion of a metal in its environment as the result of a chemical, electrochemical, or physical process.

The following tend to intensify corrosion at the metal-water interface, either by increasing the rate or by increasing the localization of attack.

Since corrosion is essentially a chemical reaction, the rate increases as the *temperature* increases. Therefore, corrosion rates are likely to be higher on heat-transfer surfaces than on non-heat-transfer surfaces for the same water composition. The corrosion rate for most metals is greater under *acid* conditions. Amphoteric metals such as aluminum and zinc will be attacked in either *acid* or *alkaline* environments.

The presence of a *depolarizing agent* such as oxygen in the water will tend to accelerate corrosion. Although it is generally true that the higher the oxygen concentration the more rapid the corrosion will be, a point can be reached at which the oxide film is maintained and the corrosion reaction is retarded.

Extremes of *velocity*, either high or low, affect the corrosion rate. Erosion may be caused by excessively *high water velocity* even when there is no suspended matter present. Softer metals, such as copper and many of its alloys, are particularly susceptible to erosion even at relatively *low velocities*. Low velocity also encourages localized corrosion and ineffective distribution of corrosion inhibitors. Conditions that cause one portion of the *surface to differ* in properties from another will tend to localize corrosion. *Deposits* may lead to differential oxygen attack of the metal surface as localized corrosion. Corrosion products and a wide variety of biological organisms including bacterial slimes, algae, and mollusks are frequent deposits. *Construction*, such as crevices, often create conditions almost identical to those deposits. The *coupling of two different metals* tends to accelerate the electrochemical corrosion of the more anodic metal. *Conductivity* is the water property which has the greatest influence upon the rate of electrochemical corrosion. The higher the conductivity, the greater the corrosion current that can flow.

Generally speaking, under any given set of conditions, the rate of electrochemical corrosion will increase as the difference between the coupled metals on the electromotive series or the galvanic series increases. The area relationship of the anode and cathode has a direct effect on the corrosion rate. Failure will usually come much more rapidly in a system which has a small anode and large cathode. For example, the seawater exposure of a joint prepared by riveting two sheets of copper with steel rivets will lead to rapid failure, whereas two sheets of steel joined with copper rivets will last much longer. Mechanical stresses on a section of the metal will tend to promote localized corrosion.

Most of the economically feasible methods for combating corrosion do not *prevent* it but, rather, reduce its rate. Generally, the following control measures should be considered: selection of corrosion-resistant materials that provide protective coatings; appropriate mechanical and process design; and modification of water composition to permit use of a less resistant metal.

The selection of corrosion-resistant materials of construction is the most effective control measure, but, unfortunately, it is usually the most expensive. Even when the general water composition is known, minor details of construction or water constituents or conditions can cause failures of the materials that otherwise would appear to be satisfactory.

Steam Generation

More than a few micrograms per litre of any substance is regarded as an undesirable pollutant in water to be fed to a boiler producing steam at a pressure in the range above 13 790 kPa (2000 psi). Even for the pressures of 4137 to 10 342 kPa (600 to 1500 psi) in many contemporary power plants, dissolved salts as well as suspended solids are often limited to the milligrams per litre range in the makeup. At lower pressures, operation with appreciable dissolved solids is accepted practice. General values for water quality guidelines for boiler feedwater and boiler blowdown quality as developed by the ASME Research Committee on Water in Thermal Power Systems are listed in Table 1.

Cooling of Industrial Processes

Almost any quality of water, including seawater, has been used for industrial cooling in once-through systems, where heat removed from process equipment increases the temperature of the water on its way to some other use or to waste. In many such systems, it is not even considered worth the cost to clarify the large flow of cooling water to remove suspended solids. When silt accumulates on heat-transfer surfaces sufficiently to impair their performance, it is removed intermittently by either mechanical or chemical means. In many areas, reduction of temperature in water discharged from once-through cooling systems now is required before returning effluent to the original source.

A more or less universal nuisance in once-through cooling systems is the accumulation of slime organisms, unless they are kept under control by periodic addition of chlorine to the water.

TABLE 1—*Boiler-water concentration limits.*

Boiler Pressure at Outlet, psig[a]	Total Solids. mg/litre	Alkalinity (Total). mg/litre	Suspended Solids. mg/litre	Silica. mg/litre
0 to 300	3500	700	350	125
301 to 450	3000	600	250	90
451 to 600	2500	500	150	50
601 to 750	2000	400	100	35
751 to 900	1500	300	60	20
901 to 1000	1250	250	40	8
1001 to 1500	1000	200	20	2.5
1501 to 2000	750	150	10	1.0
to 2001	500	100	5	0.5

[a] Metric conversion: 1 psig = 6.895 kPa.

Inorganic coatings, frequently of a slimy character, also result from the deposition of hydrous oxides of iron or manganese, or both, from the cooling water. Harder deposits of calcium carbonate scale are produced only if the once-through cooling water is practically saturated as it reaches the heat-transfer surface.

Where heat is removed from the cooling water by evaporation, as in a spray pond or a cooling tower, solids originally dissolved in the initial supply are concentrated in the water recirculated to the cooling operation. As a result, the conditions necessary for deposition of a scale of calcium carbonate are more frequently attained.

Since a cooling tower inevitably functions as a giant air washer, a recirculating cooling system is always being seeded with airborne bacteria and other minute living organisms. It also accumulates dust, becomes saturated with oxygen, and collects such gases as carbon dioxide, sulfur dioxide and trioxide, hydrogen chloride, hydrogen sulfide, or ammonia released by the burning of fuel or by chemical processing. Fouling of heat-transfer surfaces, corrosion of metal lines and equipment, and damage to the surfaces of cooling towers by chemical attack, bacterial attack, or both, are commonly controlled by a variety of water-conditioning techniques.

Processing Materials

Some industrial processing operations can be conducted with almost any quality water. An example is the washing of fines from bituminous coal. In other processes, only demineralized water of the highest quality is employed. The manufacture of microelectronic components is an example often cited, but the production of electrolytic tin plate free of pinholes requires water of similar high purity. Between these extremes lie many special situations. There is no standard approach to providing water for industrial operations. Consider a few of the many criteria:

Color due to the natural decomposition of vegetation, to the oxidation of dissolved iron or manganese, or to various constituents of municipal or industrial wastes must be minimized in water used for processing natural and synthetic fibers, washing and dyeing the fabrics woven from them, and manufacturing clear plastics or quality paper of high brightness.

Suspended solids in a range of particle size from those which can be readily removed by sedimentation to those so small that they remain dispersed for long periods of time are an almost universal pollutant of river water. In relation to the trouble they cause in most process operations, the cost of their removal is sufficiently low as to justify clarification, either as an initial step or as an additional benefit of softening by precipitation.

Dissolved salts in water that might be considered of the highest quality for drinking must nevertheless be considered as pollutants if they cause operating difficulties, impair product quality, or impose costs for treatment to remove them.

Water for rinsing steel surfaces to be electroplated or painted should not leave hygroscopic salt deposits on the dried metal because subsequent blistering of the finish in humid atmospheres may otherwise occur.

Iron and manganese cause a general staining of all water fixtures, dulling of shades in dyeing of textiles, and introduce undesirable color in washing of clear plastics, white paper, and textile fibers and the products woven from them.

Calcium and magnesium in water used for washing textiles tend to cause uneven dyeing. Water low in hardness is required for some electroplating processes, washing and bleaching of paper, pulp, leather tanning, and laundering.

Copper and mercury at levels so low as to be barely detectible cause cracking of alumimum alloys.

Incorporation in Product

Taste and odor are vital considerations in water used for brewing beer or bottling nonalcoholic carbonated beverages, for food processing, and pharmaceutical industries.

Color is a critical characteristic in water for club soda.

Dissolved salts should be low in water used for making artificial ice to minimize opaque accumulations of solids in the last water frozen.

Calcium and magnesium in water used for cooking peas and other vegetables for canning toughen them undesirably.

Keeping Water Reusable

From the very beginning of the Industrial Revolution, industry has had to accept costs due to natural impurities in water. The early history of the steam boiler contains references to the "fur" deposited from hard water, which must be removed frequently to avoid blistering and failure of the boiler shell directly above the furnace. Deposits of relatively insoluble compounds of calcium and magnesium—the "hardness" in the water—as an insulating scale on heat-transfer surfaces in contemporary condensers and coolers as well as in boilers are prevented only by controlled pretreatment and chemical conditioning of the water.

Not only dissolved substances present in natural waters, but also silt from erosion of the land, as well as slime produced by bacteria present in water, foul industrial equipment, interfere with heat transfer, or impair the quality of products.

Even the oxygen dissolved in water from the air, vitally necessary to the normal balance of life in a stream or lake, accelerates failure of pipelines and equipment by localized corrosion.

The fact that a water supply either in the natural state or after treatment in a municipal water plant meets the standards set for drinking water does not mean that this water is suitable for industrial use. Further treatment usually is needed to minimize its total cost.

While natural impurities can always cause some kind of trouble wherever water is used by industry, man has compounded his problems exponentially in two ways. While multiplying his numbers, he has increased tremendously his control of power and his capabilities for manufacturing products to meet many new wants in addition to old needs. Throughout the industrial expansion of the past two centuries, he has conveniently flushed his sanitary and his industrial wastes into the nearest stream or lake.

From the strictly economic viewpoint for our society as a whole, the optimum control of this pollution would be that which leads to the lowest total of all the costs to all the groups using and reusing the water through its complete path back to the reservoir of the oceans. But water also has aesthetic and recreational values which are leading us as a society to pay more than the minimum number of dollars which would be needed for the optimum level of control on a strictly economic basis.

Keeping water reusable provides a promising alternative to transportation of water from a diminishing number of sources at increasing distances from the point of use, and to the recovery of usable water from the oceans. However, the cost of controlling entry of the wastes of society into our presently available water will not be small.

Chapter 5—Treatment of Process Water and Waste Water

The purification of water for industrial use can be very complex or relatively simple, depending upon the properties of the raw water and the degree of purity required. There are many methods and combinations in use, but all are covered in three basic processes: physical, chemical, and physicochemical treatment.

A fourth basic process, biological treatment, is often employed where waste water must be purified before it may be discharged. This process takes advantage of the ability of living microorganisms to induce a variety of chemical and physicochemical reactions. Treatment of waste water is usually a much more complicated operation than the production of process water of appropriate quality.

This chapter discusses these processes as they are used in the treatment of industrial water and waste water and outlines some of the technical problems and basic considerations involved.

Physical Treatment

Physical treatment pertains to those processes in which there is separation of impurities from water without chemical change. The common methods are sedimentation, straining and filtration, multiliquid phase separation, degasification, dilution, removal of entrainment, distillation and stripping, underground discharge, and ocean discharge.

Sedimentation

Sedimentation is the process by which the force of gravity acts on particles heavier than water and causes them to move downward and settle out. Surface waters contain varying amounts of suspended material, and this process is used to clarify raw water either by simple sedimentation or with the addition of chemical coagulants. The tanks in which this action takes place are called sedimentation basins.

Particle size, weight, shape, frictional resistance, and viscosity play an important part in the design of such tanks. Theoretical calculations usually are based on modifications of Stoke's law and the assumption that the particles are spheres. Many factors must be considered in design, and all of these must be modified as judgment and experience dictate. The theory of design will not be given here; it will suffice to state that effective clarification can be accomplished in tanks that are properly designed and operated.

Settling basins may be constructed of earth, wood, concrete, or steel. They may be rectangular or circular. The usual period of retention ranges from 4 to 12 h. Where the water contains large amounts of settleable solids, the basins often are provided with mechanical scrapers which move the settled sludge to a sump from which it is forced out by the hydraulic head of water in the basin. In other instances, manual sludge discharge valves are provided to remove some of the settled material; it is necessary to remove such units from service at regular intervals for thorough cleaning.

Inlet and outlet distribution of the fluid must provide for uniform flow in the basin if efficient operation is to be attained. In rectangular tanks, the influent is distributed by a trough equipped with adjustable sluice gates or plug valves, and the effluent is usually discharged over a weir or series of weirs. Circular units are provided with a center distributor and an overflow launder at the periphery of the tank.

Short-circuiting often plagues the operation of rectangular basins, thereby decreasing the theoretical retention time. This can be overcome by improving the inlet distribution or by effective use of muffle boards at the inlet and sometimes just ahead of the effluent weir.

Depending upon the character of the silt and suspended matter, plain sedimentation may provide as much as 70 percent removal; where coagulants are employed, removals may be as high as 95 percent.

Many industrial waste waters contain organic and inorganic settleable solids that must be removed before final discharge. These solids respond to the process just described, and settling basins of similar design are used for the purpose. Retention periods are usually much shorter than for raw waters, rarely exceeding 2 to 3 h. Long retention periods are detrimental where the solids are all organic, because bacterial action may take place. This may result in anaerobic conditions and the generation of odors. The settled sludge will have a tendency to float if considerable gas is evolved, and this will tend to nullify the operation.

Air flotation is very effective for removing flocculent solids that settle very slowly or have a tendency to float. The air is dispersed in the liquid under pressure and the pressure released just prior to discharge into a receiving basin. The finely divided air floats the solids to the surface, where they are skimmed off. Effective separation is provided at minimum cost by this method.

Straining and Filtration

Strainers and filters may be used where it is necessary to remove floating or suspended solids from water, either as a further step after sedimentation or where space precludes installation of settling basins.

Several types of strainers are in commercial use. Cloth, metal gauze, rotary drum, and rotary disk are the usual kinds. Cloth and metal gauze filters are used where the suspended materials are fairly fine and in low concentration. Cheesecloth or similar material is rolled around a perforated mandrel and installed in a cast iron housing. The water passes through the filter into the drum and the finely suspended material is retained on the cloth. When the pressure drop reaches a predetermined value, the unit is taken out of service and the cloth washed or replaced. These units will do a good job of straining but are bulky and have a fairly high loss of head.

Metal gauze is becoming popular as a strainer. Here the size of the mesh can be rigidly controlled down to several micrometres and selective straining can be performed.

Rotary drum and disk strainers are quite widely used for coarse separations. The drum type comprises a rotating drum covered with a screen of the proper mesh size for the purpose and installed inside a housing. The drum is driven at slow speed by an electric motor. Valving is provided to backflush automatically a portion of the screen in its rotation and thereby keep it clean. These units are built to handle up to several thousand litres per minute at a low pressure drop. This unit may be modified by replacing the screen with perforated porcelain disks.

A drum strainer is used where floating solids must be removed from waste water. This is a drum frame covered with screen and rotated in a concrete channel. The water flows through the screen and out of the center of the drum. Provision is made for backwashing the screen as it rotates. This unit is for gravity flow only.

The disk unit is a perforated disk set at an angle in a channel where the water must flow through the disk. The solids are scraped or brushed off the portion of the rotating disk that is above the water surface. This is a gravity-flow unit.

Filtration of water is carried out in either pressure or gravity units containing graded sand, calcite, magnetite, anthracite, charcoal, or finely divided, relatively insoluble materials such as diatomaceous earth. Silica sand is the most common filtering medium for cold, neutral waters because of low solubility, low cost, and the relatively high specific gravity of sand particles. Pressure filters are usually designed for a downflow rate of 81 to 122 litres/min/M^2 (2 to 3 gal/min)/ft^2 of surface area, and a reverse-flow backwash rate up to 68 litres/min (18 gal/min). The filter medium usually is specified on the basis of effective size and uniformity coefficient. The effective size of filter medium is usually specified to be not more than 1.65 and is always greater than 1.0.

Crushed anthracite coal, because of its relatively low solubility, is usually specified as the filter medium where hot, strongly acid, or strongly alkaline waters must be filtered. The anthracite filter medium usually is backwashed at lower velocities than sand of the same size. Anthracite filter medium weighs only about 80 kg/m^3 (50 lb/ft^3), approximately one half the bulk density of sand.

Diatomaceous earth is often used as a filter medium. In one type, the diatomaceous earth is supported by a porous stone or wire mesh element and removed by backwashing. In other types, the filter material is deposited on a rotating filter drum in a fairly thick layer. A doctor blade continuously scrapes off a thin film and thus exposes a fresh surface. Precoated filters have the advantage of high-quality effluent, low weight, high capacity for their size, and sometimes lower first cost. They have the disadvantage of high pressure drop, high operating maintenance and repair costs, and rapid depreciation and obsolescence. Poorly designed units are often undependable in operation even in the care of a competent and reliable operator. A diatomite filter must have two to four times the filter area of a sand filter of equivalent capacity. Even with the larger area, the pumping power needed may be two to four times higher than for the equivalent sand filter. There are numerous types of precoat filters which employ a variety of precoat materials.

It should be understood that filtration will not remove true color from water. This can be eliminated only by use of a suitable coagulant dispersed in the water prior to filtration.

Multiliquid Phase Separation

One or more nonmiscible liquids can often be physically separated from water as a result of differences in specific gravity. Gravity separations of this kind are performed on a small scale in laboratory separatory funnels and on a commercial scale in specially designed equipment [*1*].[1] The oil and water separator for oil refinery waste water is an example of one large-scale application of this process [*2*].

Frequently there is not much difference in the specific gravities of the liquids, and one of them may be dispersed in a finely divided, globular state. Thermal convection currents under such conditions may be strong enough to prevent efficient operation of the equipment. It is therefore always desirable to minimize thermal currents by careful design of gravity separator systems. An equalizing basin ahead of the treatment unit will minimize temperature and other fluctuations that may disturb proper operation. Agglomeration of the dispersed phase by chemical or physical means will greatly increase the efficiency of the separator.

Centrifugal equipment is used for multiliquid phase separations where the value of the separated product justifies the relatively high capital cost of the equipment. Use of a centrifugal separator to remove traces of suspended water and solids from lubricating oil is an economical application of this process. The differential separating force between the two or more liquids can be greatly increased with such equipment. The strength and cost of the materials from which centrifugal separators are constructed place a limit on their size and capacity.

Air flotation is widely used in this type of separation. The oily water is put

[1] Italic numbers in brackets refer to the list of references appended to this chapter.

under a pressure of 207 to 345 kPa (30 to 50 psi) and air is diffused into the liquid. The pressure is released just prior to discharge into a separating tank where the fine air bubbles rise to the surface carrying the particles of oil with them. A rotating skimmer sweeps the floated oil to a collecting trough from which it flows into a receiving tank. These systems can easily produce 90 percent separation with very short retention periods, sometimes of no more than 30-min duration [*3*].

Desgasification

Stripping operations, such as physical deaeration and aeration, are processes for removing undesirable dissolved gases from water. One or more dissolved gases, such as oxygen [*4*], carbon dioxide [*5*], ammonia, or hydrogen sulfide, are removed by exposing large surfaces of the liquid to a vapor phase deficient in the gases to be eliminated.

Degasifying equipment can be classified as ebullition, tray or drip, and spray units. In the ebullition type, a suitable gas is bubbled through the liquid for a period sufficient to change the vapor pressure equilibrium and enlarge the liquid surface. This principle was widely used in the past for hydrogen sulfide and carbon dioxide removal; it is now employed mainly to separate carbon dioxide and oxygen in deaerating feedwater heaters, usually operating under a few pounds pressure.

Tray or drip gas-stripping equipment exposes large surface areas to the desired vapor pressure conditions by slowly flowing the water in thin layers over plates, channels, slats, or packing and allowing it to fall or trickle in droplets or thin sheets Deaerating feedwater heaters operate on this principle to remove dissolved oxygen and carbon dioxide from boiler feedwater. The heaters are usually operated under a few pounds pressure and at temperatures above 100°C (212°F). Degasifiers used to remove carbon dioxide where alkalinity is controlled by acid addition, or by blending hydrogen zeolite effluent with sodium effluent or after cation exchange, operate on this principle. Closed wooden tanks containing many stacks of trays allow the water to drip down while air blown up through the tank escapes at the top.

Spray and spray-ebullition gas strippers utilizing atomizing nozzles, ebullition, and entrainment to divide the water into fine droplets for exposure to the desired vapor pressure conditions are finding wide use, not only in deaerating feedwater heaters, but also with vacuum deaeration of carbon dioxide and oxygen from cold water and ammonia from hot water. Vaccum deaeration is carried on in one or two stages, usually in vertical steel tanks where the vacuum is maintained by steam-jet ejectors.

With the exception of vacuum deaeration, some means must be employed to maintain the partial pressure of the undesirable gases well below the point at which stripping will cease. In a gas-stripping basin or tower, the air that is pumped or blown through the equipment carries the undesirable gas away to the atmosphere. Steam with a low partial pressure of free oxygen is the stripping agent in deaerating feedwater heaters. A vent condenser is usually included to permit the incoming feedwater to absorb most of the heat in the stripping steam.

Dilution

High salt concentrations in waste water from the oil and alkali industries present a difficult disposal problem. Similar problems occur in other chemical plants where sodium sulfate and organic solids are present in high concentrations in effluents. Regulatory agencies have set limiting concentrations in the receiving streams that restrict the amount of dissolved matter and suspended matter that may be discharged.

Where inorganic salts such as sodium chloride, calcium chloride, and sodium sulfate must be discharged, there are two methods in use. One is by dilution with uncontaminated water, and the other is by controlled discharge. In those plants where the waste stream is small and there is available considerable uncontaminated waste water (for example, from cooling operations), the two are blended to conform with the concentration allowable in the plant discharge. Where the amount of clean water is insufficient for diluting all the concentrated waste, any surplus of the latter is held for controlled discharge.

Controlled discharge takes advantage of the increased stream flows during winter months or rainy seasons to dispose of concentrated wastes that would otherwise overload the receiving water. The wastes are stored in ponds and released during periods of heavy runoff at a rate that will not exceed the allowable concentration in the river. This operation may require large areas of land for storage lagoons, but it is often the most economical method of handling the problem.

When there is sufficient flow in the receiving stream to assimilate the biochemical oxygen demand (BOD) load from organic matter, dilution can provide satisfactory stream assimilation and eliminate areas of heavy oxygen depletion. This method has certain limitations but it has been used successfully in some areas.

The dissolved salts and sludge in evaporators, boilers, and cooling towers are concentrated in the circulating water and these concentrations must be controlled by blowdown. Blowdown is thus a dilution process whereby concentrated solutions and suspensions are replaced by more dilute water. Intermittent boiler blowdown usually discharges directly to an atmospheric drain tank, with the result that all of the heat of the liquid and of the flashed steam are lost. Continuous blowdown systems make it possible to recover this heat. Heat-recovery systems are available for both high- and low-temperature operation. Heat-recovery equipment for high-temperature blowdown may consist of a flash tank to salvage flash steam or of a surface heat exchanger for transferring the blowdown heat to the feedwater just before it enters the boiler. Heat-recovery flash tanks or surface exchangers for low-temperature blowdown usually transfer the blowdown heat to the cold feedwater in or ahead of the deaerating feedwater heater. Heat-recovery systems for high- and low- level blowdown can be used in series where the overall heat balance of the plant makes such equipment economical.

Figure 1 shows the percentage of the boiler water that is flashed to steam as it is throttled from various pressures to atmospheric pressure. It also shows the total heat of the boiler water at various pressures.

Blowdown from cooling towers is often called purge water. Windage or other water losses are sufficient in some cases to limit the concentration of salts of the cooling tower water. Where additional dilution is required, a continuous stream of water is run to the waste water system.

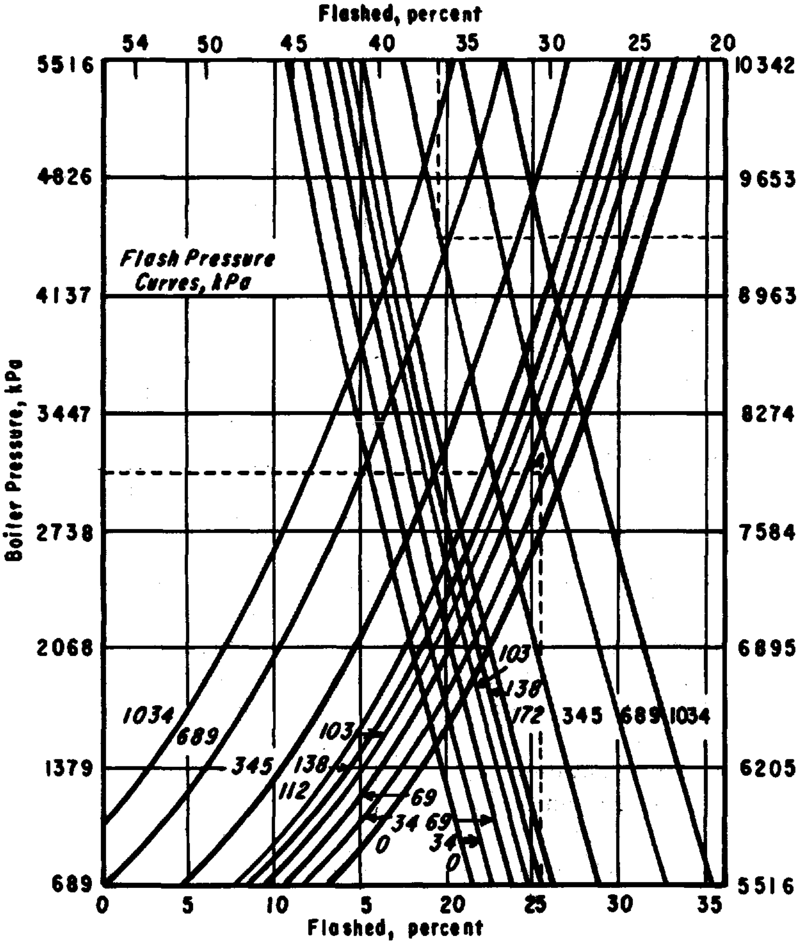

FIG. 1—*Flashed steam recoverable from continuous blowdown systems.*

Removal of Entrainment

One of the fundamental problems in boiler design and operation is the mechanical separation of solutions and solids from the steam. All boilers must include entrainment separators. The simplest method is to provide sufficient disengaging space above the normal waterline in the steam drum. It is economical for industrial steam generators to use dry pipes, baffles, or special types of separating devices to reduce the size of the steam drum. Most modern steam drums are furnished with carefully designed and proved internal equipment. Steam separator equipment is mechanical in nature and operates by gravity, centrifugal force, and surface tension or by a combination of these forces to remove liquid and solid contamination. Preliminary washing of the steam by feedwater or steam condensate may be done in steam separating equipment. Devices for overcoming entrainment of liquids in gas will not appreciably separate a mixture of gases, such as steam and carbon dioxide, or steam and hydrocarbon vapors.

Entrainment separation efficiency in a steam boiler is controlled not only by the mechanical equipment, the steam rate, and the water level in the boiler drum, but also by the surface tension of the dissolved solids and the liquids in the boiler water. There is usually a limit for dissolved solids above which, at normal steam rates, priming and carryover will occur. No general standard for allowable dissolved solids can cover all types of steam generators. While operators at one plant will insist that concentrations must be kept below 1000 mg/litre dissolved solids, operators at another plant with identical equipment, but with different water conditions, may be able to operate satisfactorily with 5000 mg/litre.

The same general principles apply to reduction of solids carryover in the

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NOTE—For boiler pressures between 689 and 5516 kPa (100 and 800 psig), use "flash" pressure curves slanting from lower left-hand to upper right-hand corner and the bottom axis. For boiler pressures above 5516 kPa (800 psig), use "flash" pressure curves slanting from lower right-hand to upper left-hand corner and top axis.

This chart is used to calculate the percentage of boiler water discharged by a continuous blowdown system that can be flashed into steam at a reduced pressure and recoverable as low pressure steam for heating or process.

EXAMPLE—A boiler operates at a pressure of 3103 kPa (450 psig). Continuous blowdown amounts to 4540 kg/h (10 000 lb/h). What percentage of blowdown water can be recovered as flashed steam at 5 psig pressure?

SOLUTION—Locate 3103 kPa (450 psi) on left-hand axis. Follow horizontally toward the right to the intersection with 34 kPa (5 psi) "flash" curve (point *A*). Drop vertically downward to the bottom axis and read 25.5 percent. Twenty-five and a half percent of 4540 kg/h (10 000 lb/h) blowdown = 1158 kg/h (2550 lb/h) of flash steam at 34 kPa (5 psig) pressure.

These curves have been prepared from the formula:

$$\text{Flashed steam, percent} = \frac{H_B - H_F}{V_F} \times 100$$

where:

H_B = heat of liquid at boiler pressure in Btu/lb,
H_F = heat of liquid at flash pressure in Btu/lb, and
V_F = latent heat of vaporization at flash pressure in Btu/lb.

vapor from evaporators in process operations. This is especially important where barometric condensers are used to provide vacuum, because the tail water is usually discharged directly to the sewer, and minimum solids are desirable to keep product losses and the BOD of the waste water to a minimum.

Distillation

Distillation is the time-honored method for preparing high-quality pure water. Both dissolved and suspended solids can be removed almost completely by this purely physical process of evaporation and condensation. The condensate from a water distillation unit with good steam separator equipment, and at normal evaporating rates, should contain no more than a few milligrams per litre of dissolved solids and may contain only a fraction of 1 mg/litre. The suspended and dissolved solids of the feedwater remain in the evaporator salines and are removed by blowdown and descaling operations.

The high quality of its product gave the distillation process an initial advantage over other processes for the preparation of boiler feedwater. Distillation transfers a large part of the boiler water treatment problem from the plant boilers to low-pressure evaporators where it can be more successfully handled. Single-effect and multiple-effect evaporators have found wide use in plants where large quantities of low-level heat or exhaust steam otherwise would be wasted. Low-level, or so-called waste heat, is not worthless; its cost is too often underestimated in the overall plant heat balance and in the original plant design.

Compression distillation equipment may be economical where low-level heat is not available in sufficient quantity or is being put to more valuable use. These units, employing the heat-pump principle of salvaging the latent heat of evaporation, have the heat economy of 15 or more effects of multiple-effect evaporation. Compression stills may be electrically driven or may be powered by other prime movers. Diesel-driven compression distillation units can produce from 67 to 112 kg (150 to 250 lb) of distilled water per pound of fuel oil.

In industries where only a few milligrams per litre of dissolved solids are allowable in the process water, either distillation or one of the deionizing processes (discussed later in the "Chemical Treatment" section) can be used. The choice will depend largely upon the concentration of dissolved solids in the raw water.

Distillation equipment should be so designed that the scale and sludge problem can be handled with minimum labor. The problem is similar to that of a boiler except that the temperature usually is lower. Heat-transfer rates at lower temperatures are more vulnerable to the insulating effects of scale and sludge deposits.

Extremely high-quality distilled water can be obtained by multiple or fractional distillation. In the latter process, part of the product is condensed and refluxed to scrub entrained salts and solids from the steam being produced in the vapor generator. It is doubtful whether this quality will surpass that from a well-operated mixed-bed deionizer.

Underground Discharge

Underground discharge is a method for disposal of liquid wastes into permeable strata in the earth. It is a satisfactory method only in areas where other methods are extremely expensive or unavailable. The permeable strata must be so located that the liquid waste pumped into them will not contaminate strata used for water supply. These permeable layers are very deep, about 1200 to 1500 m (4000 to 5000 ft) being usual. Furthermore, injection wells are very expensive.

The waste water must be sterile and free from suspended solids. Extensive pretreatment is essential to remove silt, suspended solids, oil, and emulsions. Chlorination is generally provided to make sure that it is free from microorganisms. Additional pressure above that developed by the depth to the aquifer is necessary to force the water into the strata; this may be as high as 14 000 to 20 000 kPa (about 2000 to 3000 psi).

This method has been used in only a few locations because of the extensive study required and the high cost of the installation. It does have its applications, however, and should not be overlooked.

Ocean Discharge

Ocean discharge of waste water is practiced by plants in coastal locations. Actually, it is a dilution method. Consideration must be given to the path of ocean currents in the area of the outfall to ensure that the waste water will not be carried to the shore and contaminate bathing beaches. The major cost for this method is construction of an outfall to such distance that safe disposal will result.

Desalination

It has been estimated by many experts that by 1980 we will require nearly 2.2×10^9 m^3/day (600 U. S. billion gallons of water per day), which is double our present demand. Recognizing the need, and the benefits to be gained from saline water conversion, Congress enacted the Saline Water Act in 1952, and extended it by amendment in 1955 to provide for a program of research and development having as its primary objective the development of economical methods of producing freshwater from sea and brackish waters. The Department of the Interior, through the Office of Saline Water, sponsors scientific research and development through Federally financed contracts and grants, by research in Federal laboratories, and by stimulating and coordinating private activities in this field.

In 1958, a new law authorized construction and operation of not less than five demonstration plants to test some of the more advanced conversion processes. The methods selected were:

A. Multiple-effect long-tube vertical (LTV) distillation.
B. Multistage flash distillation.
C. Forced circulation vapor compression distillation.
D. Electrodialysis.
E. Freezing.

These demonstration plants have been built and operated. Complete data including costs on these plants have been published elsewhere. A brief description of each will be given here.

Method A—The seawater plant at Freeport, Tex., has a capacity of 3785 m^3/day (1 Mgd) and uses multiple-effect LTV evaporation.

Like many distillation processes, this plant is based on a system of multiple effects to achieve the degree of heat recovery necessary for a favorable economy ratio. The plant regularly operates at a ratio of 10+1 or 4.5 kg (10 lb) of product water to 0.45 kg (1 lb) of steam. The basic unit in the multiple-effect process is the LTV evaporator, which operates with a downward flow of seawater as a film inside the vertical tubes. Steam heats the outside of the tubes, and the vapor given off by the first effect becomes the steam source for the second effect. Brine effluent concentration is three- to four-fold. Product water regularly runs less than 50 mg/litre total dissolved solids.

Method B—The seawater plant at San Diego, Calif.,[2] has a capacity of 3785 m^3/day (1 Mgd) and uses multistage flash evaporation. The process involves flashing vapor from the brine at successively lower temperatures and correspondingly higher vacuums and condensing the vapor on tubes in the upper portion through which the incoming seawater is being carried.

Method C—The brackish water (about one-half the salinity of seawater) plant at Roswell, N. M., has a capacity of 3785 m^3/day (1 Mgd) and uses forced-circulation vapor compression. Start-up heat is added by means of a boiler. During operation, however, additional heat for the evaporator is added by a large compressor that compresses the vapor, adds heat, and vaporizes more brine. Inlet pressure to the compressor is essentially atmospheric at 103 kPa and 100°C (15 psia and 213°F); outlet pressure is 186 kPa at 111°C (27 psia at 232°F).

Method D—The brackish water plant at Webster, S. D. (total dissolved solids, approximately 2000 mg/litre), has a capacity of 946 m^3/day (250 000 gpd) and uses the electrodialysis process. This process involves the transport of salt ions through permeable membranes driven by an electric current. The positive ions move toward the negative poles, the negative ions toward the positive poles, and the membranes are permeable to either positive or negative ions. Water spaces between the membranes in the stack are thus alternately enriched and depleted of salt ions.

Method E—The seawater plant at Wrightsville Beach, N. C., has a

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[2] Relocated, 1964, at U. S. Naval Base, Guantánamo Bay, Cuba.

capacity of 757 m^3/day (200 000 gpd) and employs the controlled crystallization freezing process. This process uses direct-contact heat exchange between a secondary refrigerant and seawater, and centrifugal separation of ice and brine.

Solar distillation of seawater as a source of freshwater is an old process that includes all those methods in which the energy of the sun is collected and used immediately, or after a period of time, in evaporation of freshwater from seawater. While energy from the sun is abundant, it is intermittent and of low intensity. In general, solar distillation units consist of sloping glass or plastic plates covering a long, narrow, black-surfaced basin. The transparent sloping surfaces transmit solar energy which is absorbed in the basin. The seawater in the basin, warmed to a temperature as high as 71°C (160°F), vaporizes into the air space, condenses on the cooler transparent cover surfaces, and runs down the sloping cover to troughs and storage.

In addition to the processes described in the foregoing, salt removal by reverse osmosis is being evaluated in several demonstration plants, and this process shows considerable merit for brackish water.

Chemical Treatment

Chemical treatment pertains to those processes in which separation of the impurities from water involves chemical alteration of the contaminating material. It may include precipitation, ion exchange, sequestering reactions, gas removal, oxidation and reduction reactions, chemical control of biological growths, and sterilization.

Precipitation

When certain soluble salts are added to an aqueous solution, some of the free ions may react to form comparatively insoluble compounds. The precipitate can be separated by filtration or by decanting the clear liquid after settling. Precipitation occurs in accordance with definite laws governing the combining weights of the reactants and their solubility products [*6*]. Many of the methods described in the following depend upon precipitation of impurities.

Softening—The earliest commercial chemical precipitation process was the addition of hydrated lime ($Ca(OH)_2$) to water for removal of bicarbonate hardness. Lime converts bicarbonate hardness to relatively insoluble calcium carbonate:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + 2H_2O$$

The process can be carried out in either batch or continuous equipment. In either type, close control of the lime dosage is necessary to approach the theoretical minimum hardness. Chemical cost is usually low if the lime particles are sufficiently small and if good agitation is provided. Fine particles result from proper slaking of quicklime or through dispersion of hydrated lime [7].

Removal of carbonate hardness by heating the water to drive off the dissolved and half-bound carbon dioxide accomplishes the same result as adding lime:

$$Ca(HCO_3)_2 + \text{heat} \rightarrow CaCO_3 + H_2O + CO_2$$

Water containing noncarbonate hardness is only partially softened by adding lime alone. Noncarbonate hardness can be removed by adding soda ash (sodium carbonate):

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$$

Soda ash usually is combined with lime to remove both kinds of hardness in one step. The two reactions can be carried out simultaneously, hot or cold, in batch or continuous equipment. A coagulant generally is used to improve the separation of the solid phase.

Magnesium can be precipitated in a lime-soda softener by increasing the hydroxide alkalinity of the effluent to the point at which magnesium hydroxide is relatively insoluble. This can be accomplished with hydrated lime or caustic soda:

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl$$

If magnesium is precipitated by lime, there is no appreciable reduction in hardness unless additional soda is used to precipitate the calcium that replaces the magnesium. It is economical in some locations to use caustic soda alone instead of lime and soda for precipitating magnesium. This eliminated lime-slurry feeding problems and particle size difficulties.

Theoretically, magnesium can be precipitated only as described in the foregoing. At several installations, however, where high-calcium hydrated lime alone was being used for calcium bicarbonate precipitation, it has been found that about 60 percent of the magnesium was being precipitated, even though only a few milligrams per litre of hydroxide alkalinity were present. This small amount was insufficient to precipitate the magnesium as the hydrate, but certain unusual equilibrium conditions produced the unexpected result. Total reduction of hardness was within normal limits in these instances, but the amount of calcium precipitated was less than normal. The operations were carried out in the cold in sludge-blanket units.

Most continuous-process installations for lime-soda or caustic soda softening utilize accumulated sludge in suspension to promote growth of larger precipitation particles. This arrangement carries the chemical reaction and absorption processes to practical completion in a short time. The unit for performing this operation is known as a sludge-blanket precipitator. In older plants, settled sludge was mixed with the incoming water to produce the same effect. However, efficiencies were not as high as with the new units, and the older method has been more or less abandoned.

Temperature plays a very important part in chemical reaction. Where low hardness is desired and hot water can be used, as in boiler feed, temperatures from 104 to 146°C (220 to 295°F) are employed. A hardness of about 70 mg/litre is the best that can be produced at temperatures of 10 to 27°C (50 to 80°F), but this can be reduced to about 25 to 30 mg/litre at 104°C (220°F) and to 10 mg/litre at 146°C (295°F).

Zero hardness is desired for boiler feed makeup, and it is evident that the lime or lime-soda method will not provide this. Phosphate softening following hot lime-soda treatment is often used as a second softening stage; it is used for single-stage softening when the initial hardness is 30 mg/litre or less [*8*]. The theory involved is the precipitation of the calcium ion as the triphosphate, an insoluble material:

$$3Ca(HCO_3)_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6H_2O + 6CO_2$$

Any of the phosphates may be used; they are added in aqueous solution. Where the calcium hardness is mainly bicarbonate, phosphoric acid provides alkalinity control as well as lower total solids in the effluent. The reaction is carried out at a pH of 10 or higher with maintenance of a few mg/litre of hydroxide residual. The resultant hardness in the treated water is about 1 mg/litre as $CaCO_3$. Caustic soda is used for precipitation of magnesium ion when phosphates are used to precipitate calcium.

In the past, especially in European practice, barium carbonate was used instead of lime for softening. This method has not found favor in America, where it is used in only a few specific instances.

Internal Boiler-Water Softening—Usually it is unsatisfactory to depend upon external softening alone for boiler makeup water, especially for high-pressure boilers. Internal boiler water treatment may be required to convert scale-forming salts to soft sludges to be removed by boiler blowdown. Chemical compounds whose solubilities increase with a rise in temperature can be made to form nonadherent sludges [*9*]; those whose solubilities decrease with increase in temperature often form hard, adherent scale. Internal boiler-water treatment in actual practice is far more complex than these general principles indicate. This results from the wide variety of compounds and mixtures of compounds that can be formed in the boiler, and from the effects of organic matter and rates of evaporation on crystal structure [*10-13*].

It is not desirable to precipitate large quantities of minerals in a boiler, and internal boiler-water treatment preferably should be applied as a supplement to external chemical or physical treatment. Internal treatment alone may be satisfactory for low-pressure boilers, for which only moderate amounts of reasonably soft feedwater are required.

Bicarbonates and carbonates introduced with the feedwater or with internal treatment decompose in the boiler to produce carbon dioxide in the steam and to form hydroxides in the concentrated boiler water:

$$2HCO^- + \text{Heat} \rightarrow H_2O + CO_3^{--} + CO_2$$

$$CO_3^{--} + H_2O + \text{Heat} \rightarrow 20H^- + CO_2$$

The hydroxides produced in this manner can precipitate the magnesium in the boiler water as magnesium hydroxide:

$$20H^- + Mg^{++} \rightarrow Mg(OH)_2$$

During the decomposition of the bicarbonates and carbonates, some of the calcium of the boiler water is precipitated as calcium carbonate:

$$Ca^{++} + CO_3^{--} \rightarrow CaCO_3$$

The rate of decomposition of the bicarbonates and carbonates may be so rapid at boiler pressures above (34.5 kPa) (5 psig) that the calcium hardness is entirely precipitated and the hydroxide concentration becomes excessive. One method of solving this difficulty is by using phosphates [*14*]. Another method of solving this difficulty is by using chelating agents such as the sodium salts of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). These agents form highly soluble complexes with metallic ions, thereby preventing scale formation on heating surfaces.

Iron, Manganese, and Chromium Removal—Iron and manganese can be removed by precipitation, using lime or caustic soda to adjust the pH to the proper range. Groundwaters often contain iron and manganese that must be removed. These waters usually have very little color or turbidity except that due to those minerals. The iron is generally bound with carbon dioxide as the bicarbonate, and aeration is a necessary pretreatment to release the carbon dioxide and precipitate some of the iron. The addition of alkali converts the ferric iron to a hydroxide which settles out. For iron alone, a pH in the range of 8.5 is sufficient, but when manganese is present a pH above 9 is required. A coagulant is generally required to aid subsidence of the precipitate. Chlorine is often used to accelerate the rate of oxidation. Retention basins are necessary for separation of the precipitate. These may be followed by sand filters to provide a satisfactory final effluent.

Waste waters from plating operations may contain chromium, usually in the hexavalent form. Chromium in this form is toxic to aquatic and human life; it must be removed prior to final discharge.

The chromium is first converted to the trivalent form by lowering the pH to 2 with acid and adding a reducing agent such as ferrous sulfate, sodium bisulfite, or sulfur dioxide. The chemical reaction is as follows:

$$2CrO_4^{--} + 3SO_2 + 4H^+ \rightarrow 2Cr^{+++} + 3SO_4^{--} + 2H_2O$$

The trivalent chromium is then precipitated as the hydroxide with lime and pH adjustment to some value between 7.8 and 8.5. Residual chromium can be reduced to very low limits by this method.

Emulsion Breaking or Demulsification

Organic oil emulsions in waste waters present a disposal problem because the emulsion will contain considerable organic matter with a high BOD, and breaking the emulsion will release free oil which may not be discharged to surface streams. In many cases these emulsions can be broken by acidification below pH 4, but the resultant acid water is extremely corrosive and must be handled in acid-resisting structures. pH correction is required after sedimentation and before discharge to the receiving stream.

Demulsification with calcium chloride and adjustment to pH 9 with soda ash is a method that has gained acceptance. The calcium chloride dosage is high, about 2000 mg/litre, but exceptional breaking and precipitation of the emulsion have been obtained with a resultant high-percentage recovery of oil. The chemistry of this procedure is not fully understood, but full-scale installations have proved the feasibility of the process.

Ion Exchange

It may be necessary to remove the cations or anions, or both, from water to provide a satisfactory supply for process and boiler feed uses. A preceding section described removal of cations by precipitation; this process had no effect on the anions present, and other means are required to remove them.

Certain insoluble substances possess a capacity for exchanging ions bound in their molecular structure with other ions in water. The exchanged ions are released by regeneration of the exchange resin. Negatively or positively charged ions may be exchanged, depending upon the nature of the resin. A wide variety of solid materials possess this reversible property. A characteristic difference between ion exchange and precipitation processes is that the former produces only solutions for waste disposal while the latter yields both liquid and solids. This important difference may be the deciding factor in a choice of process. Disposal of sludge from a precipitation process may make it uneconomical as compared with ion exchange. On the other hand, waste water from an ion exchange process may present a disposal problem.

Natural and synthetic substances (zeolites) have been used for many years to remove calcium and magnesium ions from water. These ions are then replaced by sodium ions when the zeolite is regenerated:

Softening:

$$\text{Sodium zeolite} + Ca^{++} \rightarrow \text{Calcium zeolite} + 2Na^+$$

Regeneration:

$$\text{Calcium zeolite} + \text{excess } Na^{+} \rightarrow \text{Sodium zeolite} + Ca^{++}$$

The process will operate equally well if the calcium and magnesium ions are replaced with potassium ions or with any other positive ions that can exist in a relatively concentrated neutral solution.

In the early years of the industry zeolites were developed from natural greensand. Suitable treatment opened up the pores in the grains and hardened the surface. Exchange capacity, which was dependent upon pore area, was relatively low, about 6.4 kg/m^3. Capacities of 0.292 kg were developed by either acid or heat treatment. The natural zeolites were not resistant to high- or low-pH water, and pretreatment of the raw water was often necessary because they were easily fouled by iron or organic matter. Synthetic gel zeolites were later produced and had higher capacities, but their use was rather restricted and they have gradually been abandoned in favor of the newer synthetic resins.

With advances in the art of ion exchange, carbonaceous and synthetic resin zeolites were developed that would withstand both acid and alkaline solutions and provide both cation and anion removal. Carbonaceous zeolites are limited to about 18.3 kg/m^3 while the resins have a maximum capacity of about 1.9 kg on the cation cycle.

In hydrogen cycle operation, the material exchanges hydrogen ions for calcium, magnesium, sodium, and other positive ions; it is regenerated with sulfuric or hydrochloric acid:

$$\text{Hydrogen zeolite} + Ca^{++} \rightarrow \text{Calcium zeolite} + 2H^{+}$$

The effluent from hydrogen ion exchangers contains free mineral acidity, and it may be desirable to operate such installations in parallel with sodium cycle exchangers or to mix the effluent with untreated water to neutralize the acidity. The combination of sodium and hydrogen cycle ion exchange makes it possible to remove the hardness and reduce alkalinity at the same time. The bicarbonate hardness is converted into dissolved carbon dioxide, which can be removed by degasification.

Where the anions must be removed from the water, the process usually is operated in two stages. The water first flows through a hydrogen-regenerated cation unit, and the acid effluent is then passed through an acid-absorber anion exchanger.

In this two-step process, the acid effluent is usually degassed to remove free carbon dioxide before passing through the acid-absorbent exchanger to complete the deionization. The degassing step can be eliminated if a strongly basic, acid-absorbent exchange medium is used. If the hydrogen exchange of the first step is complete, the product from the final unit will be neutral and low in ionized solids. If the effluent from the hydrogen cycle contains positive ions, these ions with their negative components will pass through the acid-absorbent units and appear in the final effluent. It is therefore essential to have good operation of the hydrogen cycle in this process. Depending upon the solids in water, the two-step units will produce an effluent with a conductivity of about 10 to 50 μmho. Two or more stages, or a mixed-bed unit, will be necessary if higher purity is required.

Weakly ionized materials in water passed unaffected through the older type of ion exchangers. Thus, silica was not removed by the original two-step hydrogen exchanger and weakly basic acid absorber. If the silica is converted into the strongly ionized fluosilicic acid by addition of fluorine compounds at some point in the process, the fluosilicic acid can be removed by the weakly basic acid absorber. The development of strongly basic acid absorbers has solved economically the problem of ion exchange removal of silica without the use of fluorine compounds.

In general, silica removal has been carried on along with anion removal using highly basic anion resins. Where softening and silica removal are required but not complete demineralization, the use of strongly basic anion exchangers following normal sodium-regenerated cation exchangers has served the purpose economically. The capacity of anion resins for silica removal has been found to be a function of the caustic soda dosage used for regeneration. Silica reductions to 1 mg/litre or less from 35 mg/litre have been obtained by this method [*15*].

Initial cost, process, and control problems of two-step deionization are now being reduced by the use of mixed-bed deionizers. The hydrogen exchange and acid-absorbing materials are mixed intimately in a single bed in these units. A mixed-bed unit performs like multiple stages of the two-step process and can deliver water with extremely low ion content. The breakthough of ions at the end of the operating cycle can be made extremely sharp with mixed-bed units. During backwashing, the two media separate by differential density, with the hydrogen exchanger below the acid absorber. The acid absorber can be regenerated with caustic soda and rinsed through the spent hydrogen exchange material. The hydrogen exchanger is then regenerated by introducing acid through a distributor located just below the anion absorber medium. Another method of regeneration is to introduce simultaneously the caustic soda at the top of the anion resin and acid at the bottom of the cation resin bed, removing the spent caustic and acid together through a common collector located at the interface of the beds.

Ion exchange must complete with distillation for the production of high-purity industrial water. The choice between the two processes depends largely upon the total concentration of ionized and nonionized substances in the water supply, and whether sterile water is required from the process.

Other forms of mixed-bed or multiple-bed ion exchangers are of commerial importance. One involves simultaneous sodium and chloride exchange, in which both kinds of ions in the regenerating solution serve a purpose. The sodium ions regenerate the cation exchange material, liberating calcium and magnesium ions, while the chloride ions regenerate the anion exchange material, liberating bicarbonate ions. These units will replace hardness with sodium ions and bicarbonates with chloride ions. The two ion exchange materials need not be completely mixed; the unit can be operated with the material in the layers that develop during backwashing. This method is feasible, but it is not widely used. Two stages are employed more often, the first to remove calcium and magnesium, utilizing sodium chloride for regeneration. In the second stage, the anion material absorbs the bicarbonate ion and replaces it with chloride ion. Here a mixture of sodium chloride and caustic soda is used for regeneration. Although the salt performs the regeneration, the caustic has been found to lengthen the life of the resin, which results in higher capacity [*16*].

Ion Exchange in Waste Treatment—Ion exchange is being used to recover chromium from waste waters. The chromic acid waste is first passed through an anion exchanger to remove the chromium in accordance with the equation:

$$H_2Cr_2O_7 + 2R\cdot OH \rightarrow R_2\cdot Cr_2O_7 + 2H_2O$$

The actual removal is believed to occur in two or more successive reactions:

$$H_2CrO_4 + 2R.OH \rightarrow R_2\cdot CrO_7 + 2H_2O$$

$$H_2CrO_4 + R_2\cdot CrO_4 \rightarrow 2RHCrO_4 \text{ (or)} \, R_2\cdot Cr_2O_7 + H_2O$$

The anion material is regenerated with caustic soda, which releases the chromium as sodium dichromate:

$$R_2\cdot Cr_2O_7 + 2NaOH \rightarrow Na_2Cr_2O_7 + 2R\cdot OH$$

The products of regeneration are then passed through a cation exchanger to convert the sodium dichromate back to chromic acid:

$$Na_2Cr_2O_7 + 2HR \rightarrow 2NaR + H_2Cr_2O_7$$

This treatment recovers the chromic acid and concentrates it for reuse.

The chromic acid content of plating waste waters varies from 100 to 500 mg/litre CrO_3. The recovered chromic acid has a concentration of about 30 000 mg/litre or 3 percent CrO_3, which is sufficiently high for reuse. The waste water has been rid of dilute chromic acid and it can be reused or discharged to a stream.

Ion exchange has also been used for recovery of certain ionized organic compounds. These include nicotine from water used to wash the gases from cigarette drying, and tartaric acid from winery wastes. Nonionized fruit sugars have been recovered from cannery wastes and citrus peels, and pectins from grapefruit wastes, by ion exchange. These are special applications but show the wide range of applicability of this process to the treatment of waste waters for product recovery.

Ion Exclusion—A technique, known as ion exclusion, has been evolved which has many possibilities in waste-water treatment and certain process operations. It allows separation of ionic and nonionic materials, such as sodium chloride from ethyl alcohol, sodium chloride from formaldehyde, and sodium sulfate from glycerin. Thus, separations that were never economically possible are now quite feasible.

The method provides for alternate feeding of the aqueous solution of ionic and nonionic materials and water into an exchange column. One volume of feed solution is usually followed by one or more volumes of water. An aqueous solution of ionic material comes out of the column first, followed by an aqueous solution of the nonionic material. The separation of the ionic material from the nonionic material may be quite sharp.

Separations of this kind are possible because of the peculiar behavior of an ion-exchange bead in an aqueous solution of a mixture of an electrolyte and a non-electrolyte. In such solutions, the electrolyte tends to be more concentrated around the bead, while the nonelectrolyte tends to have the same concentration within and outside the bead. This difference in concentration between the two solutes is the basis for the process. The ionic material appears to be rapidly flushed through the void spaces between the individual ion beads, while the nonionic material is retained in the column for a longer period since it diffuses through the resin beads as well as around them.

Resins used in ion exclusion do not need to be regenerated because they never become exhausted; the only operating cost is for water and pumping [*17*].

Ion Retardation—Another ion-exchange process for separating water-soluble materials is ion retardation. This has resulted from development of a resin that has both anionic and cationic exchange sites located in the same bead. The resin will therefore adsorb both anions and cations from the feed solution. The resin sites are so closely associated, however, that they partially neutralize the electrical charges in each other; the adsorbed ions are thus weakly held and may be displaced from the resin by water alone.

Ion retardation is a column operation in which alternate portions of feed and rinse water are passed through the column, as in ion exclusion. It permits separation of two electrolytes, such as ferrous sulfate from zinc sulfate, sodium hydroxide from sodium chloride, and ammonium chloride from zinc chloride. It will also separate electrolytes from nonelectrolytes, and salts from very large nonelectrolyte molecules.

Like ion exclusion, this technique holds promise of adding another tool to the fractionation of process streams and treatment of waste waters.

Sequestering

The foregoing subsections have been devoted to water-treating processes in which chemical constituents are removed as precipitates or by ion exchange. A third chemical method is that of sequestering the impurity into soluble complexes. In the sequestering process, certain normally positive ions, such as calcium and magnesium, are so strongly held in a complex negative ion that the equilibrium concentration of the free metal ion is extremely low. The concentration of free metal ions can be depressed by this process to the point where the insoluble soaps will not form. Water so treated may have a soap hardness of zero, and it can even redissolve precipitated calcium soap.

Nearly 100 years were required between Thomas Graham's first studies of sodium metaphosphate and the general recognition that a soluble negative complex ion of calcium does exist. The discovery [*18*, *19*] of the soluble phosphate-calcium complex was made with sodium hexametaphosphate. Many of the poly-phosphates display this property in various degrees. Other chemicals have been found in recent years which are able to sequester hardness in true soluble complexes. Polysilicates are available that form soluble complexes with iron [*20*].

Relatively large concentrations of treating chemicals usually are required to sequester effectively even moderate concentrations of undesirable constituents. Thus the sequestering process finds its most economic application as a supplementary or final treatment after the bulk of the undesirable constituents have been removed by a process having a lower unit cost.

Oxidation

Surface- and groundwaters may contain odor- and taste-producing substances that make them unfit for drinking and for some process uses. These substances are usually organic, and often they can be removed by oxidation.

Spray ponds provide one method for accomplishing this. Water is dispersed in the air as fine droplets by spraying it over a pond through nozzles. The intimate contact between water and air provides the desired oxidation. Usually any dissolved gases are released at the same time. A forced-draft degassing tower may be used in place of a spray pond; it should provide about the same efficiency.

Oxidation with chlorine, chlorine dioxide, or ozone can be used to convert objectionable organic matter into innocuous compounds. A short contact period, usually not over 10 min, is required for complete oxidation. Certain waste waters may contain taste-producing materials, such as phenol, in small volume but high concentration. Biological treatment under these conditions would entail a very large capital expenditure, but the operating cost would be low. The capital investment can be reduced materially by using chlorine or chlorine dioxide, because the operation would be the equivalent of a waste treatment unit. The waste-water flow would be the water supply to the chlorinator and it would be discharged as a treated effluent. The operating cost for such an arrangement might be rather high, but the low capital investment would make it attractive in many instances. The effluent will contain excess chlorine, and some retention is necessary before release to a stream.

Normal biological methods are usually prohibitive where waste waters contain more than about 3 percent of soluble organic matter, because of the large dilution necessary for effective purification. A method known as wet combustion has been developed which provides efficient air oxidation through operation at elevated pressure and temperature [*21*]. The waste water is heated to not less than 350° C and the pressure raised to 13 800 kPa (2000 psi). Air is blown through the liquid under these conditions, and effective oxidation of the organic material takes place, with purification efficiency well above 90 percent. Power requirements for this process are very high, but with effective power and heat recovery, the economics of the operation are satisfactory.

A catalytic oxidation method has been developed for organic wastes plus water that are produced in the vapor phase and that can be prevented from condensing prior to treatment [*22*]. The waste feed is raised to 300° C and, together with air in the ratio of 300 to 700 percent of the requirement for oxidation, also heated to 300° C, is fed into a converter containing copper or manganese chromite catalyst maintained at about 600° C. The reaction is exothermic, and means must be provided to remove enough heat to hold the catalyst at 600° C. Conversion efficiencies of 90 percent and above can be achieved by this method, with organic concentrations as high as 8 percent; the method is uneconomical at concentrations below 1 percent.

Iron in water above 0.3 mg/litre and manganese over 0.2 mg/litre are generally objectionable. Both can be removed from most waters by lime-soda or caustic soda precipitation process. They also can be removed by oxidation, precipitation, and filtration because of the comparative insolubility of hydrated ferric and manganic oxides. Aerated water is passed through contact filters in which the filter medium acts as a catalyst for the oxidation reaction. Manganese is more dependent on catalytic contact than is iron in this process. Silica sand is often a suitable contact medium for iron removal, but complete manganese removal usually requires pyrolusite (manganic oxide) or special manganese zeolite. These manganese zeolite units are not cation exchangers but are contact oxidizers that are regenerated by treating zeolite with manganous sulfate and potassium permanganate. The higher oxides of manganese are deposited on the zeolite granules during regeneration. Contact with this material oxidizes ferrous and manganous ions to insoluble hydrated oxides, which are then removed by filtration. Such units are employed most economically as a final treatment to remove the last trace of iron and manganese from effluents that already have been treated by a less expensive, but less efficient, process.

The sodium-cycle ion-exchange process will remove ferrous and manganous salts simultaneously with hardness if these metals are present as bivalent ions.

Neutralization

Neutralization of acidity or basicity may be necessary to provide satisfactory process water or for treatment of waste water. Many groundwaters contain such high concentrations of carbon dioxide that the water is quite acidic. Aeration will remove most of the carbon dioxide, but not all of it, and the pH may still be so low that the water is corrosive for general purposes. Accordingly, neutralization is provided to raise the pH to the desired value.

Calcite filters, which consist of pressure vessels filled with pulverized marble, can be used if the quantity of water is small. The carbonic acid is neutralized by the calcium carbonate and the water is stabilized at the same time. Stabilization means that the alkalinity-pH ratio is automatically adjusted to provide a water neither corrosive nor scale-forming.

Alkali feeds are used where large volumes of water are needed. The solution feeder comprises equipment for continuously feeding a water solution of caustic soda, soda ash, or lime slurry. Provision is made for controlling the rate of chemical addition to maintain the desired pH value. The control may be manual or automatic, through a pH recorder-controller. Neutralization is not instantaneous, and a contact period must be provided, usually not more than 5 min. The alkali solution may be fed by gravity or by pumping into the stream to be treated. Liquid storage tanks are usually designed for 12- to 24-h operation between refills.

Chemicals may also be fed dry. Only soda ash or lime may be used in dry feeders because caustic soda is too hygroscopic to permit uniform feeding. The dry-feed machines operate either on the volumetric principle, in which a measured amount is displaced each stroke, or gravimetric, whereby the flow of dry material is weighed continuously. The dry chemical discharges into a mixing box where it forms a solution or a suspension. It is then allowed to flow by gravity, or is pumped, to the point of application. These machines can be made to operate in proportion to flow rate or to pH response. Hoppers over the machines provide chemical storage of 8 to 24 h.

Where lime or lime-and-soda methods of softening are employed, the effluent will contain caustic alkalinity. This excess alkalinity generally must be neutralized. This is done by adding acid, usually sulfuric or carbonic. The amount of acid fed is determined by the resultant pH value desired. The usual control is by a pH recorder-controller.

A 10 percent acid solution is normally used to treat relatively small volumes of water. Concentrated acid is fed if the volume is large. A metering pump is preferred for acid feed in large-volume operations. The pump can be controlled for ratio-flow control, pH control, or a combination of both. Acid-resistant storage tanks, piping, and pumps must be used.

Both alkaline and acidic waters are encountered in waste treatment. Free mineral acids and free alkalies must be neutralized before discharging such waters. This means neutralization to the methyl orange or the phenolphthalein end point, respectively. Rarely is it necessary to go above pH 4.6 or below pH 8.3. The neutralized waste water will not reduce the total alkalinity in the receiving stream. It is very difficult to maintain pH values above 5 since slight increments in alkali feed cause wide swings in pH as neutrality is approached.

Where acid and alkali waste waters are discharged in the same plant, blending these may be all that is necessary for satisfactory neutralization. Any deficiency of one waste can be made up by a separate chemical feed, and the final blended effluent can be discharged at the desired pH. The blending should be carried out in an acidproof tank providing sufficient time for full reaction. Neutralization studies in the laboratory will establish the period of retention required.

Consideration must be given to the type as well as to the concentration of acids in waste waters that must be neutralized. Such acids as hydrochloric or nitric can be neutralized with lime without trouble since the salts produced are soluble in high concentrations. With sulfuric acid, there is a very definite limit if high-calcium lime is to be used; the acid concentration must be held below 0.3 percent if calcium sulfate deposits are to be avoided. Concentrations up to 1 percent can be handled successfully if dolomitic lime is used. If other acids are present, the resultant depression of calcium sulfate solubility must be taken into account. An example of this is a blend of neutralized nitric and sulfuric acids in which the calcium sulfate solubility was reduced to 1100 mg/litre from about 2000 mg/litre.

Acids can be neutralized by upward flow through granular limestone beds [*23*]. The flow rate is usually 3340 to 5350 litres/min/m^2 (25 to 40 gal/min/ft^2) of bed, and beds 0.9 to 1.5 m (3 to 5 ft) in depth are placed in acid-resistant tanks. These beds are quite effective because of the turbulence created as the water is forced to flow upward. Sulfation must be avoided where sulfuric acid is neutralized, or the limestone particles will cement together.

Gravity flow is necessary for handling large water volumes if high pumping costs are to be avoided. Usually, both rate of flow and acid concentration will vary widely. The multistage neutralizer [*24*] can be used to deal with this difficulty. The neutralizer consists of several chambers in series, up to six in number, each provided with a mechanical mixer. The waste water flows from the top of one chamber to the bottom of the next one, thereby providing ample reaction time without short-circuiting. Lime slurry is fed at alternate chambers; the feed rate is governed by pH recorder-controllers. The first chambers of the multineutralizer function as equalizing units and the alternate ones as reaction vessels. Before designing such a system, detailed reaction-rate studies must be made to establish total retention time, reaction time, and rate dosage.

Silo storage of burned lime is usually provided together with gravimetric feeders and slakers and effective slurry storage. The slurry, usually 10 percent, is circulated past the feed valves and back to the slurry storage by centrifugal pumps. Provision must be made for holding constant back pressure on the feed valves. Excellent effluent control can be achieved with an installation of this kind for treating waste flows as high as 37 850 to 56 775 m^3/day (10 to 15 Mgd) with lime requirements of 108 t (120 tons) per day.

Degassing

Dissolved Carbon Dioxide—Dissolved carbon dioxide can be chemically removed by adding lime, soda ash, or caustic soda to form soluble bicarbonates or relatively insoluble carbonates. This method requires careful chemical control. Approximately the same result can be obtained with less control and supervision by passing the water through a bed of material with which the dissolved carbon dioxide will react chemically to form a neutral or alkaline product. The most common material for this process is crystalline or granular calcium carbonate, such as crushed calcite or limestone. The calcium carbonate slowly dissolves by reaction with the carbon dioxide to form additional bicarbonate hardness in the water:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca(HCO_3)_2$$

Such a unit also acts as a filter, and periodic backwashing may be required. The initial investment is the principal cost of the process; chemical replacement and operating costs are small. The additional hardness added to the water by the process may be objectionable [*25*].

Chemical Removal of Dissolved Oxygen—To supplement physical deaeration, dissolved oxygen also can be removed from water by chemical means. Sodium sulfite is used extensively as a final treatment to consume the small trace of dissolved oxygen which is not removed by deaerating feedwater heaters. Sulfite reacts rapidly with dissolved oxygen at boiler water temperature to form sulfate:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_2$$

It is easy to determine sulfite in boiler water, and the concentration and consumption of sulfite can be used as a convenient chemical integrator for checking the performance of the physical deaerating equipment. Sulfite at boiler water temperature may reduce certain chemicals, however, such as iron and copper salts, and a material balance may be slightly inaccurate. Ferrous iron salts and hydrazine have been used as oxygen scavengers. Colloidal iron, tannin, and other chemicals are also used for their oxygen-consuming properties.

Contact Reduction of Dissolved Oxygen—Steel wool contact filters have been used in the past for dissolved oxygen removal through oxidation of the metal, the products of corrosion largely remaining in the filter. Steel wool filters in some waters liberate ferrous salts, which consume additional dissolved oxygen beyond the filter. The slow rate of oxygen consumption by steel wool contact filters has limited their commercial use. Contact reduction of dissolved oxygen can be brought about by a reversible oxidation reduction process using an amine exchange resin. Inasmuch as this material can be regenerated by chemicals, it is similar to ion exchange.

Dechlorination and Removal of Gases by Chlorine—Sulfite, sulfur dioxide, and thiosulfate or bisulfite can combine with dissolved chlorine in a dechlorination process. The reactions may be represented by the equations:

$$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$2Na_2S_2O_3 + Cl_2 \rightarrow Na_2S_4O_6 + 2NaCl$$

Chemical methods usually are employed only for removing low chlorine residuals. Chlorine gas, on the other hand, may be used to convert ammonia or ammonium ions to chloramine, which can be removed from solution by aeration.

Sterilization and Disinfection

In general, all waters, whether surface or ground, contain bacteria, the type and number depending upon existing conditions. Groundwaters taken from sand strata usually are free of pathogens but may contain a fairly high count of soil organisms not harmful to man. Water taken from rock wells may or may not contain pathogenic organisms.

Surface streams are prone to bacterial contamination from both soil and man, the amount of the latter increasing greatly with sewage discharges. Other types of bacteria can be present in large numbers where industrial pollution is present.

Soil bacteria must be more or less completely removed from water for municipal supply, and pathogenic organisms must be absent. In industrial waters, small numbers of organisms can usually be tolerated, depending upon process use. It is thus apparent that these organisms must be eliminated if satisfactory potable water supplies are to be provided.

Where small volumes require sterilization, as in the laboratory, heating to boiling temperature is sufficient. When continuous treatment is necessary, as in a water purification plant, bactericidal agents are employed. The most common of these is chlorine, either as a gas or as hypochlorite.

Feeding gaseous chlorine requires specially constructed equipment and, while the gas may be diffused into the water to be treated, the general practice is to feed an aqueous solution of it. This results in full utilization of the gas and better control. Gas chlorination is generally employed when 6.75 kg (15 lb) or more is required per day, because there is no saving in the cost of the feeding equipment below this quantity.

Bleaching powder, high-test calcium hypochlorite powder, or sodium hypochlorite solution are used where only small amounts of chlorine are needed. These solutions are fed by gravity or pumped into the system by a diaphragm pump. The available chlorine in these compounds is much more expensive than gaseous chlorine, but the low equipment cost and simplicity of operation more than offset the difference.

The amount required to provide a residual for sterilization is in general dependent upon the amount of organic matter in the water, because this must be oxidized before there can be a residual. Most groundwater is low in organic matter, and the effluent from a filter plant is usually very low. Feed of 0.5 to 1 mg/litre under such conditions will provide a residual of 0.2 mg/litre as combined chlorine. Feed rates of 10 to 40 mg/litre may be required if the organic matter is high.

Chloramines are used where there is a large distribution system or a reservoir open to sunlight, because chlorine alone may be dissipated too quickly to ensure sterile water. Chloramines are formed by adding ammonia in a 1+4 ratio of ammonia to chlorine. The chloramines are not as active as free chlorine, and a minimum contact time of 15 min is required. Chloramines are very persistent, however, and they provide more satisfactory sterilization in long distribution systems.

It has been found that a combined-chlorine residual will not always destroy all of the microorganisms in the system and that tastes and odors sometimes occur in sequence. This problem is combated by maintaining a free-chlorine residual. This is done by feeding sufficient chlorine to oxidize all the organic matter, thereby providing a residual of free chlorine. This practice is now followed at most waterworks.

Chlorine dioxide is a product that is finding favor in eliminating tastes and odors, for it is also an excellent sterilizing agent. This is produced by reacting sodium chlorite solution with a chlorine solution at pH 3.0. The resultant solution contains both chlorine and chlorine dioxide. Its use has been successful in eliminating tastes and odors in many cases when other methods have failed, and the residual appears to persist well.

Accessory equipment is required for making a solution of the chlorite and for feeding it. Furthermore, a reaction chamber is necessary for mixing the two solutions. The chlorine dioxide and chlorine combination is more expensive in terms of actual available chlorine, but with a difficult taste and odor problem it provides the only way to eliminate it.

Sterilization of water is also effected with ozone generated by passing an electrical discharge through dry air. It must be generated at the site in expensive equipment with a high electrical demand. The gas and air mixture is bubbled through the water as in a normal aeration system. The cost of installation and operation is considerably higher than for chlorinators, except in large waterworks. In addition, measurement of residual ozone is nearly impossible; as a result, it has been used in very few locations.

Bromine possesses the same sterilizing properties as chlorine but it is a more difficult material to feed and control. So far, it has been used experimentally in some swimming pool installations.

Ultraviolet light can kill bacteria in clear water. The light must be generated at the point of use, and the equipment is complex. A few experimental units have been installed in the past, but the method has not been generally accepted.

Silver iodide has excellent disinfection properties when fed as a soluble salt. Its high cost precludes its use except during war emergencies. It was made in tablet form during World War II and was extensively used by the armed forces.

Control of Biological Growths

Various biological growths in water may require chemical treatment, either to inhibit their growth, to kill them by sterilization, or to stimulate them with hydroponics. The objectionable organic growths in industrial water systems may include pathogenic and nonpathogenic bacteria, algae, slimes, iron and manganese bacteria, sulfur bacteria, and a host of other microscopic and macroscopic organisms. Some organic growths are dangerous to health, others cause bad tastes and odors, and still others cause clogging of equipment and piping.

Chlorination processes are effective for control of most biological growths in water [*26*]. Chromates and salts of copper, zinc, and silver also are used for this purpose. Organic compounds such as phenol, chlorinated phenol derivatives, naphthenates, quaternaries, and many others under a wide variety of trade-names are available for biological growth inhibition. Copper sulfate, with or without aliphatics such as citrates to keep the copper in dilute neutral solution, is used for the economical control of algae in large bodies of water such as reservoirs and lakes. Treatment with considerably less than 1 mg/litre of copper sulfate is usually satisfactory, depending upon the type of algae [*27*] and the care that must be taken not to kill fish. The amount of the treatment need only be sufficient for a limited top water layer and not for all of the water in the reservoir. For large quantities of water used only once, the economic choice for biological growth control is usually limited to copper sulfate, chlorination, and ozonation.

In smaller bodies where the water is reused, as in circulating cooling water basins, treatment with other chemicals may be economical. Intermittent chlorination may be economically satisfactory for control of biological fouling in cooling water systems. Residual free chlorine in the order of 0.5 to 2 mg/litre is satisfactory in most cases for control of slimes and the spat or larval stage of larger organisms. Intermittent treatment with bromine also is used to a limited extent, especially for the control of such macroscopic organisms as mussels, which are resistant to chlorine.

Incineration

Incineration is not usually considered as a waste water disposal method, but there are certain cases where it is applicable. When the volume of waste water is under 40 litres/min (10 gal/min) and the soluble organic concentration is above 4 percent, the waste can be sprayed into the boiler furnace for evaporation of water and combustion of organics. The boiler furnace must be large enough to handle the vapor load. Some additional fuel will be required, and the fuel-feed and burners must be of sufficient size to handle this increase. This method can generally be used only with oil-fired boilers. If the waste water contains toxic materials, a modified unit provided with its own burner and fuel supply can be used effectively for destroying the compounds.

A great deal of study is necessary, followed by pilot operation, before incineration can be used effectively, but the technique does provide a satisfactory answer for certain waste water problems.

Physicochemical Processes

Several important water treatment processes depend upon combined chemical and physical action. These are coagulation, adsorption and absorption, crystal growth deactivators, additives for changing surface tension, and corrosion inhibition.

Coagulation

Most surface waters contain suspended matter and color. Much of the suspended matter consists of particles too small to settle rapidly, even in quiet water. Color is caused by absorption of light by suspended and dissolved organic and mineral substances. A chemical coagulant, such as alum, ferrous or ferric sulfate, or sodium aluminate, will cause the finely divided and colloidally suspended materials to be gathered together into larger particles, called floc, which will settle rapidly. A flocculent precipitate which has enormous surface area per unit of volume is produced by coagulants. This precipitate removes suspended and colloidal matter from the water by electro-physical attraction, adsorption, absorption, and physical entanglement. For example, aluminum sulfate reacts with hydroxyl ions in water to form complex aluminum hydroxides that are relatively insoluble in the pH range from 6 to 8. The particles of precipitated aluminum hydroxide, with the help of suitable mild agitation, agglomerate into visible clumps which settle by gravity. The simultaneous formation, agglomeration, adsorption, and inclusion of the suspended matter and color into the floc is the physicochemical process of coagulation.

Each coagulant has a pH range in which it is most effective. The addition of the coagulant usually changes the pH of the solution at the time the floc is formed. Acidic coagulants such as aluminum and ferrous and ferric sulfates precipitate as basic compounds and reduce the pH of the water. When the natural alkalinity of the water is not sufficient to maintain the minimum pH requirement after coagulation, it is necessary to add lime or soda. The optimum range for coagulation with aluminum sulfate is between pH 5.5

and 7.0. Above 7.0, there is a tendency for some of the alum to remain unprecipitated, and a small amount of residual aluminum will remain in the final filtered water. When the pH of the raw water gets above 7.2, the amount of coagulant necessary to drop the pH into the optimum band may be too great economically, especially if the coagulation pH is 6.3 to 6.4 for the water. Accordingly, sulfuric acid is added ahead of or with the aluminum sulfate to reduce the pH to the proper range for good coagulation. Sulfuric acid will lower the pH much faster and at less expense than the coagulant.

Ferric sulfate is an effective coagulant over the wide pH range of 5.5 to 10. It has an acidic reaction and lowers the alkalinity of the water. Ferrous sulfate, while effective over a wide range, is generally used between pH 8.5 to 10. In addition to requiring alkalinity for coagulation, there must be an oxidizing agent to convert the ferrous iron to the ferric state. Usually there is enough dissolved oxygen in the water to complete the oxidation; if insufficient, some form of aerating device is employed to increase the oxygen content. Chlorine also is frequently added for this purpose.

Many factors affect the amount of coagulant needed for optimum results. Among these are type and amount of suspended matter, water temperature, rate of mixing, and retention time. Coagulant dosage may vary from 5 mg/litre for a good water very low in turbidity and color to 100 mg/litre or more for a highly turbid one. Presettling is usually provided when turbidities continually run over 400 to 500 mg/litre, to reduce the coagulant requirement.

Continuous and proportionate feeding of the coagulating chemical is necessary for effective coagulation. In addition, control of the pH in the optimum range is essential. The coagulant can be fed dry or in solution, depending upon the amount to be fed and specific conditions. Usually quantities up to 45 kg (100 lb) per day are fed as a solution. Above this, dry-feed machines are employed with a dissolving tank so that a dilute solution is fed; with proper physical arrangement the dry material can be fed directly into the water.

The coagulant should first be thoroughly dispersed in the stream to be treated. This is accomplished in a high-speed mixing chamber having a retention of from 0.5 to 1.0 min. After the dispersion, the finely formed flocs require agglomeration by very gentle agitation so they can develop into large masses. Slowly revolving paddles in a chamber providing from 40 to 60 min retention will bring the floc to maximum development and produce one that will settle rapidly and provide a satisfactory supernatant for filtration.

Adsorption and Absorption

The processes of adsorption and absorption of organic and colloidal materials into flocculent precipitates with a resultant increase in sedimentation rate are used to remove color, taste, and odors from water. High silica concentrations also can be economically decreased by ferric and magnesium flocs. These processes are more efficient in terms of chemical consumption when the flocculent precipitate develops in the water than when a preformed precipitate is added.

Adsorption on ferric hydroxide can reduce the silica content to 2 or 3 mg/litre. The initial reduction occurs rapidly, but suitable mixing and retention time are required to attain minimum concentrations. The process operates best in the cold. Magnesium hydroxide also will remove silica and often is used in the lime-soda precipitation process for silica adsorption and precipitation. Magnesium can be added to the water as magnesium carbonate, magnesium bicarbonate, or magnesium oxide. Magnesium hydroxide requires a longer contact time than ferric hydroxide for maximum silica reduction. It differs from the ferric hydroxide process in that warming the water improves silica reduction. The pH for magnesium hydroxide formation must be above 10.2, which is the usual condition with lime-soda softening. On the other hand, the ferric hydroxide process is usually carried out separately because the pH for its most economical silica reduction is about 9.0.

Taste, odor, and some dissolved gases often can be removed from water by adsorption on activated carbon. This material can be added as a powder to the filter influent and removed from the filter bed during backwashing. Activated carbon filters of granular or powdered activated carbon are available for filtered water service. Activated carbon may be partially regenerated by steam or other gases. Activated carbon filters are also used for dechlorinating water.

Crystal Growth Deactivators

The surface deactivation properties of numerous chemicals are employed in a variety of treatment processes for retarding or inhibiting crystal growth. The polyphosphates have this property in various degrees. Tannin, lignin, and many other organic materials have surface deactivation properties. Crystal surfaces are believed to be covered with molecular or submicroscopic films of the surface deactivator, thereby reducing, altering, or inhibiting further crystal growth.

Threshold treatment is an example in which calcium carbonate deposits are inhibited, although concentrations above the normal solubility of the scale-forming material are present. Calcium phosphate precipitation in feedwater equipment can be inhibited in the same manner. This technique is also used to retard precipitation of ferric iron in water containing dissolved oxygen; thus red-water troubles frequently can be reduced by crystal deactivation.

Surface deactivation is used as an aid in keeping trace elements in solution for hydroponics, in limiting crystal size, and for many other special uses. An ever-increasing number of surface active chemicals, under a wide variety of trade names, are available to the water conditioning engineer.

Additives for Surface Tension Changes

Numerous chemicals have the property of significantly changing the natural surface tension of the water. Chemicals which markedly decrease surface tension are called wetting agents, and those which materially increase surface tension are often spoken of as foam suppressors. Wetting agents in a wide variety of commercial forms are available for many industrial uses, such as ore-separation processes, laundry operation, fire fighting, acid cleaning, and a host of others. Numerous chemicals that increase the surface tension of water also are commercially available for reduction of foaming and priming difficulties in steam generators.

Corrosion Inhibition

Water conditioning for corrosion control involves both physical and chemical processes operating together. Protective films that inhibit metal deterioration are physical barriers. The formation and maintenance of such films may be the result of chemical reactions. These physicochemical corrosion inhibition processes are briefly described in the following three subsections.

Cathodic Protection—The electrolytic theory of iron corrosion, as postulated by Whitney [*28*] and demonstrated by Walker and associates [*29*], is essential for understanding the process of cathodic protection [*30*]. According to this theory, metals in contact with water tend to go into solution, forming positively charged ions. Positive ions can go into solution in an electrically neutral system only if an equivalent number of positive ions of some other element are plated out. In the case of pure water in contact with a metal, such as iron, hydrogen ions are plated out at the interface. The reaction may be written:

$$\begin{array}{ccccccc} \mathrm{Fe} & + & 2\mathrm{H}^{+} & \rightarrow & \mathrm{Fe}^{+} & + & 2\mathrm{H} \\ \text{Metal} & & \text{Ions} & & \text{Ion} & & \text{Atoms} \end{array}$$

The liberated hydrogen forms a thin, insulating film on the metal which prevents further corrosion. Thereafter the corrosion reaction proceeds at a rate that is a function of the rate of removal of the layer of atomic hydrogen. The observed effects of dissolved oxygen, temperature, pH, salt concentration, and turbulence on this protective hydrogen film on iron and steel have been found to agree with this theory [*31*]. Any method for maintaining the protective hydrogen film will reduce corrosion.

Galvanizing steel provides a form of cathodic protection. Here the protective hydrogen film is maintained on the exposed steel cathode at the expense of the zinc anode, which slowly goes into solution. Magnesium and zinc rods or plates suspended in water and electrically connected to the steel tank are further examples of cathodic protection. In other forms of this process, direct current is supplied from an outside source to maintain the protective hydrogen film on the steel cathode, and a corrosion-resistant anode is used. A sacrificial anode, such as an abandoned pipeline, also can be used. Various types of commercial equipment are available to provide cathodic protection. Cathodic protection often is used to inhibit corrosion in cold-water tanks and pipelines. By a variation of this process, hulls of steel ships can be protected from electrolytic corrosion caused by copper-alloy propellers.

Physicochemical Corrosion Barriers—Any type of continuous film that is chemically inactive in water and is tenaciously attached to the metal will inhibit aqueous corrosion. Painting and molten-metal plating are examples of physicochemical corrosion barriers. A corrosion-inhibiting film also can be developed from the metal itself by chemical action. Metal oxide finishes and chromate, silicate, phosphate, and tannate films are examples of chemically produced corrosion barriers. The art of chemically producing and maintaining uniform corrosion-resistant films on the various engineering materials is a complex field.

A well-maintained steel boiler might be defined as a clean, thin, continuous film of water-insoluble material, reinforced by steel, and used to generate vapors. The development and maintenance of this thin continuous film, usually consisting of metal reaction products, depend on many factors. Raising the pH of the water in contact with steel to between 10.5 and 11.7 to develop a more uniform protective film is common practice for steam boilers. Other conditions such as the removal of dissolved oxygen and carbon dioxide by physical or chemical deaeration will improve the uniformity and tenacity of the protective film. Volatile nitrogen compounds (neutralizing amines) are used to neutralize carbonic acid [*32*, *33*]; filming amines are used to provide a monomolecular protective film [*34*]. Venting of such gases as carbon dioxide [*35*] from steam condensate systems results in an increased pH and improves the protective film. In open cooling-water systems, chromates [*36*] and silicates [*37*] are widely used for the development of thin, uniform protective films on steel. Organic materials such as tannin and lignin compounds are also used for this purpose.

The polyphosphates [*38*] under controlled conditions can form protective films on steel and cast iron. Polyphosphates, organics, and chromates are often used together for cooling-tower corrosion inhibition. Where serious deposits of calcium carbonate scale will not develop, it is sometimes desirable to increase the pH in cold, hard-water lines [*39*] by a controlled lime treatment to reduce corrosion. All the aforementioned processes are used for the purpose of developing and maintaining a thin, uniform, tenacious film to keep corrosion of pipe and equipment at minimum levels.

Inhibition of Biological Corrosion—The chemistry of biological corrosion is still in its infancy. It is believed that dilute sulfuric and nitric acids can be produced on the surface of metals by biological reactions in polluted waters. Elimination of the acid-producing organisms should prevent biochemical corrosion of ferrous and copper-alloy tubing. These organisms can be controlled by the same general processes used in physical and chemical regulation of biological growths.

Liquid-Phase Separation

With the steadily increasing demand for water, considerable thought has been given to the purification of seawater, and it is here that liquid-phase separation is being widely investigated.

The development of ion-selective membranes has led to their use in this work. Membrane electrolysis employs a stack of alternating cationic and ionic selective membranes which provides a series of parallel cells through which the raw water flows. An electric potential across the stack causes the cations and anions to move in opposite directions and to pass through the appropriate selective membranes. As a result, ions tend to leave alternate cells and to concentrate in the cells between them. Thus the stack continuously discharges two streams, one relatively demineralized and the other proportionately concentrated in the abstracted ions. The process shows promise as an economical method for desalting brackish water.

Osmoionic demineralization is another method being studied for purifying salt water with ion-selective membranes. No electricity is required, because the method uses osmotic pressure to move ions through the membrane. The procedure is effective for desalting brines with chloride concentrations in the range of 3000 mg/litre.

Dialysis and electrodialysis have been used in the treatment of certain waste waters. These methods separate ionizable salts from colloidal suspensions. The ionized salt passes through a membrane and leaves the colloidal material behind. Depending upon the material to be separated and the conditions at hand, electricity may be used as an additional driving force. These methods are being used for alkali and acid separation and recovery from process liquors.

Biological Treatment

Interest is awakening in the time-honored process of percolation of raw wastes through a bed of graded media.

Sand percolation is one of the oldest recognized methods of water purification. The process had the ability to remove color, turbidity, and bacteria by means of biological activity within a gelatinous growth on the media grains. The biologically active material provided the major purification; the graded media, or sand, served as a support for the bio-mass (known as schmutzdecke). Good purification resulted at application rates of 2300 to 2800 litres of filter per square metre per day (2.5 to 3.0 million gallons per acre of filter per day). Intermittent dosing or trickle-spray fluid application of the raw waste may be used to increase the throughput of percolation units, but higher rates tend to favor more advanced processes. Influent pretreatment may also provide minor improvement in application rates.

Biological purification is widely used for treatment of waste water containing dissolved organic matter. Bacteria break down the complex compounds into simple, stable ones; the usual end products are carbon dioxide, water, nitrate, and sulfate. This change is brought about through the metabolism and cell synthesis of the microorganisms present. Usually these processes are carried out in the presence of excess dissolved oxygen, and the operation is then known as aerobic decomposition. Another group of microorganisms can thrive in an environment devoid of dissolved oxygen. Under these conditions the process is known as anaerobic decomposition. Although most biological treatment today is aerobic, there are some wastes which respond better to anaerobic decomposition.

There are two broad types of bio-oxidation equipment, trickling filters and activated sludge. The trickling filter is a bed of graded rock, usually 0.9 to 1.8 m (3 to 6 ft) deep, but sometimes as deep as 3 m (10 ft). The bed diameter may vary from 4.5 to 61.0 m (15 to 200 ft). The rock is supported by an underdrain system for collection of the liquid flowing over it. A rotary distributor on the top provides for uniform spreading of the waste water on the bed. The underdrain system has air ducts which allow air to circulate through the bed by natural draft; this provides the oxygen necessary for good biological action. The stone provides a large surface for growth of the organisms that accomplish aerobic decomposition. The units are classed high or low rate depending upon the rate of operation. Up to 4700 litres/m^2/day (5 million gallons per acre per day) (Mgad) is considered low rate, while 9400 to 28 200 litres/m^2/day (10 to 30 Mgad) is high rate. Biochemical oxygen demand is the design criterion. The volume of the filter is based upon decomposition of 0.34 to 1.72 kg/m^3 (1 to 5 lb of BOD/yd^3) of stone per day. The diameter is fixed by the rate of application and volume of waste water to be handled per day. Actual design should be developed only after pilot plant studies of the waste water in question. Efficiencies of single filter units range from 35 to 85 percent removal of BOD. Where higher efficiencies must be provided, a second unit is installed to operate in series with the first to provide two-stage treatment. Under such conditions, 80 to 95 percent purification can usually be obtained.

In the activated sludge process the waste water to be treated is held for a period of time in a tank in which air is blown through the liquid. This develops a lush bacterial suspension which brings about aerobic decomposition. The retention time will usually range between 4 and 24 h. BOD in kilograms per day is the design criterion for these units and the loading will vary between 0.24 to 2.4 kg/m^3 (15 and 150 lb/1000 ft^3) of aeration tank volume. The air required is supplied by rotary compressors or centrifugal blowers. The difuser system may be perforated pipe, nozzles, carborundum plates, or tubes. Turbomixers of various design characteristics are also used.

Purification efficiencies will range from 75 to 95 percent depending upon the waste water and the concentration of bacteria in the aeration tank water. Higher efficiencies can generally be obtained with higher bacterial concentrations, but this must be balanced against an increased air requirement. The concentration of bacterial slime (reported as suspended solids) will range from 2000 to 5000 mg/litre.

Biological purification produces sludge, whether by trickling filters or by activated sludge. This must be removed from the effluent before final disposal. Settling basins providing from 1½ to 5 h retention permit the solids to settle. Scrapers move the settled material to a central point for removal. The sludge produced by trickling filters is removed completely from the system. In the activated sludge process, a portion is returned and mixed with the raw waste water entering the aeration tank. The excess over that necessary to maintain a satisfactory concentration of suspended solids in the aeration tank is removed from the system.

The wasted sludge must be disposed of in some manner. This can be a problem because of its fairly large volume, inability to dry readily on a sand bed, and evolution of offensive odors. Bacterial decomposition of the wet sludge under anaerobic conditions will yield a sludge that dries well and has little odor; this process is widely used for sludge treatment. Closed concrete tanks providing from 25 to 60 days retention and heated to about 32°C (90°F) hold the raw sludge and allow bacterial decomposition to occur. The volatile solids are broken down from about 75 to 80 percent to about 50 percent and, in so doing, carbon dioxide, methane, and nitrogen are given off as gases. If a sufficient volume of gas is evolved, it can be burned for heating the tanks and also used for operating gas engines in the plant.

There have been many adaptations of the activated sludge process to serve particular purposes. Among the best known of these are the Guggenheim, Kraus, contact areation, dispersed-growth aeration, and biosorption methods. These have all been described in various texts and they will not be discussed here.

Where the effluent from the treatment plant must discharge into a very small stream, the amount of organic material remaining in the treated water may be too large for inoffensive assimilation; in such cases, additional purification becomes necessary. Here use is made of the oldest type of biological unit, the slow sand filter. This is simply a sand bed which is dosed intermittently with the effluent from the treatment plant. Slime growths develop on the sand and additional purification and straining take place. The effluent flowing from the underdrains is clear and has a very low BOD. The rate of flow through these filters is extremely low and extensive land areas are required, but they can do a most effective job.

Modifications of the slow sand filter are the percolation bed and spray irrigation. These use large areas of land where the soil is sandy and little or no clay is present. Percolation beds make use of the sandy soil above the ground water table and require 1.5 to 2.5 m (5 to 8 ft) of depth for good operation. Low dikes are built and means provided for dosing the areas once a day Dosing is normally equivalent to flooding to a depth of about 5 cm (2 in).

The waste is usually diluted with water to provide a BOD of 300 to 500 mg/litre and applied to give a BOD loading of 0.11 to 0.22 kg/m^2/day (100 to 200 lb per acre per day). Under such conditions, purification efficiencies of 90 to 98 percent have been obtained. In the sand, biological growths develop which utilize the soluble organic material in the waste water as food and thereby provide purification. Air is drawn into the soil during the dosing period; this provides the oxygen needed by the organisms.

Spray irrigation utilizes the same general principle. Rotating sprays or fixed sprays spread the diluted waste over a large area, which can be crop land or wooded areas. The spray period usually lasts from 8 to 12 h per 24 h. Sandy soil is a requisite, and purification is effected by biological growths in the soil. The sprayed waste water should be low in suspended solids to avoid plugging of the soil. While this method has been developed primarily for disposal of cannery and milk wastes, it is applicable to almost any easily oxidized, nontoxic waste.

A modification of the activated sludge process is the oxidation pond. In this adaptation, the waste water is held in a shallow pond for a period of days. Aeration from the atmosphere takes place and bacterial growths develop. These ponds can remove 95 percent of the BOD and kill 99 percent of the coliform bacteria; thus purification is generally sufficient to allow discharge of the effluent into streams. These stabilization ponds have been quite widely used in the paper industry and they are gaining acceptance in the textile and chemical industries. They are used as a low-cost method for municipal sewage treatment.

Summary

An attempt has been made to enumerate the principal water treatment processes serving industry at the present time. New processes will undoubtedly be developed in the future. The discussion has been limited to the main technical and economic features. Literature references have been given for readers desiring greater detail.

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Chapter 6—Technology of Industrial Water Reuse

The growing water shortage in many parts of the world has made water reuse a popular topic of concern. However, reuse actually is an ancient practice. Since there is a fixed amount of water on the earth, it is clear from the law of conservation of matter that the same water must be used over and over again to fulfill the many needs. The perpetual cycling of water from atmosphere to earth to ocean and back again to the atmosphere of course is not uniform throughout the world. In some places, water evaporated from the oceans is returned rather quickly by mountain streams with little or no use. In other cases, precipitation may percolate into groundwater systems, from which much of it may not emerge again for thousands of years. But sooner or later the natural laws which control the hydrologic cycle guarantee that all water will return to a point of use. Reuse is the inevitable result of this process.

The current emphasis on reuse of water results from the fact that water users and water uses are increasing throughout the world. Industrialization is responsible for the greatest increase in water requirements. Since the amount of water is fixed, it is obvious that the available supply must be handled more often between the time it precipitates from the atmosphere and the time it evaporates from the ocean. Each successive user along its path automatically becomes a reuser, and the more numerous the reusers, the more important becomes the subject of technology of water reuse.

Significance of Terms "Use" and "Reuse"

Considerable hysteria has been created by writers who imply that all water drawn from a resource for a given purpose is lost to the needs of other prospective water users. A thoughtful person will recognize immediately that the terms "water withdrawal," "water use," and "water consumption" are not synonymous. An industry may draw large quantities of water from a surface stream or a well, use it only once in a closed cooling circuit, and pass it on to the next user downstream. Another industry may draw very little water from the source, but use it over and over again with relatively little actual water loss. Occasionally an industry will consume virtually all of the water it withdraws. The carbon black industry is an example, because the process of making carbon black results in evaporation of most of the water back to the atmosphere. Despite this variation, the average water consumption (loss to the atmosphere, etc.) for industries as a whole, including steam-electric power plants, is only about two percent of the water withdrawn from the original source. In other words, 98 percent of all industrial water is simply passed through the plant and becomes reuse water for the next operation downstream.

The requirements of individual industries vary markedly, as one might expect. Major users, such as the chemical and metal industries, withdraw 25 to 30 times as much as minor industries, like the leather products industry. Within a given industry, one factory located in a particular part of the country may use 10 to 25 times as much water per unit of product as similar plants located elsewhere. New factories are likely to be more efficient water users than old ones, because of increasing competition for available supplies. Large installations tend to use somewhat less water per product unit than small operations, and factories in arid regions are far more water conscious than similar ones in humid areas. This pattern is evidence that industries are reasonably flexible in tailoring their water requirements to fit the local situations. It is safe to say that almost every individual factory can reduce its primary water needs by improving its water-use philosophies, introducing conservation practices, and increasing reuse techniques. Where cooling is the principal use of water, and this generally is the case, substitution of a recycle system for a once-through system can reduce intake requirements by as much as 90 percent. This, and other reuse practices, could easily counteract the twofold increase in industrial water intake predicted for the year 1980.

Today, industry as a whole uses five times more water than it draws from the original water source. In other words, it practices 500 percent reuse. Tripling the amount of reuse would make it possible to double our industrial production without increasing water intake. Of course, the quantity of water lost through evaporation and wastes would need to remain the same. In view of this possibility, it is not surprising that the number of reuse systems is increasing. A 1959 Census of Manufacturers, published early in 1961 and summarized in the *Journal of Industrial and Engineering Chemistry* later that same year [*1*],[1] showed that overall water reuse in industries other than steam-electric generation increased by about 45 percent in the five-year period between 1954 and 1959. An increase in reuse of 25 percent was observed among industries which had not reported reuse during earlier surveys. While this census was restricted to industries withdrawing 75 000 m^3 (20 million gallons) or more of water per year, it included the major users, who account for 90 percent or more of the total quantity of water withdrawn (excluding steam-electric generation). This remarkable increase in efficiency

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

of water use resulted from the variety of return flow and on-site reuse systems discussed in the following text.

Reuse of Returned Flow

About 98 percent of the 5.3 × 10^9 m^3/day (140 billion gallons) of water withdrawn daily by U. S. industry is returned to the sources from which it came. Roughly 80 percent of this is used as cooling water and thus is contaminated only with heat and concentrated dissolved solids by evaporation. The remaining 20 percent carries a great variety of contaminants in an equally great variety of concentrations. The nature of the industrial complex and the receiving stream play a major role in determining the significance of the quality of this return. If the receiving stream is sluggish or if the ratio of withdrawal to streamflow is great, the chemical, physical, and biological processes which normally restore a water to acceptable quality may be relatively inefficient, and downstream users may receive water of relatively poorer quality. As an extreme example, the quantity of water withdrawn from the Verdegris River in Kansas during the low-flow period is approximately 17 times the natural flow.

Regardless of the volume of flow in the source stream, concentration of industries along its banks can create quality problems by steadily increasing the ratio of wastes to available dilution water and reducing the distance and recovery time between users. A survey in 1959 showed that there were 254 industrial installations of 10 different types on the Delaware River and estuary. Such a complex yields a return flow with sundry contaminants in relatively low concentrations which must be removed from large volumes of water before the supply will meet certain critical process needs of downstream users. The expected increase in industrial activity in the next several decades will markedly increase the volume and variety of return-flow contaminants. This could be a serious problem to the return-flow reusers unless waste treatments keep pace with the increasing waste discharges. Organizations such as the Ohio River Valley Water Sanitation Commission, and numerous industries, already have made considerable progress toward evaluating and eliminating discharge quality problems. Standardization work by ASTM Committee D-19 on Water and similar groups is providing the tools for improved evaluation.

One should not assume that it always will be possible or even desirable to eliminate significant treated waste water discharge from all surface streams.

Groundwater

Short-term reuse systems are not nearly as applicable for groundwater sources as for surface-water sources. However, underground water may be the principal, it not the only, supply in certain areas with limited rainfall and few surface streams. This is true in parts of the southwestern United States. In such areas, pumping groundwater at rates exceeding recharge of the groundwater reservoir (aquifer) results in declining water tables and land subsidence. In coastal areas, declining water tables can result in serious saltwater intrusion. These circumstances have increased interest in groundwater recharge operations. Returning treated waste water to groundwater aquifers also is attractive because the infiltration process further restores water quality. In 1955, artificial groundwater recharge operations with treated waste water came to about 190 000 m^3/day (50 million gal/day). Long Island, New York, has a requirement for returning all cooling waters to the groundwater aquifers to maintain water level and prevent seawater encroachment.

Groundwater recharge can be accomplished either through direct injection wells, or by spreading water in ditches, ridge-and-furrow systems, or recharge basins. Recharging through injection wells is three to seven times as expensive as the surface operations, and involves the risk that water may clog the aquifer or contaminate the supply because of unfavorable chemical or geochemical reactions. Bypassing the corrective influence of the soil mantle also is a deficiency of the well recharge method. In its present stage of development, well injection is best suited to cooling water return where heat is the only significant pollutant involved. Even here, differences in pH, gas content, or oxidation-reduction potential might create significant problems, particularly if unstable constituents, such as ferrous ion, are present in the groundwater supply.

Returning water to the ground by spraying, ponding, and spreading is considerably better insurance that reusable groundwater will result. Of course these methods are applicable only to areas with favorable percolation properties. In Wisconsin, ridge-and-furrow irrigation with cheese processing wastes and spray disposal of paper mill wastes are carried on extensively with little trouble from groundwater pollution. Spray disposal of food processing wastes also is practiced extensively in New Jersey. Israel's national water system provides for recharge with both flash flood water and waste waters. A major portion of the country's total supply (both surface water and groundwater) is combined in a flexible integrated system which provides for maximum efficiency in use and reuse.

The years to come will see more efforts directed toward returning water to groundwater reservoirs for the multiple purposes of reducing evaporation loss, restoring quality, and preventing seawater encroachment and land subsidence. It is important to recognize that this type of reuse is hindered by the rather serious limitations of flow through porous media as compared with the free flow of open channels. However, water technology must make maximum practicable use of groundwater rechargd.

Cooperative Reuse Systems (Tandem Systems)

Sewage

A cooperative or tandem reuse system is a special case of return flow in which one user passes waste water from his operations directly to another user instead of returning it to a general source of supply. The most common waste water used in such an operation is domestic sewage effluent. This is because sewage plant effluent often is readily available and nearly always is of relatively qood quality. A classic example of a tandem reuse system involving reuse of municipal sewage water is Bethlehem Steel Company's reuse of Baltimore city sewage effluent. Bethlehem originally used well water for critical cooling operations, which required quality better than that of Baltimore harbor water. Eventually, increasing cooling demands and decline in water table in the aquifer beneath Sparrows Point, Md., necessitated search for another supply. Thorough study showed reuse of city sewage effluent to be the most practicable solution to the problem. This system of tandem reuse was started in 1942, and has increased from 9.46 to 47.3 × 10^4 m^3/day (25 million to 125 million gal/day), in 1960.

Tandem use of sewage effluent has the advantage of reducing demand on the primary supply and thereby extending its life. Supplying Bethlehem Steel from Baltimore city's resources would scarcely be possible. Another excellent example of the same situation is Texaco's Amarillo refinery, where an agreement was made with the city to operate the refinery on sewage effluent rather than to compete with the city for the limited groundwater resource. The cost is lower than for city water in this case.

Numerous industries use sewage effluent from their own housing developments, particularly where source water is in short supply. For example, the Santa Rita Copper Company, in New Mexico uses sewage waste in precipitation processes and then reuses it in leaching operations. Information on numerous other installations has been published [*2*].

Use of Industrial Waste

Tandem reuse of industrial waste water also is practicable to some extent and probably will be practiced increasingly because of the heavy concentration of industry in certain areas. Where limited water resources pose serious restrictions on the amount of water which can be withdrawn, this plan often is preferable to a plan involving competition among the industries for primary withdrawal. Where industries are located close together and the receiving stream is highly contaminated, water withdrawn, treated, and used by an upstream plant sometimes is of better quality than water drawn directly from the stream. If this is true, it is to the advantage of the downstream user to draw the waste directly from the first user than to pump from the original source. In the 1959 Census, the chemical industry reused 4.1 × 10^8 m^3 (109 billion gallons) in this manner. English coal mines practice tandem reuse when water-rich and water-poor mines are located close together.

The quality requirements of the second user in a tandem reuse system determines the treatment that must be applied to the waste-water effluent of the first user. Before being used as Bethlehem Steel Company's cooling water, Baltimore's sewage effluent must be subjected to supplementary settling and chlorination, in addition to the normal combined trickling filter-activated-sludge treatment.

On-Site Reuse Systems

The figures cited earlier for withdrawal and reuse show that there is considerable in-plant recycle of water after it is taken from the water source and before it is discharged as waste. This is accomplished with "on-site reuse systems," which may be divided into several principal types—simple recycle, multiple recycle, and cascade—but combinations of two or more generally are used.

Simple Recycle System

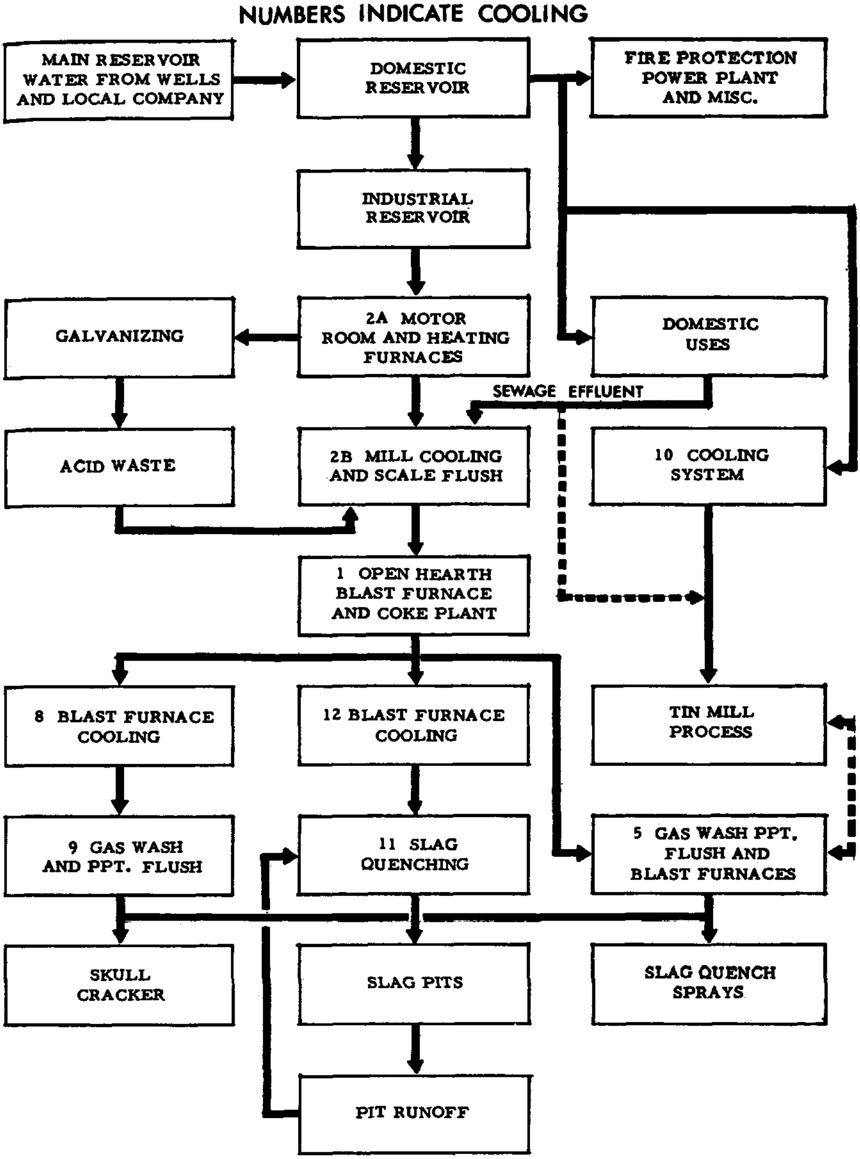
The condensate return system of a steam electric generation plant is the most common and familiar type of a simple on-site recycle system. Because of the care which must be taken in treating boiler feedwater, economic considerations require that the water be used to the maximum practicable extent once it is in the boiler system. This is accomplished by returning the steam condensate to the boiler feedline by way of the condenser, and by way of any waste heat exchangers which may be included in the system to improve economy. The returning condensate is partially degassed in the condenser and frequently is further degassed in a pressure-closed deaerator to minimize dissolved oxygen. It also may be subjected to other treatments, such as ion exchange or special filtration processes, to ensure maximum purity before it is returned to the boiler feedwater line. Were it not for inevitable losses through steam leaks and the need to waste a small part of the boiler water to carry away corrosion products and reaction products of internal boiler-water treatments, this recycle would satisfy the entire water requirement. Since these loses cannot be avoided, the returning condensate is fortified with a small amount of treated makeup water from the main water source. Condensate recycle in a well-kept boiler plant constitutes about the most perfect reuse system available.

Multiple Recycle System

In a multiple recycle system, parallel circuits carry various grades of process and cooling water of qualities suitable for the processes involved. This plan has the advantage that the several waste streams are kept separate for simplified, individual treatment and product reclamation. It also allows for individual control of temperature, pressure, and flow rate. While the circuits of a multiple cycle may operate with individual cleanup systems (ion exchange, etc.), it is more common to maintain quality in each circuit by continuously blowing a part of the circulating water to waste or to a less critical use in the same industrial plant. Where the waste water is passed to another process or cooling circuit, the system becomes a compound multicycle-cascade type. The Dow Chemical Company's Midland, Mich., plant has an elaborate multiple recycle system which handles high-pressure service and cooling water, domestic water, high-grade cooling and process water, and demineralized boiler feedwater, in five separate supplies involving many miles of distribution lines. This complex system uses eight times as much water as it draws from the original water source. Eventually all of the circuits are integrated to form a semicascade system and the final waste water is mixed and treated in a central location. In such complex operations, it is common to reclaim chemicals as by-products from the various circuits as well as from the final cascade. It is also common to mix the discharges to gain advantages from reactions of components. Thus an alkaline waste might be neutralized by mixing it with an acid waste. Final waste that cannot be reclaimed economically is discharged into a biological waste treatment plant or into disposal wells.

Cascade System

A cascade system differs from a multiple recycle system in that a single effluent stream flows from one process to another, increasing its waste content as it goes until it finally is no longer useful for any part of the operation. The water withdrawn from the source of supply first flows to the equipment or process which requires the coldest or cleanest water, and from here it passes to successive operations where progressively higher temperatures and poorer water qualities can be tolerated. Thus, the waste of one operation becomes the supply of the next. Either single passes or recycle circuits may form the various steps of the cascade, but considerable recycle is characteristic of most cascade systems. Almost every industry employs cascade to some extent. A cascade system does not reduce water loss or decrease the waste which eventually must be treated or discarded. On the other hand, it generally reduces the number of water-cooling and waste-treatment facilities required, and, of course, increases the percentage of reuse. Its principal shortcoming is the need for designing heat exchangers and processing equipment to tolerate the relatively poor quality of water in the later stages. It also is more difficult to reclaim specific by-products from the integrated waste stream that results from a cascade system. The Kaiser Steel plant at Fontana, Calif., is the classic example of this type of reuse system. Here a mixed plant supply of well water and local company water is used for stepwise cooling of motors and heating furnaces; mill cooling and scale flushing; and cooling open hearths, blast furnaces, and coke plants. After this, it is divided into parallel streams for further cascading. These streams handle less critical operations like gas washing, precipitative flushing, and blast furnace cooling. The streams finally are mingled and used for quenching slag. The diagram of the circuit presented in Fig. 1 shows that some water is diverted for use in the tin mill, and that some is reclaimed from



Kaiser's Fontana, Calif., system of multi-recycling cascade is so effective that the plant withdraws only 5320 litres (1400 gal) of water per ton of steel produced, whereas as much as 247 000 litres (65 000 gal) are required in some plants. It can be said that the water is wrung dry in this 3000 percent reuse system.

FIG. 1—*Example of water reuse system.*

the slag pit. Much of the final waste water is lost by evaporation from the slag pit.

While a cascade system does not reduce the amount of water lost by evaporation and may actually increase it to some extent, it does markedly increase the ratio of water used to the water withdrawn. In the case of Kaiser's plant, each gallon of water is used 30 to 40 times, so that the plant withdraws only 5320 litres (1400 gal) of water per ton of steel produced, whereas as much as 247 000 litres (65 000 gal) of water per ton are withdrawn in some plants. Such a cascade plant is more costly to build, but it has the advantage of ability to operate in an arid zone where it might be impossible to operate otherwise.

Examples of cascade reuse can be found in almost every industry. In Holland power plant blowdown (boiler waste) is used for coal washing. Stack gas wash water and mine waste are used for the same purpose. Any number of stepwise combinations can be used to advantage where shortages provide the incentive.

Process Integration Systems

In some cascade and recycle systems, production of particularly troublesome waste necessitates high dilution of final concentrated effluents or extremely costly waste disposal systems. The black liquors produced by sulfite and neutral sulfite semichemical (NSSC) paper mills are examples. Until recently there was no profitable process for reclaiming raw materials from such liquors, and the relatively high percentage of organic matter contained in them caused rapid depletion of oxygen and consequent pollution in receiving streams. Use of the waste in road-binding operations and spray disposal on wastelands were the most practicable solutions to the black-liquor problem. The latter occasionally caused serious iron contamination of groundwater systems due to complexing actions of organic components.

Occassionally, troublesome wastes can be handled by ingenious integrations of industrial processes. Sonoco Products Co. of Hartsville, S. C., has perfected such a system for handling black-liquors. Formic and acetic acid are first reclaimed from the waste water, which is then combined with kraft mill waste to generate raw materials useful in the kraft process. It is possible to reclaim 98 percent of the NSSC black-liquor water in evaporators. A flow sketch of this integration system was shown in *Industrial and Engineering Chemistry* [3]. Numerous other possibilities for improving reuse through process integration can be and have been exploited in controlling industrial waste problems.

Quality Problems in Reuse

Heat Dissipation

The extent to which water can be used is determined in large part by the effectiveness of quality control treatments in the reuse system. Since approximately 80 percent of all industrial water is used for cooling, elimination of heat contamination is a major consideration. In recycle systems, cooling is accomplished with spray ponds, cooling towers, evaporative condensers, and air-cooled heat exchangers. All but the last depend on the cooling effect of evaporation. Approximately 1 percent of the circulating water is evaporated for every 6 deg C temperature reduction, and the loss is the same regardless of the type of system in which the evaporation is taking place, provided the relatively small windage losses are disregarded. Even when there is a considerable wind-loss factor, cooling tower water consumption generally is no more than twice that of a once-through system, in which the water flows directly to the source stream. The effectiveness of an evaporative cooling system, like cooling of heated water in a river, is determined by the wet-bulb temperature of the environment, since this is the absolute lower limit to which the water can be cooled by evaporation. The actual terminal temperature may range from a degree or two below atmospheric temperature, at high humidity, to -1°C (30°F) or more below atmospheric temperature when the air is very dry. Thus, evaporative coolers are most effective in arid regions.

Forced-draft cooling towers with bottom fans and countercurrent air flow are gaining favor over induced-draft (top-fan) and natural-draft types. All types of cooling towers are more efficient than spray ponds for industrial cooling applications because of the better contact between water and circulating air.

Evaporative condensers combine cooling-tower and process-cooler functions in a single operation. In a typical installation, cooling water is sprayed on condenser tubes of a refrigerating system to condense refrigerant and release heat to a circulating air stream, thus dissipating heat. The plan is best suited to unit process cooling operations. A single installation in General Electric's Electronics Park Site has 68 evaporative condensers.

Air-cooled heat exchangers waste no water by evaporation, but they can cool only to within a few degrees of atmospheric temperature, and thus are limited to relatively high-temperature applications. Compounding systems to cool as far as possible with air and then to continue temperature reduction in a cooling tower or evaporative system of another type often is an economical way of handling cooling loads.

Organic Deposits

Open cooling systems are likely to develop algae and bacterial slime growths. In the United States, organic growths generally are controlled with chlorine or with nonoxidizing bactericides and algicides, whereas the British chimney-like cooling towers depend on light-tightness for elimination of some of the nuisance organisms. Antirot and fungal control treatments are available for protection of construction materials and fill in wooden towers, but slow deterioration is inevitable.

Corrosion and Mineral Deposits

Corrosion also is a pertinent consideration in the metallic components of recycle systems. This is handled by use of resistant components and by inhibition with soluble oils, phosphate or chromate compounds, silicates, zinc compounds, and dianodic mixtures as required. Organic and mineral acids frequently are fed to maintain proper pH, and minimize deposit formation. It is also feasible to control pH by diverting a part of the cooling water through an acid-type cation-exchange resin instead of by direct feed of acid. The so-called "starvation process" employed in Great Britain is an interesting form of this treatment. Here a carboxylic acid type of exchange resin is used which reacts only with carbonate alkalinity, thus making it impossible to overacidify the circuit or to generate free mineral acid. The process requires no more acid for regenerating exchangers than would be required to treat the circuit directly.

Troublesome scale and sludge deposits will accumulate in any recycle system if evaporation yields concentrations of water components above saturation values, or if circulation rates are inadequate to keep undissolved solids in suspension. Deposit formation generally is avoided by draining a part of the circulating water to waste to maintain acceptable concentration ranges and by replacing this waste with fresh makeup water. The percentage of waste water can be calculated from a knowledge of the composition of feedwater and behavior of the wastes involved. Information for calculating tolerable calcium sulfate contents is given in *Industrial and Engineering Chemistry* [*4*].

Safe disposal of concentrated blowdown wastes is a pertinent consideration in every reuse system. A variety of organic and some inorganic wastes can be separated by standard processes like coagulation, sedimentation, demulsification, skimming, flue gas stripping, filtration, centrifugation, and biological and chemical oxidation. Certain soluble inorganics require more costly treatments, like evaporation, electrodialysis, and ion exchange.

Profitable Aspects of Water Reuse

Wherever possible, an attempt should be made to recover by-products from waste waters of reuse systems in order to defray a part of the cost of operation. The extent of by-product recovery is limited only by the resourcefulness of the technical staff. Paper mills reclaim large amounts of usable fiber from wash waters; refineries salvage oils from their integrated wastes; mines recover much coal from washers; platers obtain copper from chemical baths and spent ion exchangers; steel mills dredge oxide from scale pits in sizable quantities; and brewers recover from process waters vitamins and antibiotics that otherwise would go to waste.

In some instances, by-product reclamation processes also generate high-quality water for reuse. For example in the plating industry, ion exchange resins simultaneously remove metal ions continuously from circulating wash waters and generate freshwater for continued washing. The trapped metals are valuable for recharging the plating bath, as mentioned in the foregoing.

The benefits derived from by-product recovery can be very sizable. Whether or not such reclamation is economically practicable depends on the size of the operation.

Reuse systems also can save money in initial water costs. Price advantage in reuse will increase as increased industry results in greater contamination of primary water supplies and primary treatment costs increase accordingly. Depletion of local water supplies and need for long-distance transport also will generate a price advantage for reuse systems.

One should not overlook the intangible profits of reuse, including reduction in chemical, thermal, and biological pollution; flexibility for plant expansion without providing larger water mains and sewers; relative simplicity of treating and otherwise handling concentrated waste waters which result from recycle; and maximum freedom from water pollution by upstream users.

Planning a Reuse System

The time will come when every existing industry must think seriously about improving its water use facilities and this inevitably will mean increased reuse. By the same token, new industries should give serious consideration to the role of reuse in their proposed operations. In either case, the following elements will be pertinent to developing a sound plan:

(*a*) Quantitative and qualitative water requirements of all process operations.

(*b*) Relative cost of alternative water supplies.

(*c*) Water use efficiencies of various plans and counterplans.

(*d*) Adaptability of various reuse systems to the operations involved.

(*e*) Overall economic advantage of alternative systems.

(*f*) Severity of ultimate waste disposal problems.

In any evaluation of this type, it is important to remember that water use is a very dynamic operation because of our rapidly changing industrial economy. Thus, flexibility should be an integral part of plant design and continuous appraisal a recognized aspect of water use.

Future Outlook on Industrial Reuse of Water

Anyone with industrial experience will be quick to recognize that reuse of water can involve some very troublesome features. Pages already have been written on the effects of small quantities of detergents in return-flow operations, and these troubles have been generated by minute quantities of the contaminant in question. Certain components of process waters could easily generate corrosion problems that require much more careful attention to water-handling equipment than now is required. Experience shows that initial investment almost always is higher in a plant designed primarily for high-percentage reuse.

One should also be careful not to overlook the very real problem of disposing of concentrated wastes which all recycle systems must generate sooner or later. While these wastes occur in relatively small volumes, their disposal to streams in periodic slugs can produce serious local effects, which are often more serious than continuous discharge of dilute waste from a once-through system. Much of the success of reuse depends on discovering ingenious methods of disposing of these wastes without their being returned to the water courses. Processes like the slag quenching employed by Kaiser, or deep-well injection employed by Dow Chemical Co., are steps in this direction.

These disadvantages will not discourage water reuse. Increasing demands for industrial water and expanding legislation for pollution control will cause a steady increase in the cost of industrial water supplies and effluent treatment. As the cost of the primary supply approaches the cost of recycle and cleanup, reuse systems will become increasingly attractive and more prevalent. To keep pace with this trend, more attention must be given to methods for sampling and testing waters and waste waters. The work of ASTM Committee D-19 is aimed in this direction.

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Chapter 7—Self-Purification and Other Natural-Quality Recovery Mechanisms

Water is the most plentiful liquid on earth. It is a requirement for all life, whether it is used in metabolic processes, as a solvent of minerals, or in the disposal of waste. Indeed, it is difficult to name a natural phenomenon in which water, in one form or another, has not had an essential role.

Nature has provided for the conservation of this abundant and valuable liquid by endowing it with a considerable capacity to rid itself of foreign substances. This process, known as self-purification, is an inherent system for water. Man's only problem with the system is that the water does not always clean itself quickly and completely enough for the next intended reuse. Almost all of the processes used by man to clean the water are accelerated natural-quality recovery mechanisms. The water may be moving in streams, or be relatively static as in lakes or the oceans, but the natural processes of purification are proceeding toward completion. Advantage is taken of this intrinsic ability of water to purify itself by using it as the final polishing treatment for all municipal and industrial waste discharges.

Streams contaminated by natural, human, or industrial wastes are rendered stable by self-purification. Eventually, this water becomes innocuous and is again reused by man or nature. This purification is accomplished by combinations of the physical, chemical, and biological forces present in the water environment. The extent to which each force operates is dependent upon the contaminating substance and the particular water environment in which it is present. Physical forces separate suspended solids; chemical forces cause reactions which neutralize the nocuous wastes; and biological forces stabilize the water by using the contaminating substances as nutrient sources and by enchancing both physical and chemical phenomena. Generally, the biological forces are the most active and the most important in the self-purification of a stream.

The Dynamic Equilibrium

Water, as vapor, is present in the atmosphere in amounts that we express as relative humidity. Condensation of this vapor causes the formation of droplets of water which are pure until they fall through a contaminating atmosphere as rain, hail, or snow. The purity of the water is further affected by contact with the soil or other surface.

The atmosphere usually contains a number of contaminants, especially in areas of heavy air pollution. Such pollutants may be in the gaseous, liquid, or solid state. Some solids, such as dusts, are laden with bacteria, yeasts, and molds. In addition, the air contains the spores of microorganisms which exist in the atmosphere without benefit of being attached to solid particles, or entrapped in aerosoled liquids. Some bacteria and viruses, also occur in the atmosphere as free-floating agents. Thus the atmosphere possesses a distinct and variable microbiological flora.

The microflora of the atmosphere provide one of the sources of living matter constituting a normal stream biota.When the water of the atmosphere falls to earth, the microorganisms and other matter present in the air are washed out and settle upon the ground. Many of these microorganisms become entrapped in the soil, while others are carried directly into streams with the rainfall runoff. In addition, the water picks up microorganisms that are indigenous to the soil, which nearly everywhere is teeming with these microscopic life forms. In this manner, water accumulates a wide variety of microorganisms by the time it flows as a natural stream. The higher aquatic biota vary widely depending not only on the microflora but also upon the geochemistry, temperature, and the land character of the stream banks through which the stream flows. Thus the runoff from a mountain is totally different chemically, physically, and biologically to the runoff from a swamp.

After water has formed one of the surface streams of the earth, it establishes very characteristic biological flora, chemical composition, and physical properties. The stream continually comes to equilibrium with its environment, or changes due to the area through which it runs. The stream biota reflects changes in the qualities of water received by the stream. For example, if such waters contain domestic wastes (those derived from human populations), the stream biota will respond with increases in the population of organisms which are able to use these substances as food until either the food is consumed or some other growth requirement becomes limiting. As though to rid their environment of the unnatural or unusual added material, the complete biota of the stream changes. This ability of the stream to change its biota, its chemistry, and its physical properties in order to restore its original state of purity may be termed "the dynamic equilibrium." The forces of self-purification—physical, chemical, and especially biological—are constantly interreacting to improve the quality of the water.

The Natural Balance

Nature provides each stream a balanced biota, whether a clean mountain stream with little contamination, or a heavily laden swamp stream, or a heavily polluted stream. Each of these streams is characterized by a well-balanced flora and fauna, both in the water and on the bed of the stream. This condition may well be compared to those conditions existing in a balanced aquarium. This natural order is not always in concert with man's desires for further use of this water resource, but the balance is maintained. The many forms of aquatic life from the smallest bacterium to the largest fishes, are distributed in the stream in accordance with the environment. The environment influences both the number and the species present in any portion of the stream. By creating such a balance, nature provides for enough of each species of aquatic life so that the water quality is improved. Each type of plant and animal life is dependent upon the existence of other living organisms within the same realm. For example, the presence of organic or other oxidizable matter is required for bacterial growth. Protozoa depend upon such bacteria, as well a algae, for continuation of life. The rotifera and crustaceae use all these microscopic forms as a source of food, while, in turn, the large aquatic plants and animals require certain forms of the smaller members of the stream biota for their existence. Thus nature provides for an interdependence and balance of life forms in a stream environment.

Pollution

The definition of water pollution generally accepted is: Any impairment of water quality by man that is prejudicial or injurious to its suitability for other defined uses. Note that this definition does not require that something be added to the water, but considers as pollution any degradation in quality as a result of man's use of the water. Thus, a river downstream from an impoundment may be degraded if the stored water discharged has lost its dissolved oxygen or if its temperature is too low for summer recreational uses such as swimming, even though its temperature possibly has improved for a trout habitat. Pollution through increased turbidity may be caused by withdrawal of sand and gravel from the river bottom, with the waste wash water and silt returned to the stream.

Although the effects of temperature increase or decrease are presented in detail in Chapter 8, it needs to be pointed out that not all temperature changes of normal ambient river water are "thermal pollution," since the change may not be degrading the quality for other defined uses. When a water discharge temperature is considerably below that which is normal in a given stretch of river, it has been observed that temperature recovery to normal values is much slower than the concurrent rise in dissolved oxygen to saturation in the same stretch of river. Under conditions where the dissolved oxygen content recovers in 8 km (5 miles), the temperature of very cold water discharged from an impoundment may require as much as 64 km (40 miles) for recovery.

Degradation in water quality may occur below impoundment discharges at certain times of the year, for other reasons. Water in the lower layer (hypolimnion) of thermally stratified impoundments may become anaerobic for several months of the year. Discharged water entering the streams below the impoundment may be low in oxygen during warm summer months, when dissolved oxygen content may be most critical for a waste discharge. Because of anaerobic conditions in the hypolimnion, the stored water may contain hydrogen sulfide, iron, and manganese. Hydrogen sulfide lost to the atmosphere below the dam may be a nuisance there. Iron generally oxidizes rapidly and is precipitated on underwater surfaces; these surfaces become visible during low flow periods. Manganese creates more difficult problems of removal or treatment for users downstream. Cold water discharge from the hypolimnion may increase the efficiency of power plant or industrial condensers and may promote trout fishing, but the low temperatures will prevent swimming, and also change the balance of numbers and species of aquatic organisms.

When mineral acids or alkalies are added to a stream, either intentionally or accidentally, many natural factors may be involved in recovery mechanisms. Observations of a stream reduced to pH 2.5 by release of a mixture of hydrofluoric and fluosilicic acids indicated surprisingly rapid recovery to a normal pH. There was complete absence of obvious toxicity in the river a few miles downstream from the point of hydrofluoric acid addition, apparently because of reaction with silicates in river bed minerals. The reaction of hydrofluoric acid with silica apparently produced silicon tetrafluoride, which was lost to the air. This self-purification process was chemical, rather than biological, but development of a normal biological pattern quickly followed disappearance of the acid, there being ample soil organisms available for reinnoculation of the river area, once excess hydrogen ion toxicity had been removed.

A balance of biological forms is normal for all streams. Although various species of plant and animal life may predominate in each stream, no two streams are identical. Clean, pure streams, however, have certain characteristics in common. One property of such a stream is its ability to dispose of a reasonable amount of pollution. This may be accomplished without an appreciable disturbance of the normal biota. If a stream receives an unusually large amount of waste, the biota will change in an attempt to stabilize such pollutants. However, if the quantity of such foreign materials exceeds the capacity of the stream biota to render them innocuous, the higher aquatic life may be completely destroyed for a stretch of the river. As the unusual food concentration decreases, a new and different group of organisms develops as a response to the new levels of oxygen and food.

Recovery of Polluted Streams

Forces of Self-Purification

Fortunately, the forces of self-purification usually prevent such complete destruction of one of mankind's greatest assets. These forces, closely related and mutually dependent, are physical, chemical, and biological in nature.

The physical forces include the action of gravity, light, aeration, dilution, and turnover. By gravity, the heavier suspended impurities are removed by sedimentation of individual particles. Finely divided suspended solids and colloidal matter settle out of the water as aggregates or coagulated masses. Photosynthesis causes the removal of carbon dioxide and increases the concentration of dissolved oxygen. Color is removed from water by the bleaching action of sunlight and by absorption on colloids. Turbulence in a stream, as by flowing over a rocky botton, causes aeration which adds oxygen to the water by adsorption from the atmosphere. Carbon dioxide and gases of decomposition escape to the atmosphere by the same phenomenon. Influents consisting of water from tributaries, domestic sewage, and industrial wastes are diluted by the receiving stream. Such dilution assists in the rapid recovery of a stream. The turnover of pools in a stream, similar to that which occurs in lakes, is another physical factor which aids stream recovery.

The chemical forces of stream self-purification include oxidation, reduction, neutralization, and coagulation. Oxidations render suspended and dissolved organic matter harmless, the products generally being mineral matter and gases. Incompletely oxidized mineral matter may be oxidized to completion, or hydrolyzed and deposited, by precipitation, on the bed of a stream. Likewise, chemical reductions may result in the liquefaction or gasification of organic matter in the process of anaerobic decomposition. Mineral matter may be put into solution by such reductions. Ground or stream water containing dissolved carbon dioxide, in contact with carbonate rocks, dissolves calcium and magnesium carbonates as their bicarbonates. This contributes alkalinity to the water, serving either as a pH buffer or as an actual neutralizing agent for organic or mineral acids. A stream is usually dependent on entering water of recent subsurface origin for maintenance of its alkaline reserve. These neutralizations tend to maintain optimum conditions for the biochemical reactions of stream purification. Coagulation causes the precipitation and deposition of dissolved and colloidal substances on the stream bed. The removal of such materials permits other forces of stream purification to become more active.

The biological forces are not only the most important but are the most active forces; they are closely associated with the food requirements of the microbiota present.

Bacteria known as heterotrophs can cause the degradation of practically any organic substance with sufficient time. Newly synthesized economic poisons, however, constitute especially refractory substances. Instead of degrading within a reasonable time frame, they tend to accumulate within the protoplasm of the biota. Many of the economic poisons, including endrin, chlordanes, and DDT, are very sparingly soluble in water. Instead of bacterial degradation, the molecules are taken into the fauna and migrate to the fatty tissues. The molecules in the fatty tissue are relatively innoccuous until the organism experiences stress or starvation, or both, when death may occur. It is an interesting philosophical question whether the reduction in the concentration of the insecticide in the flowing water by biological uptake constitutes stream purification where the molecules may still endanger the biota or one who uses them for food, or both.

Less toxic, newly synthesized organic molecules will persist for days rather than for hours with normal food substances. Very few studies have followed the fate of such compounds as trichlorophenol or dichlorotyrosine.

Many groups of the heterotrophs have rather specific nutritional requirements so that the identity of the bacteria which respond depends on the presence of specific molecules of normal food. Thus, the genus *Klebsiella* is found in streams below industries processing cellulose, because the members of the genus can decompose partially degraded cellulose while very few other genera of bacteria can do it. The ability of different groups to respond to a wide variety of foods greatly assists in the purification process. Many groups of such bacteria have relatively specific nutritional requirements, and their demands for sources of food material greatly assist in the purification of a stream. Fats, carbohydrates, and proteins are all converted by aerobic or anaerobic processes to products of a simpler chemical nature. Often, several groups of bacteria cooperate to degrade such compounds in a series of interdependent steps.

Other bacteria, known as autotrophs, live in inorganic environments and complete their life cycle without the benefit of preformed organic matter. The sole sources of carbon for such microorganisms are carbon dioxide, carbon monoxide, or carbon suboxide. Minerals essential for the continuation of life are obtained from inorganic salts. The autotrophs are divided into groups that have specific nutritional requirements. Some live by oxidizing elemental sulfur, sulfides, thiosulfate, or tetrathionate. Others reduce sulfates to sulfide or to elemental sulfur. Nitrifying bacteria convert ammonia to nitrate. Iron organisms oxidize ferrous iron to the ferric state. Other groups of autotrophs are capable of oxidizing phenols and cyanides. In fact, as our knowledge of autotrophism grows, we realize that there are few, if any, unstable inorganic compounds that cannot be converted to stable products by such microorganisms. As in other reactions caused by bacteria, this conversion often proceeds through a series of individual reactions resulting in a specific product which, in turn, is utilized by another group of microorganisms. An example of this is the oxidation of ammonia to nitrate, where Nitrosomonas oxidizes ammonia to nitrite, and Nitrobacter oxidizes the nitrite to nitrate. The autotrophic bacteria thus can convert many unstable compounds to stable material which can be utilized by higher forms of life.

The action of bacteria-destroying agents, known as bacteriophages, has a very important role in ridding a stream of pathogenic microorganisms. Such bacteriolytic viruses are present in sewage and in the intestinal tract of man and animals. They specifically destroy, by lysis, certain pathogenic bacteria, especially the etiologic agents of the typhoids and dysenteries. Also, the pus-forming bacteria, staphylococci and streptococci, are rapidly destroyed under favorable conditions. Present knowledge does not indicate that bacteriophages have any effect upon the microorganisms normally occurring in streams.

The algae utilize carbon dioxide, an end product of bacterial decomposition, and liberate oxygen. This aids in the reaeration of streams and induces rapid stream recovery. In addition, certain inorganic and nitrogenous substances, also occurring as the result of bacterial activity, are converted to cellular material. The algae then serve as a source of food for many of the higher forms of aquatic life.

The protozoa live on organic and nitrogenous matter. Many species prey upon bacteria, while other species find that the algae provide all of the nutrients necessary for their life process. Some protozoa contain chlorophyll, and are similar to the algae.

The rotifera, the next higher form of aquatic life, prey upon the protozoa and consume algae. Many are saprophytic organisms and feed upon decaying organic material. This group serves as a source of food for other members of the stream biota.

The crustaceae, consisting of aquatic arthropods, feed upon many of the lower forms of life, especially on the algae and smaller aquatic plants. Such animals serve to maintain a balance between the lower and higher forms in the stream biota.

Rooted forms of aquatic plants utilize the organic and mineral matter in bottom deposits. Also, such forms assist in the aeration of the stream by utilizing carbon dioxide and liberating oxygen. Aquatic plants create excellent habitats for fish and other forms of stream life.

Large aquatic animals burrow in mud deposits in search of food. The bottom sediments are disturbed and thus made more satisfactory for growth of smaller organisms. One aquatic animal will survive by devouring another. By such carnivorousness, the animal life of a stream is kept in balance.

Living things in streams are dependent upon many variables. If some extraneous factor causes an unusual increase in the population of a particular group of the flora or fauna, another portion of the biota will rise to diminish this abnormality. The ability of the forces of self-purification to return a stream to its normal condition, or to adjust itself to a new condition, represents a real dynamic equilibrium.

Zones of Pollution and Self-Purification

A whole series of events occur when pollutants, such as domestic and industrial wastes, are discharged into a stream. These changes take place along the course of the stream, usually in zones that are not sharply divided but that gradually blend into one another. Such areas shift with meteorological and hydrographic conditions. Despite this variability, classical zones of differentiation have been established that are of interest in the natural purification of streams.

The first area after the entrance of a pollutant is the zone of degradation.

If the pollution is a domestic or an organic industrial waste, the water becomes dark and turbid. Sunlight is shut out. Coagulation may occur and suspended matter settles to the bottom. A deposit of sludge is formed and decomposition starts. The bacterial flora increases greatly and reduces the supply of dissolved oxygen. There is an increase in carbon dioxide. Fish may be very active, especially if the waste will serve as food. If the pollutant is an inorganic industrial waste, its toxicity might inhibit most of the aquatic life. When this occurs, dilution must take place before any stream can begin to recover. The water flora typical of this zone appears as decomposition progresses. Specific groups of bacteria will predominate, depending upon the type of waste. Algae may develop; if so, they will consume carbon dioxide, and help to replenish the supply of oxygen. The presence or absence of odors will depend upon the efficiency of reaeration. The growth of green plants is inhibited by the color and turbidity of the water, which reduce photosynthetic activity. The number of microorganisms, other than bacteria, decreases because of unfavorable conditions.

Eventually the zone of degradation gives way to a zone of active decomposition. Here, the dissolved oxygen is nearly depleted and aerobic microorganisms gradually disappear. An anaerobic condition may result, and putrefaction will occur, with accompanying foul odors. Bacteria will continue to flourish, anaerobic microorganisms taking up the work of the aerobes as the supply of dissolved oxygen is entirely used up. But as soon as the stream becomes partially reaerated, the aerobes will again predominate. The growth of algae will rid the stream of excess carbon dioxide and help to reestablish a favorable oxygen balance. Large aquatic plants and animals will be present only in areas of favorable oxygen supply.

Following this zone is the area of recovery and clean water. The water gradually becomes clear, and the bottom deposits do not evolve offensive odors. The dissolved oxygen increases probably to saturation. There is enough carbon dioxide to supply a normal aquatic flora. Bacteria decrease in number as the predatory microorganisms develop. Various protozoa, rotifera, and crustaceae are present. Algae become established, and the larger aquatic plants reappear. The more tolerant fish are present, until the zone of clean water is reached. The clean water is characterized by the normal flora and fauna previously discussed.

In natural streams, there is a considerable overlapping of these zones. Some zones are completely eliminated. At times, certain zones may cover extensive portions of a stream. The whole cycle of self-purification is adaptable to innumerable conditions. The process may be retarded, interrupted, or accelerated by the entrance of new waste materials or tributary waters. Each stream operates under conditions peculiar to it alone.

Effect of Pollution on Dynamic Equilibrium

The dynamic equilibrium, or the capacity of a stream to recover after receiving pollutants, is affected by domestic and industrial wastes. Streams receiving domestic wastes such as sewage undergo the classical cycle of zonal self-purification. The same is true, in most instances, for organic industrial wastes. A notable exception is that some wastes are toxic and inhibit, or prevent, the operation of stream purification processes. The same is true of many inorganic wastes.

Acid mine drainage is a pollutant that is indigenous to bituminous coal regions. It is characterized by being highly acidic and containing large concentrations of ferrous iron. It is formed by the oxidation of sulfuritic materials (represented by the formula FeS_2) of both operating and abandoned bituminous coal mines. A chemosynthetic autotrophic bacterium (Ferrobacillus ferrooxidans) enhances the reaction several fold where the pH of the water is in the range from 2.8 to 3.5. Dissolved oxygen is utilized by these ferruginous effluents through the oxidation of ferrous iron to the ferric state. Owing to the presence of Ferrobacillus ferrooxidans, which increases the oxidation rate, the area in which dissolved oxygen is being consumed is kept to the shortest possible stream distance. After the deposition of iron, as basic ferric sulfates and hydrates, the stream makes a rapid recovery and supports most of the normal forms of aquatic life.

Importance of a Well-Adjusted Stream

From the public health aspect alone, it is essential to have well-adjusted streams. Such a stream, owing to its dynamic capacity to respond to the entrance of foreign materials, will quickly rid itself of pollutants. It will remain a clean, healthy stream, and will be a distinct asset to the community. But the capacity of the stream to respond to pollutants can never be exceeded without paying the penalty of retarding the self-purification process.

A normal stream, through its inherent capacity for purification, will be free of disease-producing bacteria, and will not be toxic for any normal aquatic flora or fauna. In addition, the recreational benefits derived from healthy streams will be well worth the care and effort required for their maintenance.

Water Quality Criteria

It is difficult to establish exact criteria for the measurement of water quality. There is a wide variation in the mineral content of natural waters. Water from an unpolluted well in the Corn Belt, pumped into an Appalachian stream, would constitute a contaminant in the minds of most persons familiar only with the Appalachian groundwater. Water entirely suitable for human consumption may require treatment for use as boiler feedwater. Essential industries may produce critical wastes. The use of non-man-contaminated natural water may need to be hedged with about as many restrictions as those applying to sanitary or industrial waste.

Biological reactions provide one of the most important means for stream purification. A water treatment plant or a waste disposal plant, sewage or industrial, requires machinery and control devices, trained operators, and waste land for disposal of residues. A stream, given half a chance, performs the function of these man-built plants with no equipment or supervision whatever. All that is required is some intelligence in controlling the concentration and rate of addition of domestic or industrial effluents to a stream.

Chapter 8—Thermal Loading of Water Supplies

The discharge of heated water to streams, lakes, esturies, and groundwater can cause various effects. Some of these are detrimental while others are beneficial for subsequent uses of the receiving water. The heated discharge has been recognized as a problem in water quality and it is attracting increasing attention. Although ill effects are relatively minor at present, they may eventually become serious where thermal loading is tending to increase.

The term "thermal pollution" has been used to identify the detrimental effects of heated discharges. This is not a particularly good term because heat itself is not a pollutant. All matter contains heat, except when it has a temperature of absolute zero. The heat content of a substance is directly proportional to its mass, whereas its temperature is a measure of the intensity of the kinetic energy of its molecules. Thus it is the temperature of water that is of primary concern, rather than its heat content.

There are two related reasons for the interest in thermal loading. The first is the fact that a change in temperature will modify the environment of aquatic flora and fauna, resulting in a change in the species that can live and propagate in a given body of water. This is caused largely by an increase in the rate of biological reactions that accompanies a rise in temperature. The second is a fear that the tendency for thermal loading to increase will, in time, exceed the capacity of surface water to dissipate the added heat and thus create permanent temperature elevations over considerable areas.

There is a threefold difficulty in dealing rationally with thermal loading. In the first place, it is often assumed that any artificial temperature elevation is necessarily detrimental to a body of water. It will be shown later this is not always the case. Secondly, many people feel quite strongly that an artificial change in the aquatic environment is wrong if it injures any living thing. This is a primitive idealism that fails to comprehend the need for compromise between the desirable and the essential. Yet it contributes to minunderstandings about practical control measures. Finally, the scantiness of reliable data on the biological effects of thermal loading greatly hinders objective approaches to the problem.

Sources of Thermal Loads

Heat is added to surface- and groundwaters in many ways. Some of these are natural, some artificial. Heat is also dissipated by several mechanisms; if this were not so, the temperature of water would continue to rise.

Stream Sources

The physiographic features of surface streams vary greatly across the country. Width and depth, channel configuration and gradient, size of drainage basin and climate—all influence stream temperatures in some degree, both singly and in combination.

Excluding heat from hot springs for the moment, all natural heat in streams comes directly or indirectly from the radiant energy of the sun. The effect of solar radiation can be illustrated by the fact that the summer temperature of large rivers in western Pennsylvania rises 1° to 2°C from morning to afternoon, depending upon the amount of cloud cover. The sun also contributes heat indirectly by heating watersheds, thereby warming the rain that falls on them. The addition of heat from this source is probably a relatively minor factor because the specific heat of earth and rock is only about a fifth of that of water. Further, the cooling effect of a higher rate of evaporation would tend to increase the rate of heat dissipation. This is a complex mechanism that is difficult to generalize because it depends upon the humidity gradient above the surface.

Water flowing off the land can raise stream temperatures in some areas. This is especially true for the irrigated lands of the Far West. Water in irrigation ditches is heated by the sun. A variable proportion of this water runs off into natural streams. The effect is likely to be small where the water drains to large rivers.

The electromagnetic spectrum of the sun covers an enormous range (0.001 to 3×10^{14} A), but practically all radiation of wavelength shorter than the near ultraviolet is absorbed by the outer atmosphere of the earth, while radiation beyond the near infrared is absorbed by dust and water vapor at lower levels. The radiant energy that reaches the earth's surface is partly reflected and partly absorbed. That which is absorbed is reemitted as long-wavelength radiation. This dissipation of energy tends to lower the temperature of surface water and it accounts, in part, for the diurnal change in water temperature.

Evaporative cooling is another important factor in the dissipation of heat. The rate of evaporation of water is proportional to the air-water temperature difference and the unsaturation of the surrounding air. When the layer of air adjacent to a water surface is saturated with water vapor (at its dew point), the net evaporation is zero because the number of water molecules leaving the water surface is exactly balanced by the number condensing into it. Wind has an important effect on evaporative cooling because it sweeps away the saturated air and replaces it with air containing less moisture. The latent heat of vaporization of water is 580 kg·cal at 30°C (1045 Btu at 86°F). Thus evaporation of a cubic metre (35.3 ft^3) of water would absorb 580 000 kg·cal (2.3×10^6 Btu). This would have the theoretical effect of lowering the temperature of 580 m^3 (2.05×10^4 ft^3) of water 1°C (1.8°F).

Water is also cooled by loss of sensible heat through direct transfer to cool air in contact with it. Aside from back-radiation of energy, about 20 percent of the temperature lowering results from loss of sensible heat and the remainder from latent heat of vaporization.

Climate has a distinct effect on surface water temperature. Stream temperatures in summer range from about 18°C in the Northeast to 13°C on the Northwest Coast and parts of the Great Basin to 32°C in the Southwest and Southeast. These temperatures reflect the influence of air temperature as it varies across the country.

Groundwater Sources

It has been estimated that some 60 percent of the mean flow of streams is contributed by groundwater discharged from adjoining aquifer systems. Below the depth where the temperature of aquifers is unaffected by insolation and stream infiltration, the temperature of groundwater is practically constant in any given locality. Thus groundwater discharge tends to ameliorate stream temperatures because it is warmer in winter and cooler in summer. Shallow groundwater temperatures normally vary inversely with latitude, ranging from 3°C in northern Minnesota to 22°C in the Southwest and 25°C in southern Florida.

Below the depth at which the temperature of the earth's crust is affected by insolation, the primary control on temperature in a particular region is the relatively constant flow of heat from the interior. Other factors include the thermal conductivity of rocks and their contained fluids, volcanic or magmatic activity, and tectonic movements. The temperature of groundwater at a few tens of feet is about the same as the mean annual air temperature. Several authors report an average value of the geothermal gradient, usually measured to some depth below the zone of active groundwater circulation, of 1°C for each 30 m of depth.

Water from thermal springs can raise the temperature of streams in some areas. There are many such springs in the United States, most of which are west of the 105th meridian. The western springs arise from precipitation that has percolated into the earth and come in contact with hot geological formations. Those in the Appalachian range spring from very deep formations where the water has been warmed by heat conducted from the interior of the earth. The U. S. Geological Survey has listed 1059 springs with normal temperature at least 6°C above the mean annual air temperature. A few springs have temperatures of 100°C or more. Less than a third of the thermal springs have flows of 0.38 m^3/min (100 gal/min) or more. Thus this source of thermal loading is of minor significance. Warm Spring in Montana is the largest one on record; it discharges 303 m^3/min,(80 000 gpm) at 20° C. The aggregate flow of all thermal springs is probably less than 1900 m^3/min (500 000 gal/min).

Lakes and Reservoirs Sources

The temperature of natural and artificial impoundments is governed by physical factors similar to those that influence the temperature of streams. These bodies of water are usually quite deep as compared with streams. They therefore resemble deep, quiet rivers in certain respects. Their surface is warmed by solar radiation and cooled by evaporation and convective heat transfer. Under summer conditions in temperate climates, unless rather shallow, lakes differ from streams in that they consist of two dissimilar layers. A surface layer of variable depth lies upon a relatively stagnant layer. The surface layer is affected by insolation and the several cooling mechanisms, whereas the bottom layer is insulated from these effects and maintains a uniform low temperature. Some deep lakes, however, are nearly isothermal because of wind-induced mixing. Where cool water enters a lake, it tends, because of its higher density, to underflow the surface layer. Thus temperature variations are sometimes complex and difficult to predict.

Reservoirs can affect the temperature of streams in a manner that is not always recognized. When a reservoir is drawn down to augment low stream flows or to prepare for floor storage, the water is often discharged from the stagnant bottom layer. This cold water can have a deleterious effect on the stream biota for two reasons. In the first place, a sharp decrease in temperature can harm aquatic life just as an increase can. It is the sudden change in temperature that causes the ill effect. Secondly, stagnant reservoir water is often completely devoid of dissolved oxygen. Such water can destroy aerobic biota, notably the fishes, which are killed by asphyxiation.

Industrial Sources

Most water withdrawn for industrial operations is used for cooling. This water is discharged substantially unchanged except for an increase in temperature. The effects of these discharges are highly variable. They depend upon the temperature difference between the discharge and the receiving water, the size and configuration of the receiving stream, the rate of heat dissipation, the quality of the receiving water, and the downstream uses that could be affected. There are also certain economic considerations that are mentioned in a later section.

The generation of hydroelectric power is a special industrial use of water. This operation merely converts the potential energy of water into electric power, but it can adversely affect conditions downstream. In the first place, the operation of hydro plants is highly cyclical in many areas because the output of electricity is varied to meet changes in the demand for power. As a consequence of the variation of flow through the turbines, downstream water levels rise and fall markedly. This can cause many undesirable effects. Secondly, water flowing through the turbines is drawn from a low level in the impoundment to take advantage of the greatest possible hydrostatic head. Stagnant reservoir water may contain little or no dissolved oxygen and is generally quite cold. It can cause the effects described in the preceding section. For example, a hydro dam on the Chattahoochee River has lowered the summer temperature of the downstream stretch to 10°C from 30°C. The bass that formerly propagated in the river have disappeared because they cannot spawn in such cold water. Recently, the river has been successfully stocked with trout. On the other hand, the water is too cold for swimming. This is an example of negative thermal loading.

The electric power industry has been mentioned specifically only because it has been subjected to some of the sharpest criticism. Other industries with heavy cooling requirements contribute to the thermal loading of surface water. Their problems are similar to those of the power industry and in some cases are every bit as acute.

Municipal Sources

Domestic sewage, with or without treatment, is usually discharged to surface water at the most convenient location. This waste flow normally has a temperature well above that of the receiving water. Although it contributes measurably to the thermal load, it has consequences greater than the physical effect of raising stream temperatures. This method of disposing of sewage relies upon natural phenomena to render the material innocuous. The principal natural process involves utilization of the dissolved oxygen in surface water to oxidize the organic substances in sewage to relatively inert compounds. The rate of aerobic oxidation varies directly with temperature. Thus, as the temperature of the receiving water rises, the demand upon its limited dissolved oxygen resources increases. The increase may be great enough to use up all the dissolved oxygen. Anaerobic conditions then develop, and decomposition of the organic matter generates foul gases. At the same time, all aquatic life that depends upon aerobic conditions is destroyed. This represents a condition where a rise in temperature can have a profound effect on water quality. The situation is of course not confined to municipal sewage; the same result can occur where a heated industrial waste containing organic matter is discharged.

Many industries and some municipalities store partly treated waste water in lagoons. Some lagoons are equipped with devices that provide for discharge of the stored water in an appropriate proportion to the flow of the receiving water. In other cases, the lagoons are drawn down only during periods of local flood flows. These lagoons are generally shallow basins and their summer temperature will usually be higher than that of surface streams.

Data are not available on this source of thermal loading but the potential effects should not be ignored.

Thermal Patterns

The rate of natural distribution and dissipation of heat is a major consideration in deciding upon the size of a thermal load that can safely be added to surface water.

Field tests have indicated that the die-away of temperature in streams is roughly exponential; that is, as distance downstream from a source increases, the stream temperature approaches the natural temperature asymptotically. Thermal loads are dissipated in several ways, including back-radiation, evaporative, and conductive cooling.

Heated water discharged below the surface of a stream usually mixes rapidly with the body of water in a vertical direction. If the discharge is at the water surface, a substantial temperature gradient may persist for a considerable distance downstream, especially where the stream flow is tranquil.

Actual die-away patterns can be plotted by making a series of temperature traverses at regular intervals along the course of a stream. In predicting thermal patterns, it is necessary to measure solar radiation, wind velocity, and stream flow, as well as the decline in temperature from the source. Quite off thermal patterns are found in canalized rivers receiving a number of heated discharges. In a survey of the Monongahela River in Pennsylvania, the decrease in temperature was measured in terms of stream distance at several locations at which thermal loading had raised the stream temperature to 32°C or higher. The rate of decrease ranged from 0.5° to 3°C in several 300-m reaches. The rate of fall varied more with location than with time of year. Systems for temperature predictions on complex thermally loaded streams are not yet fully developed, but progress is being made.

The winter temperature pattern is isothermal in typical temperate-zone lakes or reservoirs under open-water conditions. There is complete vertical circulation in consequence of the uniform density of the water at about 4°C. In spring, solar heating warms the water surface, decreasing its density sufficiently to prevent mixing of the warm, upper water with the colder, denser water below. As the surface becomes progressively warmer, the density gradient steepens and the depth to which wind can mix the upper waters is diminished. The result is a separation of the lake into two isolated masses consisting of a circulating surface volume (epilimnion) floating above a relatively stagnant volume below (hypolimnion). Separating the two is the thermocline, a stratum of water of variable vertical thickness, in which the temperature decreases rapidly with increasing depth. This stratification usually persists until autumn, when cooling of the surface increases its density and leads to breakdown of thermal stability. When this occurs, the lake "overturns" under the influence of wind, and circulation of all the water results.

Wind will keep the water in circulation unless a persistent ice cover forms. In that event, an inverse type of thermal stratification will result until it is destroyed by warming and wind action. If winter stagnation occurs, it will be followed by a spring overturn and a second period of circulation.

The most significant changes in groundwater temperatures are caused by induced infiltration of surface water or the injection of warm water. Infiltration from shallow wells in several Central and Eastern locations has caused an annual variation in groundwater temperature of 8° to 18°C. In some coastal areas, it is necessary to inject water from air conditioners to restrain the intrusion of saltwater into aquifers. An example is Long Island, N. Y., where air-conditioner water is injected at temperatures 2° to 11°C higher than the water pumped from aquifers.

The rate of thermal dispersion at any point in an aquifer is mainly a function of the transmissibility of the aquifer and its extent. The thermal conductivity and specific heat of the aquifer matrix are relatively unimportant. Heat in water discharged to an aquifer through a well, or recharged from a surface water source, is dispersed both vertically and horizontally in the same manner as a dissolved solid; its rate of vertical dispersion is enhanced by convective movement due to the density contrast between the formation water and the recharge water. The pattern of thermal dispersion is also a function of the temperature of the recharge water, because the viscosity of water varies about 2 percent/deg C in the range 5° to 38°C. This causes a significant increase in the rate of groundwater flow in the thermally affected area. The thermal loading of groundwaters results in extremely complex hydraulic problems because both density and viscosity have transient values throughout the affected aquifer.

Effects of Temperature on Beneficial Uses

Surface waters provide a habitat for a great variety of flora and fauna. But the number of species that will live and propagate in a particular body of water is dependent upon the conditions of the aquatic environment. Water temperature is possibly the single most important condition of the environment because of its effect on the concentration of dissolved oxygen, the biochemical reaction rate, pH, toxicity, and the physical activity of aquatic animals.

Much of the concern over thermal loading of streams arises from its potential effect on fish. Millions of people indulge in the pleasure of sport fishing. It is a relaxing activity that helps to relieve the strains of modern living. One can easily sympathize with the asperity of dedicated fishermen when their favorite streams are threatened with a discharge of heated water.

Most species of fish can adapt themselves to a fairly wide range of water temperature, provided that temperature changes occur slowly enough. Sharp changes are often destructive, whether the temperature rises or falls rapidly. Both cold-water and warm-water species are found in the same latitude because of their adaptability to various temperature levels. There is an upper temperature level for each of the two types, however, beyond which they cannot survive. Brook trout, for example, live in a temperature range from about 4° to 24°C, whereas large-mouth bass will withstand the same low temperature but will not be harmed by an upper limit of about 35°C. Both species will survive temperatures higher than these upper limits for a relatively short time. The eggs of brook trout will not hatch at temperatures above 15°C, whereas bass will not spawn in cold water. It should be noted that fish acclimated to a temperature higher than the normal level for the species will be killed when the temperature falls to a value that is somewhat higher than the low-temperature survival limit.

There is one aspect of thermal loading upon which fishermen and aquatic biologists do not agree. In the South, as well as in the North, condenser water from power plants greatly improves fishing during the colder months of the year. Fish tend to congregate in warm water during cold weather and thus provide ideal conditions for wintertime fishing. Some aquatic biologists deplore this as an unnatural condition. The increased fish population in a limited volume of water is thought to deplete the food supply, thereby making it easier to catch fish. Large catches under such abnormal conditions would tend to reduce the size of the resident crop. As a practical matter, however, fish are plentiful where this situation has persisted for many years. One benefit is the fact that warm water serves as a refuge for species susceptible to winter killing, and some species spawn earlier in warm water than in areas beyond the heated zone.

The effect of thermal loading on dissolved oxygen concentrations is a subject upon which there is considerable misunderstanding. Oxygen is only slightly soluble in water. Equilibrium concentrations, which range from 14.6 mg/litre at 0°C to 7.1 mg/litre at 35°C, vary inversely with temperature.

An adequate supply of dissolved oxygen is essential for a healthy stream because desirable aquatic biota live aerobically. Organic matter is the food supply of bacteria and their utilization of it is an oxidative process which consumes dissolved oxygen. Bacteria multiply rapidly in the presence of an ample food supply. There organisms are the natural food of protozoans which, in turn, are devoured by more advanced creatures. This is the food chain that provides nourishment for the fishes. All the elements in this chain consume oxygen. The dissolved oxygen in streams is furnished primarily by two mechanisms: reaeration and photosynthesis. In healthy streams, the consumption of oxygen by the food chain is balanced by continual replenishment from these sources.

Aquatic biologists have agreed that, for some species of fish, the dissolved oxygen concentration should not fall below 5 mg/litre. In view of the inverse relationship between temperature and oxygen solubility, they have concluded that any increase in water temperature automatically results in a corresponding decrease in dissolved oxygen. This implies the assumption of equilibrium conditions. But static equilibria rarely occur in streams, and there is evidence for a substantial lag in the adjustment of dissolved oxygen concentrations to changes in temperature.

Many 24- and 48-h surveys have been made on large rivers and small streams in western Pennsylvania at all seasons of the year. These bodies of water receive a considerable amount of organic matter from municipal and industrial sources, but dissolved oxygen concentrations have ranged upward from 6.9 mg/litre. Also, oxygen resources were at least as high in summer as they were in winter. Bacterial metabolism and the respiration of aquatic plants and animals are continuous, whereas photosynthesis ceases at night. This has led to the conclusion that dissolved oxygen must necessarily fall to a low level at night in streams carrying a substantial load of organic pollution. Nevertheless, these surveys showed that the diurnal variation in dissolved oxygen in this area is relatively slight. However, streams with high populations of algae and other plant life will cause significant day-to-night variations in dissolved oxygen. For example, a stream with an average dissolved oxygen concentration of 7.0 mg/litre varied from a daytime photosynthesis peak of 10.4 mg/litre to a minimum nighttime sag point of 4.7 mg/litre dissolved oxygen concentration. This is not to imply that organic loads never cause a severe drop in dissolved oxygen. For example, below the outfall of a large sewage treatment plant, dissolved oxygen fell to 1.2 mg/litre from 7.1 over a distance of about a half mile downstream. These findings apply only to the area surveyed and are not to be regarded as typical. They do suggest that speculation is a poor substitute for analysis in the field.

Much of the difficulty in evaluating the effect of temperature on fish in a natural environment derives from the limited amount of reliable published data. Temperature effects are a major interest of aquatic biologists, and a great deal of data are available on lethal temperature maxima. These values have come, for the most part, from carefully controlled laboratory studies which may have no real relationship to any natural habitat. In defense of the aquatic biologist, however, it is necessary to recognize the extreme difficulty of getting good data on the effects of thermal loading on a dynamic complex of living things in a variable environment. This is a field that is now beginning to receive much needed research attention.

Recent years have witnessed a steadily growing popularity of aquatic sports. This can be attributed to the instant mobility of most of the populace, the wherewithal to purchase or rent the needed equipment, and the means to visit areas that were once financially out of reach. These recreational activities take many forms, from sailing to water skiing, water polo, canoeing, or swimming. Devotees of aquatic recreation object to an increase in temperature because swimming in warm water is not very exhilarating.

Effluents from municipal sewage treatment plants are generally discharged into nearby bodies of water. This disposal method is quite acceptable where the degree of treatment conforms with the volume of diluting water and the forces of natural purification. Aerobic biological activity is the most important of the purification forces because it converts complex organic matter into innocuous substances. Within certain limits, the rate of biological activity roughly doubles with each 10° C rise in temperature. This places a corresponding burden on the dissolved-oxygen resources of the water. A rise in temperature is advantageous where the water contains enough dissolved oxygen to accommodate the increased demand, because purification will occur more rapidly. But noxious conditions will develop wherever the demand for dissolved oxygen is greater than the supply. A rise in temperature, however, will generally stimulate the proliferation of photosynthetic organisms, especially the phytoplankton, which will help to make up the oxygen deficit during daylight and cause an added deficit during nighttime due to respiration. Warm water can therefore be beneficial in some cases, but detrimental in others.

The ability to draw a glass of cool water from a faucet would often be desirable, but the almost universal use of refrigeration makes this less important than it once was. On the other hand, the warmer the supply, the lower the cost of heating water for the laundry and other purposes. The lower the temperature of the water entering a purification plant, the more difficult the treatment becomes. For each 5 deg C rise in raw-water temperature, the cost of treatment drops 30 to 50c per million gallons processed. But warm water might promote the growth of algae that can cause tastes and odors. Thus a rise in the temperature of municipal water supplies has both good and bad features.

Industry is an extensive user of water for cooling purposes. This suggests that a source of cool water would confer a benefit so valuable that it would be a major factor in plant location. But such items as raw materials, markets, transportation, supply of workmen, and community services are usually so much more important to a successful enterprise that the temperature of the local water supply becomes a minor factor. Industry resorts to well water or refrigeration where it needs water cooler than the surface supply.

The steam-electric power industry might constitute an objection to this generalization about the limited importance of a cool-water supply. There is an inverse relationship between the temperature of cooling water and the efficiency of power generation; this is a matter of real concern in some areas.

This is necessary to protect subsequent water uses, and many kinds of specific regulations have been promulgated to ensure effective downstream protection.

It is easy to accept the abstract principle of reasonable use of streams for waste disposal because it represents economic logic. But problems arise in applying the principle in specific situations because of the difficulty of reaching agreement on the reasonableness of a particular use. This is a consequence of limited quantitative information on the actual effects of waste waters, especially those at elevated temperatures.

Summary

This chapter has described thermal loading, and the principal mechanisms by which the added heat is dissipated. The disparate effects that can result from discharges of heated water have been discussed in some detail. In particular, considerable attention has been given to the effect on fish because this commonly provokes the greatest public distress.

Due to Federal regulations, industries have or are facing the technical and economic problems associated with elimination of heated discharges.

Chapter 9—Sampling and Flow Measurement of Water

A satisfactory sample of water or waste water must meet two basic requirements: It must accurately represent the large or small mass sampled and it must be of adequate size for subsequent laboratory examination. Since industrial water and waste water must be sampled under a great variety of conditions, there is no single method that can be universally applied. The method, location, and time of sampling must be coordinated so the results obtained will serve the purpose for which the sample is intended.

Waters or waste waters are not fixed in their compositions but show appreciable changes depending upon their sources, seasonal precipitation, temperatures, wastes, and processes. This chapter discusses variations in composition of industrial water and waste water related to environment and the mechanics of the sampling operation. These should serve as guides in determining the frequency of sampling, the appropriate points, and suitable sampling apparatus.

In the study of water as an engineering material, and in the handling, treatment, and disposal of industrial waste water, flow measurement is an essential function demanding applications of many types of flow-measuring devices and equipment to suit specific conditions. This chapter includes a brief summary and description of the classes and categories of flow-measuring devices and equipment to suit specific conditions, the important points to consider in their selection, and the fundamentals of flow measurement.

Manual Sampling

Types of liquid samples are broadly classified into two major groups, one called instantaneous, spot, snap, or grab samples; and the other integrated, continuous, or composite samples. A grab sample is a collected single portion of water or waste water which serves as a spot check and is useful for investigating abnormal characteristics. A series of grab samples is necessary for tracing constituent variations. The volume of individual samples will depend on the analysis requirements. If samples are to be composited, the volume collected must be more than needed for the proportional part of the composite. To prevent serious errors in suspended solids concentration in composite samples, the original grab samples must be kept well mixed while transferring from one container to another.

Composite samples correlated with flow show the average conditions. The results are particularly useful in computing quantities of waste material discharged over a specified period of time. If the rate of flow is constant, the composite is made up of a number of uniform portions collected at frequent regular intervals. When the rate of flow varies, a weighted composite is collected. For this case, the volume of each portion is proportional to the rate of discharge at the time it is collected. Since it is generally desirable to minimize the amount of analytical work, samples are composited over 4-, 8-, or 24-h periods, depending upon conditions.

Manual sampling provides basic information useful in preparing specifications for mechanical devices designed for automatic and continuous sampling of industrial water and waste water.

Continuous Sampling

If it is necessary for sampling to extend over a considerable time, or when a continuous record of conditions at a given sampling point is required, it will be most practical to install automatic continuous sampling equipment. Correctly designed and installed, a continuous sampling device will provide more frequent samples than is practical by the manual method, will eliminate errors due to the human element, reduce costs for supervision, and eliminate the tedious routine work required by manual sampling.

Since the scope of this chapter does not permit complete description of the many automatic devices suitable for continuous sampling of industrial water and waste water, the reader is referred to other sources for additional detailed information [*1*,*2*].[1]

Sampling at Atmospheric Pressure

In general, industrial water has its origin in rain and melted snow reaching streams by direct runoff over the surface of the ground and by underground seepage. It contains very little dissolved material before starting to flow on the surface or through the earth. Where the soil and surface rocks are practically insoluble, the surface and seepage waters dissolve very little mineral matter. Mountain streams usually show little variation in composition for miles. The sampling of such water, therefore, is relatively simple except during flood stages when there are rapid changes in turbidity. This is important in the operation of a filtration plant. Normally, a sample taken at almost any location will meet the two basic requirements of satisfactory sampling. The data in Fig. 1 [*3*] are an excellent example of this.

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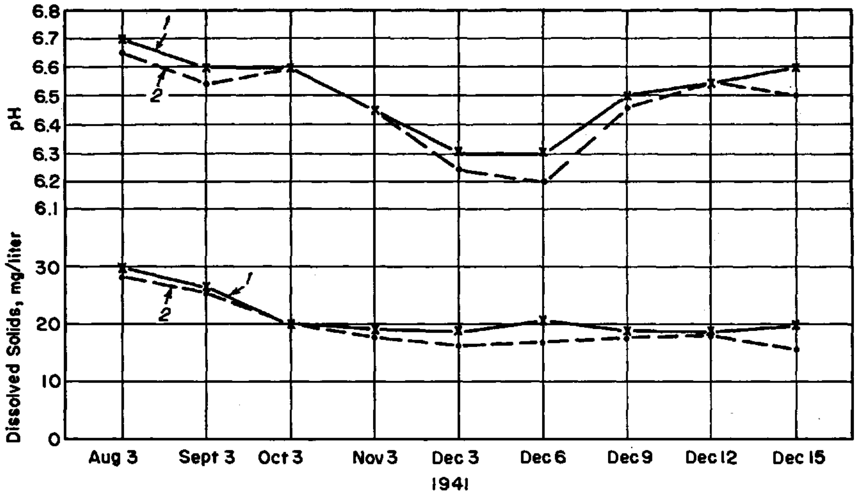
[1] The italic numbers in brackets refer to the list of references appended to this chapter.



Curve 1 = Sampling station 3 miles from mouth.
Curve 2 = Sampling station 4 miles from mouth.

FIG. 1—*Composition of Davidson River water.*

Usually, water entering rivers as a result of seepage contains larger quantities of minerals in solution than water flowing over the surface of the ground, since the contact time is much longer. Hence, during periods of drought, the concentration of dissolved material in a river is high because most of the water flows from aquifers. On the contrary, during flood stage, the dissolved mineral content of a river water is low because it is receiving the bulk of water from surface runoff. The reverse is true with respect to suspended solids. The nature of the soil and rocks over which a river flows is an important factor in determining the kind and quantity of dissolved minerals which the stream carries.

The problem of sampling becomes quite involved for rivers flowing through highly industrialized or mining areas. Here there may be little mixing, even over a considerable distance. This absence of mixing is obvious at the junction of a muddy stream and a clear one, or of two streams of different color. An extreme example of the variation in composition from bank to bank is the Susquehanna River in Pennsylvania. The eastern branch drains the northern anthracite coal fields and is usually highly acid. The western branch drains agricultural and forested lands and is usually alkaline. More than 75 miles below their confluence, these two streams still are not thoroughly mixed. The eastern branch maintains its identity as an acid water along the left bank; the western branch retains its alkaline characteristics along the right bank. Figure 2 presents typical results of cross-channel sampling of the Susquehanna River about 60 miles below the confluence [*4*].

Complete study of water composition in a river basin would require a large number of sampling stations and samples taken at frequent intervals.

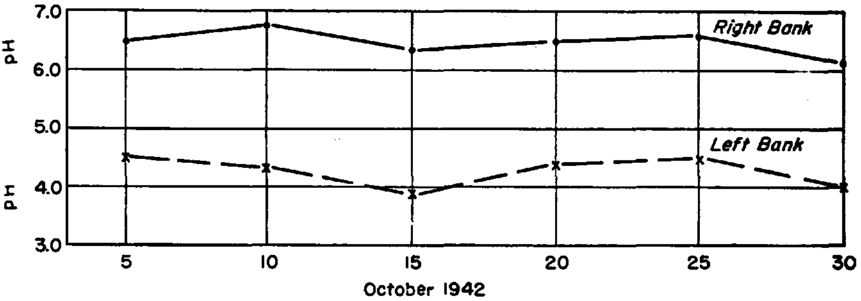


FIG. 2—*Cross-channel sampling of Susquehanna River below Sunbury, Pa.*

The cooperative studies by the Pennsylvania Department of Commerce and the U. S. Geological Survey [5] comprise such an extensive sampling program.

The sampling effort for one plant at a river location would not be so extensive. Usually, a single station and daily sampling are adequate. Occasionally, more frequent sampling is required, for example, during flood stage when the turbidity of river water changes rapidly. Figure 3 shows the course of such a change during a period of heavy rainfall.

The characteristics of water in a stream flowing through semiarid country usually change more rapidly than in more humid sections. Here, the surface rocks and soil are fairly soluble, and the runoff of each storm quickly dissolves appreciable amounts of minerals. Streams in such areas should be sampled at frequent intervals during times of changing stream flow.

For industries located on streams near tidewater, the water taken from the

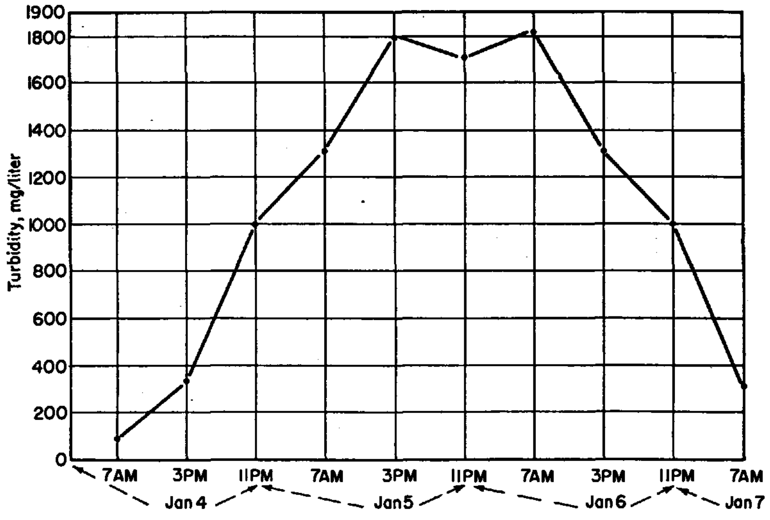


FIG. 3—*Turbidity of Miami River at Cleves, Ohio, 4 to 7 Jan. 1949.*

stream must be checked frequently at various depths to ensure the desired quality for the particular industrial use. Plants located far enough upstream to be free of salt during flood stage may encounter seawater intrusion during low-water periods. In the lower part of some estuaries, the saltwater will remain at or near the bottom, while the freshwater flows near the top. In such locations, an elaborate schedule of frequent sampling from many stations at various depths is required to make certain that seawater will not intrude unexpectedly.

Large lakes usually remain constant in composition over long periods of time. The Great Lakes, for example, need be sampled only three or four times a year to define their characteristics for most purposes. An exception to this would be for an industrial operation located near the discharge of a river or for some type of pollution.

Representative sampling of most small lakes will depend on the stream that flows into the lake basin. Some small lakes may be fed by more than one stream. The characteristics of the water in the streams therefore will govern the sampling schedule for the lake.

The composition of the water in a deep lake may vary considerably with depth, as shown in Fig. 4. The most favorable quality for a given industrial use should be determined by sampling at different levels [*6*]. Seasonal changes may make several sampling stations necessary. The concentration of dissolved oxygen and carbon dioxide varies considerably with both depth and the season [*7*]. Generally, the dissolved oxygen decreases as both depth and temperature increase.

Another factor that must be considered in the sampling of deep lakes is

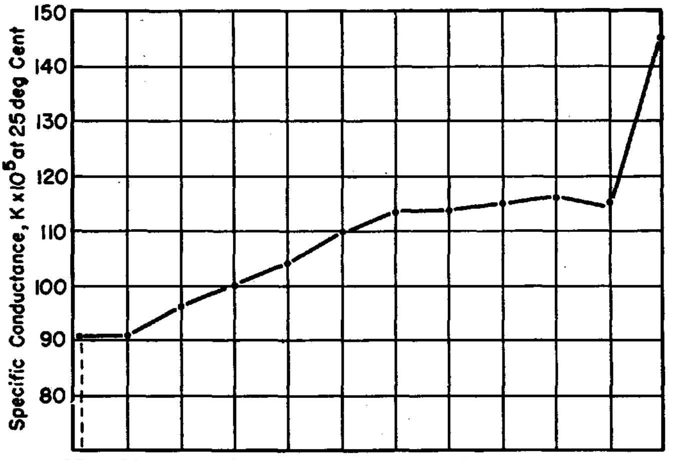


FIG. 4—*Variation in concentration with depth, Lake Mead, Arizona and Nevada (1 ft = 3.048 m).*

that they turn over during the fall. As the surface water cools and becomes more dense, the lower layers, being warmer and less dense, rise and replace the former top layers. Usually this turnover is rapid, and the resulting changes in composition of the water may be considerable.

Shallow lakes do not vary much in composition from top to bottom because mixing by the winds is generally good. The problem of sampling is therefore decided by the number and composition of streams feeding such lakes.

Reservoirs can usually be considered as lakes, but the phenomenon of a density current frequently is characteristic of deep reservoirs and occasionally of shallow basins. A density current is a stream of water that maintains its identity, with respect to both chemical composition and suspended solids, for long distances beneath the surface of the reservoir. It is caused by difference in density of the flowing water, either as a result of a difference in temperature or of the material in solution or in suspension or both. When encountered, such a density current requires a careful sampling schedule.

Sampling of Water Under Pressure

The composition of most well waters varies only slightly from year to year, and a single sampling station is sufficient. Usually two or three samples per year provide satisfactory coverage. There are exceptions, such as deep wells that have been drilled through strata containing water high in mineral content into a deeper stratum that contains water of better quality. Leaking casings or poor construction can lead to contamination of the good water. A shallow well receiving water by percolation from a nearby stream may fluctuate in composition. Such conditions necessitate more frequent sampling.

The groundwater in some areas varies in composition with the season. Such cyclic changes are usually related to solution channels in limestone, gypsum, or other soluble rock, and to variations in rainfall. Rainwater quickly reaches the water table and dilutes the higher concentrations of dissolved minerals. The concentration of the groundwater is thus lower during the rainy season than during the dry season. Figure 5 shows the composition of such a well-water supply.

A new well, or one that has been dormant for an extended period, should be pumped sufficiently before sampling, to guarantee that the delivered water is representative of normal conditions. This may require several days or weeks.

For sampling water from a pipe or conduit, it is desirable to choose a single sampling station. For example, in a cooling system with or without cooling towers, a single sampling station is desirable for chemical-treatment control. Satisfactory selection of the station may require a fairly extensive

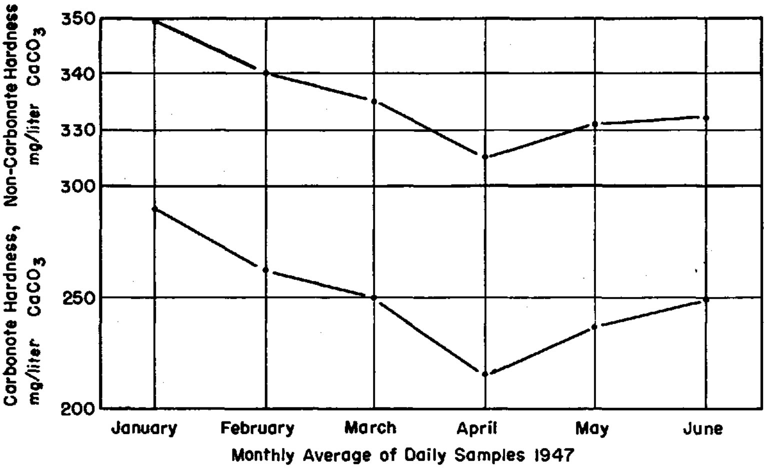


FIG. 5—*Variation in the composition of well water near Matanzas, Cuba.*

initial investigation. The most desirable location is chosen by checking samples from a number of outlets.

A factor often neglected in locating a sampling station in pipelines is the possibility of skin samples. An outlet that is flush with the inside wall frequently will not withdraw a sample that is representative of the cross-sectional flow. Differences become more pronounced with increasing diameter of the pipe. This difficulty may be overcome by having several sampling outlets extending different distances into the pipe, using a perforated sampling nozzle such as the one shown in Fig. 6. The inlets of such nozzles must face upstream. The total cross-sectional area of the holes should be such that the flow of water in the sampling line is proportional to the flow in the pipe or conduit.

Frequency of sampling should depend upon the magnitude of variations in composition of the water; that is, the schedule of samples must afford satisfactory coverage of water changes. A sampling station should not be located in any section of a pipe where the water is stagnant, such as a dead

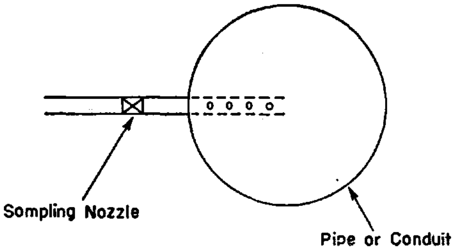


FIG. 6—*Sampling nozzle for pipe or conduit.*

end. A sample from such a location cannot be satisfactory. Physical conditions often limit the installation of sampling stations, but the best possible ones should be chosen.

Petcocks and drain valves provide convenient sampling outlets. They are used extensively and may provide satisfactory samples from small lines or dead-end samples. It is advisable to test this type of sample outlet for representativeness, instead of accepting it merely for convenience.

Industrial water in a pressure system may, in many instances, be satisfactorily sampled using weir boxes, sumps, drains, and overflows as sampling stations. Such sampling devices should not be used if unstable constituents are to be determined.

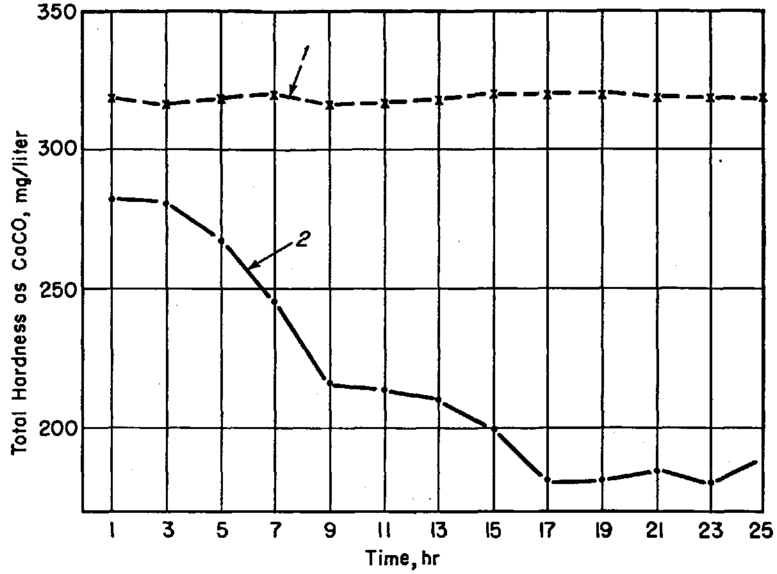
Sampling for Control of Water-Treatment Processes

The sampling of water to control the operation of a treatment process is of major importance to all types of water-treatment plants. The nature of the raw water and the quality of the treated effluent govern the number of samples taken and the type of chemical and physical tests required. If the composition of the raw water is subject to wide and frequent changes in quality, the frequency of sampling and tests must be increased accordingly. Thus changes in chemical dosages can be performed before the quality of treated effluent is affected substantially. Similarly, sampling and testing of the treated water must be frequent enough to provide data for maintenance of water quality and to indicate and deficiency in treatment due to change in chemical dosage or variation in quality of influent.

Following samples of water permit the use of instruments for continuously recording certain characteristics, such as pH, conductivity, temperature, turbidity, color, chlorine residual, oxygen, hydrogen, and silica content. Instruments may be justified by the saving in costs over manpower formerly needed for time-consuming laboratory testing, and their feasibility should be examined.

All types of water treatment plants generally require sampling points on the raw water, treated water, and other miscellaneous points if the operation is to be efficient. High-flow clarification and softening plants with sludge contact or sludge blanket treatment units generally require periodic manual sampling to measure the sludge concentration and sludge level within the unit. The frequency of sampling will depend upon the variability in concentration of the constituent used as the basis for control. Samples drawn at 8-h intervals are usually satisfactory for a water supply of fairly constant composition. On the contrary, it may be necessary to sample at less than 1-h intervals with a supply whose composition is changing rapidly or with a process that is especially sensitive. Figure 7 illustrates the two types of water.

Ion-exchange units, including zeolite softeners operating on the sodium and hydrogen cycles, and demineralizing units of multiple-bed and mixed-



Curve 1 = Well water near Cincinnati, Ohio.
Curve 2 = Maumee River at Toledo, Ohio.

FIG. 7—*Waters of constant and varying hardness.*

bed types, may require several sampling points for satisfactory control and for termination of the operating run before treated water quality has deteriorated significantly. Since this type of treatment plant lends itself to full or semiautomatic operation, flowing samples are generally employed together with monitoring instruments for continuously recording pH, differential conductivity, and hardness. Complete reliability in silica monitoring instruments must be attained in terminating the service run of demineralizers as the exhaustion point of the ion-exchange material is approached. A practical silica recorder accurate in the range of 0.02 to 0.05 mg/litre and manual sampling are important to the successful operation of this specific treatment method. Manual samples taken toward the end of an operating run and again following regeneration and return to service are usually necessary, depending upon the type of installation and the degree of instrumentation. The time for removing these two samples must be established by sampling over a short-time interval or on a volume-of-water basis, near the end of two or three demineralizing cycles and two or three rinsing cycles. The composition of some water treated by ion exchange changes rapidly toward the end of the service cycle and may require a sampling interval as short as 1 min.

Sampling at Elevated Temperatures

The requirements for sampling just discussed may also apply to hot-water service, with the addition that the sample must be cooled to approximately room temperature. Failure to cool will result in flashing and an unsatisfactory sample. Figure 8 shows a suitable type of cooling coil. Another common type is a pair of concentric tubes coiled to any convenient helical diameter. The cooling water flows through the outside tube and the hot-water sample flows in the opposite direction through the inner tube.

Sampling of water from boilers, feedwater heaters, or evaporators also must be accomplished under pressure using a cooling coil. Manufacturers frequently equip pressure vessels with satisfactory sampling outlets. The continuous blowdown line of a modern boiler is often used. In such cases, to avoid flashing, it is advisable to locate the sampling outlet between the boiler and the flow-control valve of the continuous blowdown line. It is sometimes necessary to check various possible sampling stations on some boilers to locate the most desirable one for the purpose.

A satisfactory sample of steam, particularly from boilers operating at high pressure and temperature, is extremely important. The ASTM Methods for Sampling Steam (D 1066-75) [*8*], gives complete details of the apparatus, including several types of sampling nozzles, piping, fittings, sample condenser, and cooling coils, necessary for getting a steam sample.

Because of the ease with which the approximate purity of steam con-

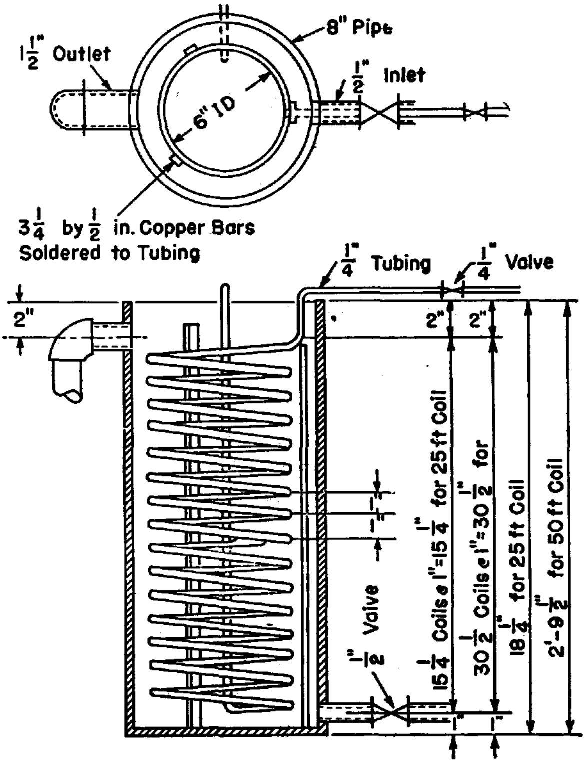


FIG. 8—*Water-cooling coil (1 ft = 3.048 m; 1 in. = 25.4 mm).*

densate can be determined by conductivity measurement, this method is preferable to evaporation of large volumes of sample and is used almost exclusively for continuously recording sample purity. Ionizable gases such as carbon dioxide and ammonia dissolved in the condensed steam sample contribute to the conductivity measured, and corrections for their pressure are necessary. Chemical analyses may be made to find their concentration in the sample. Automatic steam degassers are available which will practically remove these dissolved gases.

The schematic diagram of Fig. 9 shows the principal parts of one type of apparatus used in steam purity analysis in which inaccuracies in conductivity resulting from ionizable gases and volatile amines are eliminated.

Condensate analyzers employing ion-exchange degassing increase the sensitivity of detection of inorganic contaminants and eliminate interference by amines but not by carbon dioxide. Carbon dioxide, however, is usually at very low concentration in the modern power plant.

A steam sample is condensed at the atmospheric boiling point in a condensing chamber where practically all the free carbon dioxide and a small percentage of the ammonia are removed by venting. The effluent from this chamber passes through a conductivity cell and a small hydrogen exchange unit. Hydroxide and carbonate alkalinity, volatile amines, and ammonia are removed in this step. Cations of mineral salts are replaced by hydrogen ions. Passage through a reboil chamber eliminates bound carbon dioxide and provides a constant-temperature final sample for a second conductivity cell. Since the conductivity of the corresponding acids is several times greater than the original mineral salts, the sensitivity of conductivity measurement for mineral carry-over in steam is increased.

For maximum accuracy of steam purity determination, the sodium content of a condensed sample of saturated or superheated steam is measured by flame photometric techniques. It is possible to measure the sodium content of condensed steam with a precision of 0.4 μg/litre where suitable apparatus and proper technique are used. The ASTM Tests for Sodium and Potassium in Water and Water-Formed Deposits by Flame Photometry (D 1428) [*8*], describe the method and apparatus. The sodium electrode method of determining steam and condensate purity is another method coming into increasing use or supplemental use in the modern power plant [the ASTM Methods for Continuous Determination of Sodium in Water by Ion Selective Electrode (D 2791)] [*8*].

Sampling at Subatmospheric Pressure

It is often necessary to sample water at reduced pressure, as in vacuum-return systems or condenser hot wells. Here, a different physical arrangement is required for sampling, and extreme precautions must be taken against leakage. Minor outleakage from a pressure system will not necessarily impair the sample, but inleakage to a sample under subatmospheric

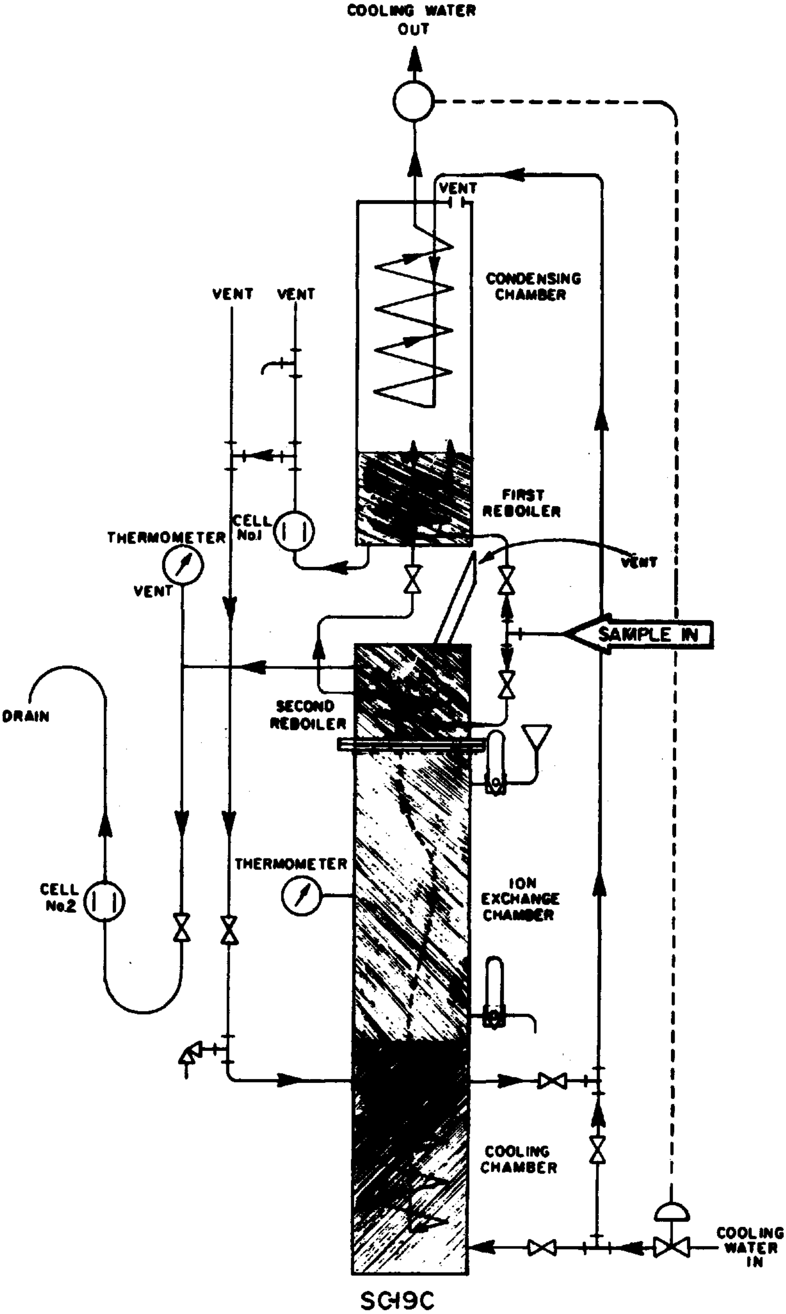


FIG. 9—*Simplified schematic steam analyzer.*

pressure will contaminate it. Leakage from pressure systems is visible, but inleakage to a subatmospheric sample is not.

Deep Sampling

To facilitate collection of samples in deep bodies of water, two types of samplers, depth integrating and point-type samplers, are in general use. Depth integrating samplers consist only of a weighted metal frame or other mechanical device for holding or clamping a glass bottle securely while it is lowered at a uniform rate throughout the vertical profile of the body of water.

For the collection of water at a specific depth, the Foerst-modified Kemerrer-type water sampler is frequently used. The sampler is lowered to the desired depth in the open position; then a messenger weight which trips the closing mechanism is run down the suspension line.

The messenger weight must meet the triggering device on top of the sampler squarely. Hence, a set of messenger weights drilled to accommodate suspension lines of different diameters permits the use of the sampler with a wide variety of ropes and cables.

When samples are required for the determination of dissolved gas content and constituents susceptible to aeration, special equipment and technique are required. The Foerst sampler can be utilized for this purpose by transferring the sample by means of a tube connected to the outlet valve projecting into the bottom of the sample bottle. Several displacements of water in the bottle should be made to assure that a representative sample is obtained. ASTM Method D 3370, Sampling Water [*8*], describes sampling methods and apparatus.

Sampling of Radioactive Water

In sampling water for the determination of its radioactivity, whether for gross or for radionuclide assay, the normal principles of sampling apply. However, because of the amount of radioactive substances in the water and the potential hazards related to working with water containing radioactive nuclides, special handling of samples may be required. The ASTM Practices for Sampling Water, (D 3370) give complete details which cover handling precautions, apparatus, frequency and duration of sampling, and preparation of sample containers. It is necessary to make certain that the sample drawn is actually representative. This may require a sample composited proportionally to flow rate or, where adequate mixing is not assured, a number of samples from different points and various depths in river, lake, well, reservoirs, processing tanks, or reactor cooling water containers.

When sampling for radioactivity determinations, precautions should be taken to reduce the magnitude of activity adsorbed on the container walls. When the nuclide amount is in the order of 10^{-12} g or less, normal adsorption losses on container walls may amount to an important percentage of the activity. Plastic materials or wax-coated containers give less difficulty in this respect than do glass or metals. Adsorption of radioactive materials on container walls often can be minimized by addition of carrier materials of chelating agents or suitable acidification. The addition of liquids such as acids, however, may change the distribution of radioactivity between the dissolved and suspended constituents.

In sampling streams or other natural waters, adsorptive losses are relatively unimportant since in such waters the easily adsorbable materials are generally carried on the surfaces of whatever suspended solids are present. In this case, treatment to prevent adsorption may result in undesired transfer of radionuclides from the suspended to the dissolved phase.

Sampling of Waste Water

Many of the problems in sampling waste water are similar to those discussed in this chapter for sampling water. In particular, information covering sampling in rivers and streams (flowing waters) entering larger bodies of water, in deep and shallow lakes (standing waters), and in tidal basins is applicable. These discussions should be reviewed as prerequisite to the added precautions outlined in this section. Objectives may differ somewhat in the case of waste water, because it is necessary not only to obtain representative samples, but to study the waste load, methods of treatment, and the possibility of recovering materials at a profit. Rigid specifications—National Pollution Discharge Elimination System permits—for the quality of waterborne wastes have been formulated by state and Federal agencies to control pollution throughout the drainage area receiving an industrial waste discharge, making a carefully supervised sampling program of plant waste waters mandatory.

Objectives

Common objectives in a sampling program should serve a number of purposes, including the determination of quantities of industrial wastes to be discharged, location of major sources within a plant, character of wastes, establishment of a basis for waste treatment, potential recovery of valuable material, and the effect of discharged wastes on the receiving stream.

Sampling Procedures

It would be rare if two waste problems were alike in all details, and the approach to waste sampling must deviate somewhat from the procedures for water; each must be handled as an individual case. Sampling must be tailored to fit the operation of each manufacturing plant and the characteristics of the waste produced. Special procedures are necessary to handle problems in sampling wastes that vary considerably in composition, depending upon the type of plant. Thus, suitable sampling locations must be decided upon as well as the frequency and type of sample to be collected. Examination of drawings showing underground sewers and manholes in manufacturing areas will help to locate appropriate points for sampling.

The degree of variation in rate of flow will determine the time interval for sampling. This interval must be short enough to provide a true representation of the flow. Although the rate of flow may vary only slightly, the concentration of waste products may range widely. Frequent sampling, that is, uniform 10- or 15-min intervals, permits estimation of the average concentration during the sampling period. This is necessary if a representative sample is to be obtained.

Sampling Points

Sampling points for waste waters are located preferably where flow conditions encourage a homogeneous mixture, such as the downstream side of a hydraulic jump, Parshall flume, or weir.

In sewers and deep narrow channels, samples should be removed from a point one third the water depth from the bottom. In wide channels, the point of collection should be rotated across the channel. In any event, the velocity of flow at the sample point should be sufficient to prevent deposition of solids. Creation of turbulence during collection of samples may liberate dissolved bases and volatiles and make the sample unrepresentative. A representative sample of a heterogeneous mixture of waste water, particularly one containing oil, is difficult to collect, but collection of a composite and analysis of an entire individual sample will give a fairly accurate estimate of the characteristics of the waste.

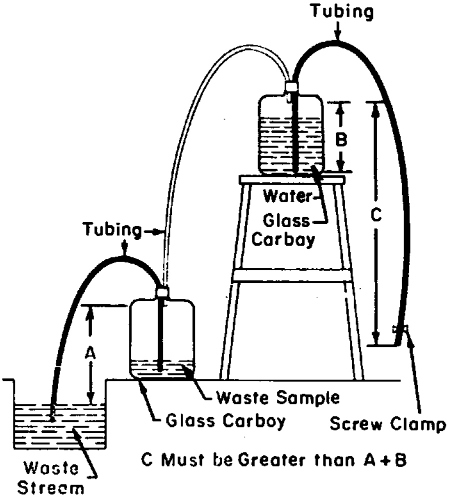
Recognized testing and precautionary measures [9] should be followed in taking samples from deep manholes to guard against accumulations of toxic and explosive gases.

Sampling Equipment

Figure 10 shows a diagrammatic arrangement of a continuous sampler suitable for uniform flows of homogeneous waste water.

Sample Preservation

Considerable research on the problem of preventing chemical, physical, and biological changes in waste water samples which might affect the biochemical oxygen demand (BOD), suspended solids, dissolved gases, cyanide, and phenol values has failed to perfect a universal treatment or method, or to formulate a set of fixed rules applicable to samples of all types. Prompt analysis is undoubtedly the most positive assurance against error from sample deterioration.



This simple jar-and-tube setup samples waste effectively when flow is nearly constant. As water drains from the upper carboy, the vacuum created siphons waste into the lower one. The rate of flow is regulated by the pinch clamp to fill the lower carboy during the sampling period.

FIG. 10—*Continuous sampler.*

Where it is imperative that stabilization and preservation be attempted, for example, when a 24-h composite is collected, it is recommended that the sample be refrigerated at 4°C.

Other methods applicable to many types of waste waters include chemical treatment, acidification, and alkalinization. Probable errors due to deterioration of the sample should be designated in reporting the analytical data.

Sampling Precautions and Equipment

The volume of water required for a sample depends on the number of determinations to be made. This is covered in detail in ASTM Method D 3370 and ASTM Method for Reporting Results of Analysis of Water (D 596) [*8*]. Generally, a minimum of 2 to 3 litres should be collected. A volume of 4 litres is desirable for the determination of all mineral constituents. In any event, the quantity submitted to the laboratory should include a surplus for check analysis. If only a few sample determinations are required, the sample volume may be reduced correspondingly. When a sample has settleable solids, the container should be large enough to allow some air space to facilitate mixing in the laboratory.

There are certain minimum requirements for sampling equipment which should be observed. For example, the sample container must not change the sample composition. It must be clean and, if glass, should be of chemically resistant type. Wide-mouth bottles are preferred for waste waters.

Rubber stoppers may be attacked by some solvents in wastes and thereby contaminate the sample. Plastic bottles with screw tops of the same material may be necessary. These are preferred for samples of condensed steam and other water in which the silica concentration is important.

Equipment for sampling purposes, cooling coils, degassers, steam sample nozzles, piping, and tubing intended for collecting acid waste water must be constructed of material resistant to the water being sampled. Such equipment must also withstand the temperature and pressure involved. Sampling equipment and piping for water or steam not in continuous use must be flushed sufficiently to remove all stagnant water.

A new system must be flushed sufficiently to remove foreign material, such as rust and oil, before placing it in service. The time required for cleansing depends on the piping and sampling equipment required. It is possible to be guided by the physical appearance of the effluent in most cases or by individual checking of samples. The sample outlet should discharge from the bottom of the sample container; this decreases the chance for atmospheric contamination. Overflowing the sample receiver also provides additional desirable flushing of the sample container. A volume of water equal to at least four to ten times the volume of the sample container should be overflowed to waste before taking the sample.

The rate of sample flow is highly important. If the rate of flow is too rapid, gas bubbles may be entrained; if too slow, the sample may become contaminated by diffusion. When samples are taken for determination of unstable constituents, unrepresentative or contaminated samples may provide highly misleading information. Continuous samplers for waste waters and steam require frequent inspection and cleaning to be reliable.

The foregoing discussion on sampling industrial water and waste water does not cover the multiplicity of situations that may be encountered. It offers partial direction for obtaining samples which accurately represent the mass to be sampled, and which meet laboratory needs for sample size. In all sampling procedures, the sample collector must exercise good judgment in deciding whether the sample is representative and if laboratory examination will provide pertinent and usable data.

Flow Measurement

Flow measurement is an essential function in the study of water as an engineering material. Since it involves principles of hydraulics and fluid mechanics that are applicable to all problems of flow measurement, a knowledge of the theory, methods, and types of equipment for measuring flow is essential. A simple measurement of the liquid depth in a standard container per unit of time serves conveniently for obtaining information on the amount of precipitation on the earth as rainfall. More complicated measurements involving rather intricate formulas and flow-measuring devices are necessary for determining the volume of surface runoff and underground seepage collected in flowing streams, flows in distribution mains and piping, and flows in sewers and open channels used for the disposal of water as industrial waste.

Flow measurement is of inestimable value in the conservation of one of man's most valuable material assets, water. Economic considerations provide an outstanding reason for flow measurement of water and waste water. Heavy costs are often involved to cover the material and labor for water-gathering systems and storage facilities, which include wells, dams, impounding reservoirs, tanks, pumps, and piping for transporting water. Installation and operating costs for treatment facilities are important factors in providing municipal and industrial water supplies. Flow measurement is an essential item in determining the cost of water delivered to consumers.

Flow measurement is important in the handling, treatment, and disposal of industrial waste water and domestic sewage, for control of discharge and making sewage service charges, and to provide records for pollution control agencies authorized to enforce laws governing disposal of waste. Flow measurement is a necessary accessory to sampling techniques; without accurate measurement, very little progress can be made with treatment methods or to establish the volume of waste that may be discharged without damage to the receiving waters.

Basic Requirements

The network of piping, underground sewers, and open channels used to convey water and waste water in modern plants presents many problems in flow measurement. There is no universal procedure, because flows must be measured under a variety of conditions. The measurement methods must be applicable to specific conditions. The type of flow device, its location, cost of installation, quality of flow data, and suitability for the service must be considered. This discussion covers briefly the kinds of flow-measuring devices, fundamentals of flow measurement, description and design of flow devices, and important points to consider in their selection. These should serve as a guide in choosing the equipment and method best suited to the purpose and in establishing a suitable location for obtaining data. The subject of hydraulics cannot be covered completely in this brief discussion, and it is suggested that reference books [*10*] be reviewed to obtain basic fundamental concepts.

Points of Flow Measurement

The points of flow measurement for water may include the sources of supply, treatment processes, and distribution systems. Collection points at sewer inlets, sewer outfalls, treatment plants, open channels, and discharges to receiving waters are recommended for waste waters.

Devices and Methods for Flow Measurement [11]

Devices used for flow measurement may fall into one of several classes: (1) head-area meters, (2) functional meters, (3) pumps, (4) displacement meters, (5) constant differential meters, and (6) inertial flowmeters. Other methods used frequently for flow measurement include surface floats, salt concentration, thermal techniques, and radioactive tracers.

Head-Area Meters—Head-area meters are used only in open channel flow or partly filled pipes; they cannot be used on lines under pressure, but are useful to measure flow from reservoirs. These meters operate on the principle that a constriction or controlled barrier in the flow channel will back up the liquid and create a higher level (head) than the level below the barrier; that head will be a function of the velocity of flow and therefore of the flow rate. Head-area meters include weirs, measuring flumes, and open-end nozzles. Several types of weirs and the basic elements of a Parshall flume are shown in Figs. 11 and 12, respectively. A typical installation of head-area meter and V-notch weir is shown in Fig. 13.

Functional Meters—Functional meters measure some function of fluid in movement and, with supplementary mechanical devices, convert that measurement into rate of flow or total flow. This principle is illustrated diagrammatically in Fig. 14. The components of a simple mechanical meter designed to function by differential pressure developed across on orifice installed in a pipe is shown in Fig. 15.

There are three types of functional meters:

(*a*) Differential-head devices produce a difference in head between two points of the device, and this differential is a function of velocity. These devices include the venturi tube, Dall flow tube, insert nozzle, Gentile flow tube, and orifice. Typical examples of each are shown in Figs. 16 through 20.

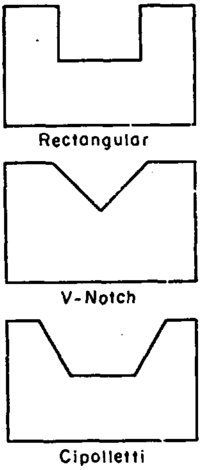


FIG. 11—*Types of weirs.*

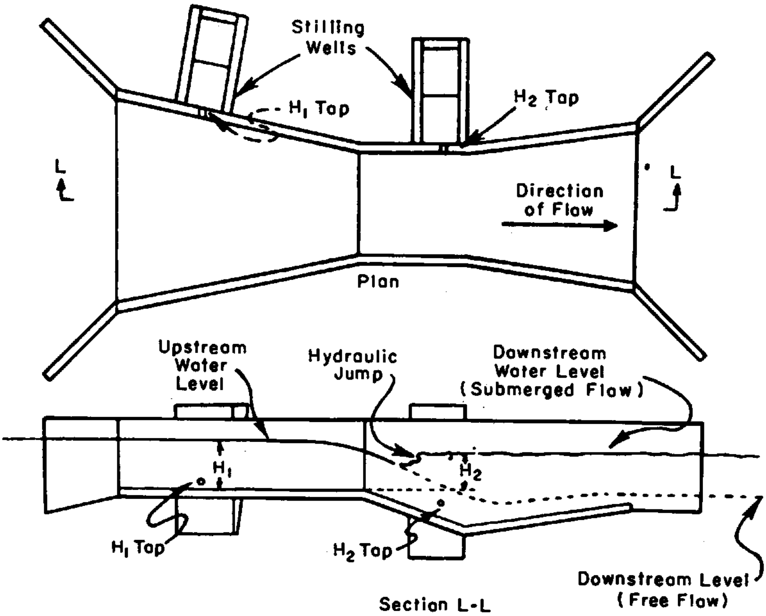


FIG. 12—*Basic elements of Parshall flume.*

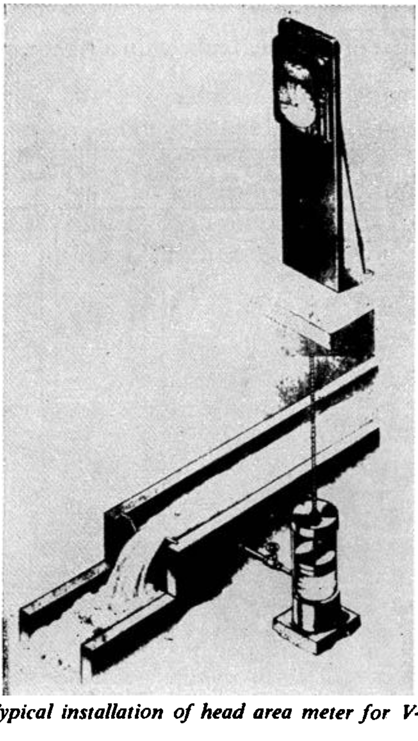


FIG. 13—*Typical installation of head area meter for V-notch weir.*

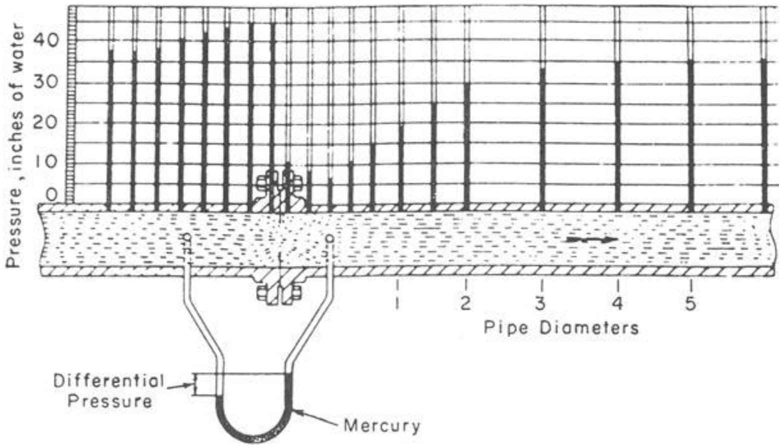


FIG. 14—*Pressure characteristics at a concentric orifice in a pipeline (1 in. = 25.4 mm).*

These devices are used in main-line metering and in metering flows at any point where water moves under pressure in a confined pipe.

(*b*) Velocity meters consist of a device by which a vane or propeller turns in direct ratio to the rate of flow past the propeller. These devices, similar to the one shown in Fig. 21, are used in main-line metering, pump discharges, etc.

(*c*) Pitot tubes consist of a vertical tube with a right-angled tip inserted in a

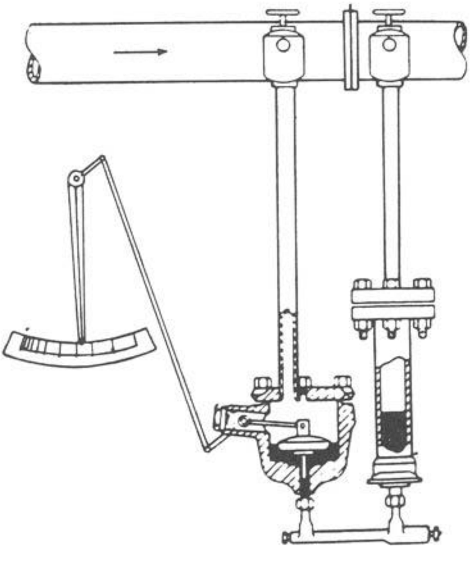


FIG. 15—*Simple differential-pressure flowmeter.*

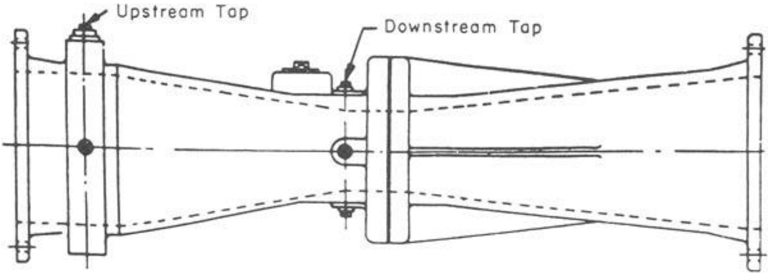


FIG. 16—*Schematic diagram of Venturi tube.*

flow, with the tip facing upstream. The height to which the fluid rises in the tube is a function of velocity and therefore of rate of flow.

Pumps—Pumps can be used as measuring devices only if the number of repeat cycles can be determined. Controlled-volume reciprocating pumps can be used easily for this purpose, but centrifugal pump discharges must be calibrated for each speed of operation, suction lift, or discharge head. Pumps are not generally used or recommended for flow measurement and should be considered only when other means prove to be impractical.

Displacement Meters—Displacement meters operate on the fill-and-draw principle. Fill-and-draw measurements of reservoirs and tanks can be made if flows into and out of the tank do not occur simultaneously. When the fill-and-draw principle is applied to a closed device, a compartment is alternately filled and emptied.

Constant-Differential Meters—Constant-differential meters, commonly called rotameters, consist of a tapered tube, smaller at the bottom than at the top, in which is confined a movable element termed a "float." The float rises or falls in the tube in proportion to changes in the rate of flow of the fluid. This device, which is illustrated diagrammatically in Fig. 22, is not used for measuring large flows; it has its greatest usefulness in measuring gas flows.

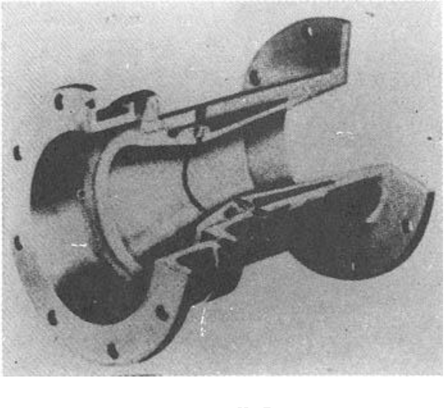


FIG. 17—*Dall flow tube.*

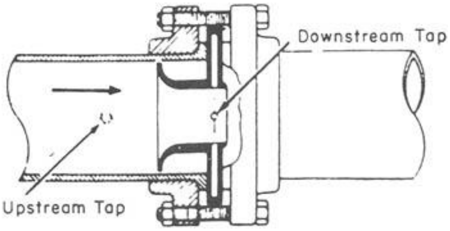


FIG. 18—*Schematic diagram of flow nozzle.*

Inertial Flowmeters—Inertial flowmeters measure mass rather than volume. They operate by indicting the inertial force of a moving mass of fluid.

Selection of Primary Units

The device that actually measures the flow of a fluid is called a primary unit (weir, Parshall flume, open nozzle, venturi tube, Dall flow tube, orfice, etc.). The primary unit is only one of two parts of a metering device. Before discussing secondary units, it is desirable to comment on factors in the selection of primary units. Weirs are infrequently used in permanent installations for measuring industrial wastes. The following three sections are devoted to the other principal primary units.

Factors that have a bearing on the selection of the primary unit include type of service, engineering considerations, installation conditions, accessories, comparative characteristics, and operator's convenience. Not all of the factors and items mentioned hereafter apply to all types of primary units; where they do apply, however, full consideration must be given to the evaluation of each factor.

Engineering considerations include such factors as allowable loss of head;

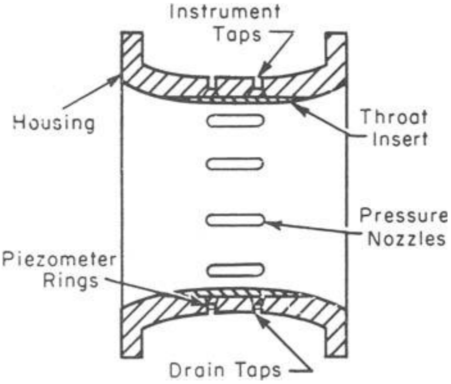


FIG. 19—*Gentile flow tube.*

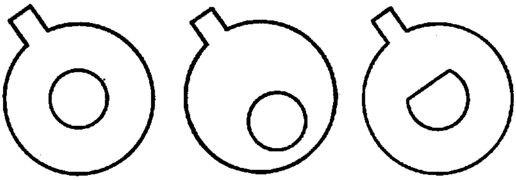


FIG. 20—*Orifice plates: concentric, eccentric, and segmental.*

throat size of the constriction; acceptable differential pressure; upstream and downstream flow conditions; type of fluid to be measured; laying length of the unit (that is, length of pipe it will replace in the line); types of ends (flange, bell and spigot, concrete coupling); distance to secondary unit; type of unit to transmit the measured data to the secondary unit; corrosion resistance required; cleanouts, inspection holes, and manholes; construction costs as affected by pits for float tubes; and forms for flumes.

Installation factors cover the position of the device (vertical or horizontal), piping arrangements, vaults, and possible bypass installations. Accessories required might consist of straightening vanes, flushing devices (intermittent or continuous), vents, vent cleaners, air chambers, floats, float tubes, sediment traps, seals, etc.

Comparative characteristics of flow-measuring devices comprise accuracy, low cost, high capacity, range, permanent loss of head, life expectancy, suitability for solids-bearing liquids, freedom from upstream disturbances, ability to handle high pressures, and ease of installation.

Secondary Instruments

A secondary instrument or receiver is the device used to convert measurements sensed by, and transmitted from, the primary measuring unit into

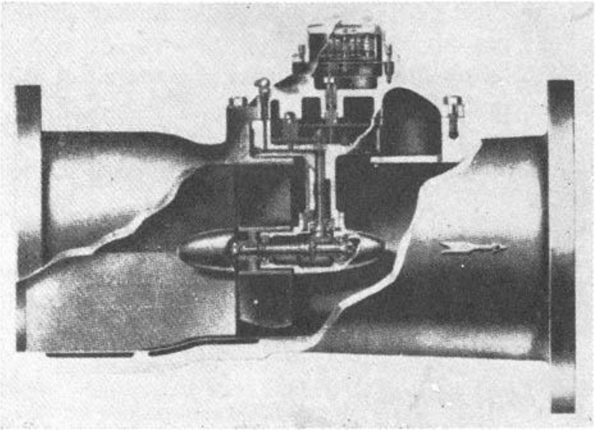


FIG. 21—*Velocity meter (Builders' Propeloflo).*

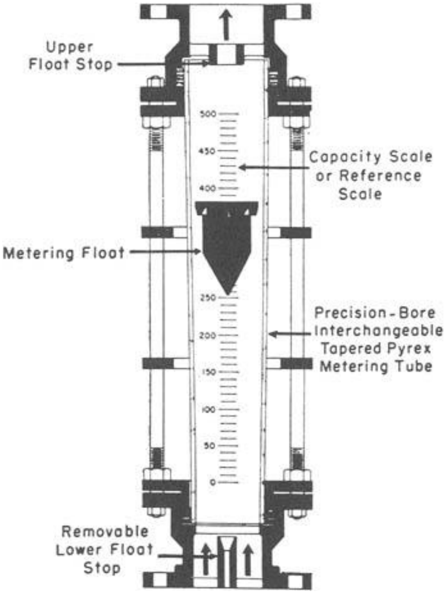


FIG. 22—*Typical rotameter.*

observable information on flow. Liquid level and pressure also can be shown on secondary instruments.

Secondary instruments are classified in two ways: (*a*) according to the type of information desired, and (*b*) according to the method of transmission from primary to secondary unit.

Classes by Type of Information Desired

Indicator—The indicator shows the rate of flow at the moment of observation, in cubic feet per second, gallons per minute, gallons per hour, millions of gallons per day, etc.

Totalizer—The totalizer shows the running total to time of observation, in cubic feet, gallons, millions of gallons, etc.

Recorder—The recorder draws a record on a chart, showing the rate of flow as a continuous record for each instant during a particular period (hour, day, week).

Combinations are available as indicator-recorder, totalizer-indicator, totalizer-recorder, and totalizer-indicator-recorder. Indicators have a single arm and dial. Indicators-recorders may have the indicator arm separate from the chart, or attached to the pen arm.

Classes By Type of Transmission

Mechanical Transmission—Mechanical transmission exists when the receiver is operated by cables directly connected to float wells, which are in turn connected to the pressure takeoffs (taps) of the primary device. Mechanical transmission also may be obtained by connecting the primary device pressure taps directly to mercury wells in the receiver unit.

Electrical Transmission—Electrical transmission is used where the receiver cannot be located near the primary unit or where there is insufficient pressure for direct connection to the secondary unit. Electrical transmission is of the time-impulse type (Chronoflo Telemeter) whereby the length of time that the signal is transmitted is proportional to the magnitude of the function being measured (rate of flow, pressure, level, etc.) This signal can actuate a receiving instrument, or control pumps, chemical feeders or valves, or both. Electrical transmission is possible over any distance from feet to miles, over telephone circuits, private a-c or d-c lines, or multiservice wires. A sequencing unit (sequence unit transmitter) will transmit signals from several transmitters consecutively over the same pair of wires. Sequencing is useful in the operation and control of well-field pumps and booster pumping stations.

Pneumatic Transmission—Pneumatic transmission is useful up to 457 m (1500 ft); it generally makes use of a varying controlled air pressure ranging from 21 to 105 kPa (3 to 15 psi). Its principal features are an absence of wiring, a continuous output signal (pressure), extreme sensitivity to change in the variable being measured, and immediate response to change in the variable.

The three types of transmission are illustrated in Fig. 23.

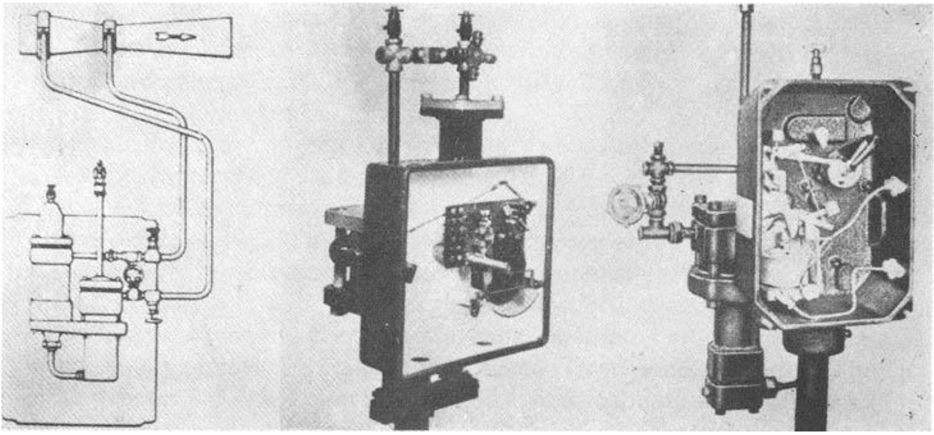


FIG. 23—*Types of transmission*: (left to right) *mechanical, electrical, and pneumatic.*

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Chapter 10—Water-Quality Monitoring

The broad objectives of water monitoring include the conservation of water quality and quantity to assure an adequate supply of water suitable in quality for both public and industrial uses and for the maintenance of fish and wildlife. Water monitoring is the continuous sampling, measurement, and analysis of the quantity and quality of various liquid streams. These streams may include waste-water streams or plant effluents; watercourses such as rivers, lakes, and estuaries; groundwater; recirculated streams such as cooling water; power plant streams such as boiler feedwater or condensate; or process effluents. Monitoring of public waters and waste waters protects the integrity of a sewer system, may prevent the upset of municipal waste treatment processes, especially biological processes, and preserves a safe public drinking supply and a healthful recreational environment. In addition to providing many of these same public safeguards, the monitoring of industrial processes provides for better products at reduced cost, improved process efficiency, and a lesser quantity of waste water that has to be treated or reclaimed.

Monitoring is no longer a solely voluntary procedure. In the United States especially, monitoring is a legal requirement of a regulatory agency carried out to determine compliance with the Federal Water Pollution Control Act Amendments of 1972, Public Law 92-500. Passage of the 1972 amendments authorized the establishment, under the Environmental Protection Agency, (EPA), of national programs for the prevention, reduction, and elimination of pollution—these to include establishing, equipping, and maintaining a water quality monitoring system for all waters. Owners and operators of any point sources are now required to establish and maintain records, to make reports, and to install, use, and maintain monitoring equipment and methods in such a manner as the EPA should provide. Under Public Law 92-500, point-source discharge into waters is prohibited unless the discharge is authorized by permit. A substantial monitoring program may be necessary to provide the information required by the permit. Such a monitoring system would also be able to provide data to answer inaccurate accusations of harmful or illegal waste-water discharges. Adequate monitoring records can document that a facility was operating in conformance with permit requirements during any particular period of time.

Earlier methods of monitoring, which largely involved wet chemical procedures, have, in the past few years, been replaced by more reliable instrumental techniques which produce results rapidly and accurately. Since no operator is required, results are more objective, and accuracy can be checked easily by proper calibration with known standards. Not only are samples analyzed shortly after collection, but the interval between sampling and results is minimized. Samples no longer need to be transported to a laboratory for analysis, eliminating several sources of error. Since the use of preservatives is unnecessary, these variations are avoided. In general, on-line instrumental monitoring obviates the inconvenience, the inaccuracy, and the delay of laboratory procedures.

Wherever possible, and particularly where continuous results are necessary, monitoring should be automated. Besides providing a greater degree of process control, data may be displayed immediately and still be retrievable for historical record. In addition to the advantages just mentioned, an automatic monitoring system may be less costly than analysis of repeated grab samples. Installation of a highly sensitive, multiparameter system when only a quick positive or negative readout is required will incur needless expense. Good reliable systems require a minimum of attention and therefore can also be operated and maintained at a reasonable cost. In general, careful selection of rugged, dependable monitoring systems will keep costs to a minimum. In an economical, automated system, the level of sensitivity of the tests should match the sensitivity of the required results.

Considerations when Employing Monitoring Instrumentation

Automatic monitoring of water characteristics provides information often not available from other techniques. One basic advantage is the promptness with which the sample is analyzed after it is collected. Other advantages are the short or zero time interval between samples, and the rapidity with which the data become available for use in evaluation or control. Some or all of these factors often contribute to the development of better methods of controlling water quality, because a complete set of the variables of interest is provided.

Economics

The economics of automatic monitoring can be attractive. Whereas a fairly large capital expenditure must be made for the monitoring equipment, the operating expenses, including maintenance, are much less than the costs of analyzing repeated grab samples in a control laboratory. Because they are completely objective, the results are more reliable, and their accuracy can be determined easily with the proper calibration and checks against standards.

The ease of checking known standards with automatic instrumentation permits more frequent restandardizations, thus increasing the reliability of analytical results.

Process Control

The monitoring of industrial process streams not only offers the direct advantages of better products at reduced costs, but also the indirect advantage of improved process efficiency, thus producing less waste material that must be treated or reclaimed. An example of such process control may be found in the steel industry, where sheet steel is pickled in acid baths. In one typical case, it was found that continuous monitoring and control of free acid concentration and iron content of the pickling baths led to an improved product, with reduced acid consumption. The decrease in acid usage meant that less excess acid had to be neutralized when the spent pickling baths were treated to precipitate ferric hydroxide, and clarified, before the effluent could be discharged to a natural body of water.

Control of Waste Treatment Systems

The foregoing example points up another important aspect of monitoring, which now is becoming widespread. This is the continuous monitoring of industrial waste treatment discharges, as well as the quality of receiving streams or other natural bodies of water, to indicate performance of treatment systems, to control waste discharges, and to prevent water pollution. Programs for monitoring various properties of the water in major surface supplies such as the Ohio and Delaware Rivers have been in operation for a number of years and have produced much valuable data.

Monitoring River Quality

Monitoring programs for quality determination on rivers and other surface supplies have several major objectives. Among these are the collection of data that can point up changes in stream quality, that indicate the approximate area of causes of change, and that develop data that provide a background of water quality for present or possible future uses. An automated monitoring program of proper design will provide as much data as desired, or, conversely, the minimum amount of data consistent with the control desired—another economic advantage. Such programs provide the mechanics of reporting data so as to permit data utilization either on a continuing basis or at times when specific causes for change can be determined. Moreover, data can be evaluated as to significance for the area or river in question, rather than be limited to comparison of one river with another. One of the major advantages is the fact that data reported represent actual conditions rather than averages.

When properly designed and operated, automated stream monitoring programs provide the necessary flexibility to permit change in analyses, or in frequency of analyses, when suggested by evaluation of data. Through automated monitoring, it is possible to maintain agreement between various agencies collecting data, by developing uniform mechanics for analytical techniques and reporting of results. Review of data provided through monitoring systems will pinpoint the factors that cause changes in observed analytical results and will suggest determinations that reveal more clearly either the reasons for or the significance of changes. At present, many agencies operate control points or sampling stations from which samples collected are analyzed regularly or intermittently. Some of these analyses are comprehensive; others cover only a few parameters. All laboratories do not use identical procedures, or even modifications of the same procedures. Means of reporting results differ widely, as do sampling procedures. Many samples are composites collected over periods of hours, days, or weeks. Neither the period of compositing nor the basis are uniform at all locations and agencies. Composites may be based on conductivity measurement agreement, equal volumes of samples collected, or on the ratio of volume to flow at the time of sampling.

And if the preceding variables are not enough to cause problems, consider other factors contributing to lack of agreement in results between various laboratories and agencies. Among these may be cited the varying intervals between sampling and analysis, the use of preservatives or variation in means of preserving samples, errors in analysis, or in calculation of results, plus a lack of appreciation of limits of accuracy and precision of analytical procedures. Failure to question the reasonableness of results at the time of analysis, or to warn the analyst of conditions that can influence analytical techniques, leads to trouble. The collection of samples at different flow conditions or the reporting of average or medium concentrations from a number of analyses will provide data of only limited value, as will determination of average load based on average flow for a time period and an average of analytical results.

The preceding subsections indicate the numerous aspects of the operation that could be stabilized and reduced to uniformity by automated stream quality monitoring programs. The monitoring units could be supplemented by alarm systems to be actuated by changes outside the normal range, and by simple checkpoint installations upstream that permit relating changes at major control points to sources causing the changes. Recorded data would permit development of inventory maps showing runoff sources that can influence water characteristics, that indicate the effect of impounded water quality and the manner of release (low-temperature reservoirs, mine water storage, oxygen depletion by excessive organic or metallic impurity loadings, etc.), and that permit ready evaluation of past water-quality records. Water-quality data could be directed toward appraisal of water suitability for current and future uses. Load data clearly defining contaminants carried by rivers and tributaries could be used for material balances and could permit evaluation of the effect of a stream on another river or body of water.

Types of Measurements

The types of measurements used in evaluating water characteristics fall into two major classifications, physical and chemical.

Physical measurements can be considered broadly (with some ambiguity and overlap) to encompass properties of temperature, density, conductance, surface tension, refractive index, radioactivity, pH, redox potential, and some others employing chromatography, colorimetry, turbidimetry-nephelometry, and specific ion electrodes. Some of these determinations are made simply by immersing a sensor in the water, while others require a portion of the water to be taken as sample and diverted through the sensor portion of the instrument.

The second major category of measurements is those involving chemical analysis procedures. Here, chemical analysis is defined as the addition of reagents, causing chemical reactions to occur, before a measurement can be obtained. Examples of chemical analysis measurements are all those that add reagents and employ various sensors which respond to pH, redox potential, color, turbidity, or conductance changes to read out the result. A brief description of these methods is presented later in this chapter.

Sample portions are collected and measured at programmed intervals when a continual analyzer is used. The time between continual analyzer results can vary from seconds to hours.

It must be understood, however, that the type of sampling system required is dictated to a great extent by the type of instrument to be used and by stability of the component to be measured. Furthermore, the instrument output or readout can be no more accurate or representative than is the sample supplied. If the instrument does not receive a representative sample, it cannot produce representative data, regardless of how well it is designed or operates.

When an instrument is to be used for direct control of water or process streams, as well as for monitoring, the delay interval between the time of sample collection and detection of the signal must be accounted for and offset by varying the modes of a process controller.

When an instrument is to be used for process control, the delay interval between the sampling time and the detection of the analytical result must not be significantly greater than the time required for the sampled flow to reach the control point.

Environmental Considerations

Misapplications, such as installing a monitoring instrument in an environment where it cannot function properly, will lead to unsatisfactory operation, high maintenance costs, and production of erroneous data. Monitoring instrument manufacturers generally specify optimum conditions for the location and operation of their equipment. If the application cannot meet these conditions, it may be necessary to use an alternative instrument, or to choose an alternative measurement for which an instrument that can operate under the prevailing conditions is available. For example, a hardness monitoring instrument located in an area that is too hot might cause degradation or decomposition of a colorimetric hardness reagent. The best solution to such environmental problems is to locate the instruments in a building or cubicle that can be air conditioned, or where atmospheric conditions otherwise can be controlled. The added cost of such housing should be insignificant when the value of the data and reduced costs of maintenance are considered.

Sampling Considerations

Preparation for the installation of an instrument consists of much more than (1) speculating on what analysis will suffice, (2) obtaining bids from several vendors and accepting the lowest one, and (3) setting the instrument on a concrete pad and flipping on the switch. It is alarming to learn that this is typical in far too many applications. This type of philosophy is normally associated with ill-defined measurement objectives and may be the result of pressure from a regulatory agency to provide immediate data on a particular pollutant.

Beginning with the premise that the correct analyzer has been chosen for a given application, the following aspects of sampling require in-depth consideration if a functional support package is to be assembled.

1. Measurement objective
2. Sample point
3. Sample probe
4. Pumping system
5. Transfer lines
6. Sample conditioning
7. Analyzer interface (stream selection)

Measurement Objective

The definition of measurement objectives may appear to be elementary; however, in numerous instances, measurement systems are incorrectly applied. An example of a misapplied measurement system is the use of a highly sensitive analyzer when something less sophisticated with a high-level alarm device is all that is required. The majority of environmental analyzers are used for either record-keeping or alarming, while only a few are used for control purposes. Illustrations of control instruments would be automatic titrators, biological activity monitors, and smoke monitors. The analyzer used for record-keeping should be sensitive and extremely reliable if the recorded data are necessary for demonstrating compliance.

Sample Point

The location of the sampling point is a direct outcome of the decision on measurement objectives. Sampling for the purpose of determining the total carbon discharge into a river is at a completely different location than that intended to detect a leak at a tank farm. Questions of major importance in locating a sample point are:

(*a*) Can a representation sample be obtained at this location? The more representative sample will be obtained immediately downstream from a turbulent area. When several streams flow together, causing minimal agitation, it is best to induce turbulence if a representative sample is to be obtained. In Fig. 1, three sewers are depicted flowing into a common sewer, one of which is partially submerged. Note the location of the sample point in relation to the area of turbulence.

(*b*) Can a measurement at this point quickly isolate the problem? Do not expect an analyzer located downstream from the junction of three sewers to be capable of identifying, during a period of high discharge, which sewer is responsible.

(*c*) Is the measurement to be used for determining the magnitude of discharge, to alarm in case of abnormal discharge, or to control pollution abatement equipment?

(*d*) Is the sample point only one of several which will be monitored by a single, centrally located analyzer?

(*e*) Will the sample point location allow sufficient lead time for appropriate action?

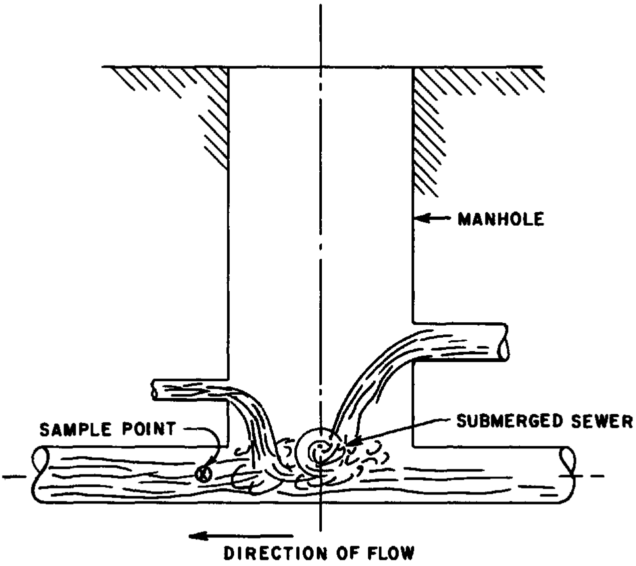

FIG. 1—*Multiple sewer junction.*

Sample Probe

The type and positioning of the sample probe are to some degree dictated by the measurement objective. If the measurement is not concerned with solids, particularly heavy solids, then the probe should not be located too near the bottom of a sewer. The reverse applies if you do not desire to encounter oils, greases, etc., which normally are surface materials.

Probe design should not be taken lightly. A well-designed probe not only can minimize the maintenance cost, but also reduce the frustation of trying to operate an analyzer without an adequate sample.

Stream contents should dictate how the probe is built. If the sewer has a low level of solids and is pressurized, it is possible to use an enlarged version of a gas sample thief. When a high concentration of randomly sized solids is present in an unpressurized sewer, it is best to mount vertically a large-diameter probe. The suction velocity should be low enough to permit the heavier objects to fall back down through the probe.

The use of relatively fine screens at the probe inlet is not recommended. This practice usually results in a high incidence of plugging.

Vertical water probes used with low-pressure safety switch protection on the pump are capable of self-cleaning. When the probe inlet becomes plugged, the pump automatically shuts off, permitting the column of water to backflush the probe. This procedure is not always adequate; if plugging becomes frequent, it may require the use of pressurized backflushing.

Pumping System

A cursory market survey on pumps will be sufficient to confuse the most inquisitive individual. Pumps vary in operating principle, dimensions, specifications, and price.

Experience has demonstrated that price should be the last factor considered when attempting to establish if a pump can perform the desired task. The following items require consideration when searching for that "right" pump for the job.

(*a*) Does the application demand explosion-proof equipment?

(*b*) Must the pump be submersible?

(*c*) Must the pump be self-priming, or will it have a flooded inlet? What is the suction lift height?

(*d*) What are the discharge pressure at the desired elevation and the distance to where the sample is to be delivered?

(*e*) Is the pump required to handle solids, strings, rags, wood, stones, sand, etc.?

(*f*) Are the materials of construction suitable for the waste material the pump will be handling?

Although open impeller pumps lack efficiency as compared to a positive-displacement pump, they are far less apt to foul or clog. Also, some sewers are so difficult to pump that it becomes necessary to use prehomogenization or delumping hardware prior to pumping.

Transfer Lines

Selection of the proper transfer line requires more thought than merely using some surplus tubing that happens to be available. The diameter of the line should be considered in relationship to the length in order to minimize the pressure drop across the line. The line should have adequate size to provide sufficient sample to the analyzer without an excessive amount of discharge pressure. The stream velocity should be high enough to maintain solids suspension, help reduce wall buildup, and minimize transfer time. Specific corrective action might be required to reduce or periodically eliminate biological growth lining the pipe. Backflushing or the use of a bactericide might be necessary to keep the line open. Again, the materials of construction should be properly selected.

Sample Conditioning [1][1]

Up to this point, the discussion has been concerned with the extraction of a sample from the sewer and its transfer to a location adjacent to the analyzer. If extensive sample conditioning is required, it should be accomplished at this point. The sample conditioner will very possibly take on the appearances of an instrument in itself. The components used in the conditioner will be dictated by the measurement objectives, and the conditioner's ability to perform satisfactorily will play a major part in obtaining the desired measurement.

Sample conditioners can be considered standard only to a point, after which they must be customized for a particular application. For example, measurements requiring only the soluble content can be achieved by phase separation, skimming, and solids separation. Obtaining a measurement of the total amount of a material, both soluble and insoluble, is not an easy task. It requires effective homogenization and blending in order to get the solids reduced to a size compatible with the sample ports in the analyzer. Mechanical reduction of solids to a size which approaches a true solution 1.0 nm mean diameter is not considered feasible.

Functions that should be considered when designing a sample conditioner are as follows.

Stream Splitting and Solids-Liquid Separation—The technique of stream splitting can be extremely useful in sample conditioning. It is an ideal method of extracting a very small sample from a larger volume and making a pressure reduction all in one step, without the use of valves or pipe reducers. Experience has taught that the use of valves, pipe reducers, 90-deg elbows,

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

and rotometers should be avoided if at all possible in streams containing any appreciable amount of solids. These components are usually the cause of plugged sample lines.

Properly designed, a stream splitter can also perform a solids-liquid separation, thereby minimizing filter loading. Illustrated in Fig. 2 are various types of stream splitters which have been used with satisfactory results. The high-pressure splitter and the multiple-stream selector are ideal for streams with low solids content. Each uses a metal finger inserted into a high-pressure stream to deflect a small sample into a secondary sample line. The V-type splitter is bent to achieve the desired volume of sample off one side

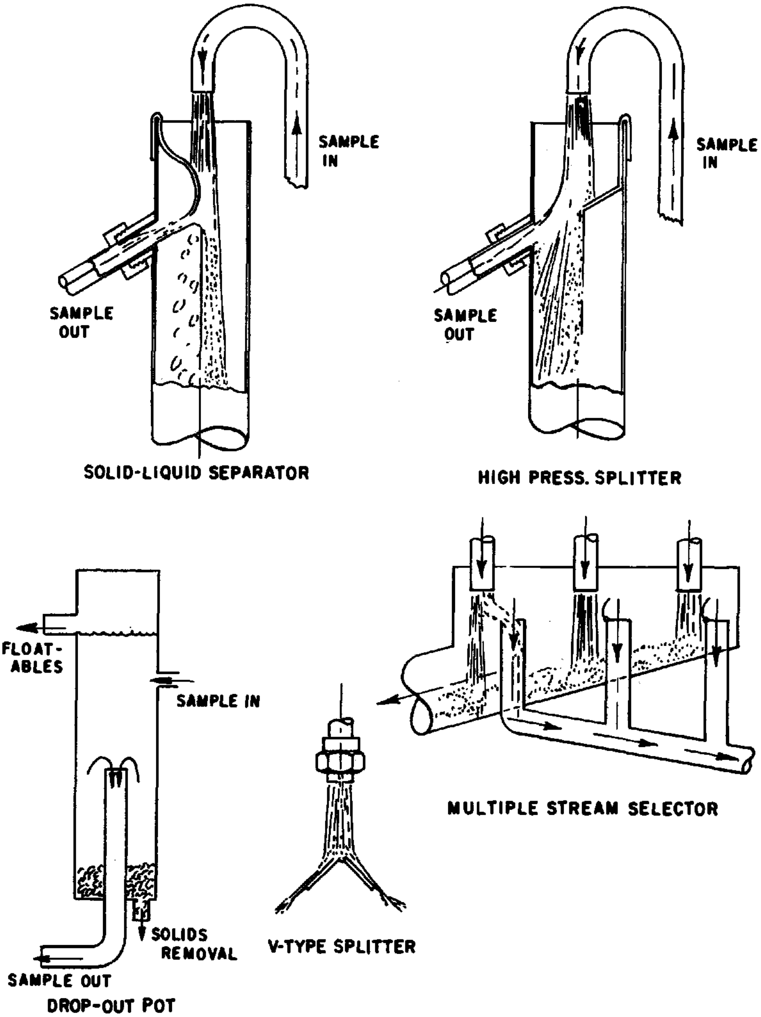

FIG. 2—*Sample stream splitters and selector.*

while the remaining sample is deflected to a return sewer line. The solids-liquid separator uses the principle of surface tension. The water adheres to the curved plate while the larger solids continue their free fall through the pipe.

Use of the simple and inexpensive dropout pot can greatly improve a sample conditioning system. This device is not as maintenance-free as the others, but it can greatly reduce the loading on a filter system if operated correctly.

Dilution—Sample dilution can serve a threefold purpose. It can reduce the solids concentration in a sample, relieving the load on the filter; it can reduce the incidence of valve plugging; and it can provide analyzer rangeability on high-concentration streams.

This approach has been used for the past several years in total carbon measurements in an effort to overcome the nonlinear response of infrared analyzers. If the carbon content in the sample can be held below 200 mg/litre, the response of the analyzer is reasonably linear. The calibration curves in Fig. 3 show the degree of nonlinearity that is encountered when the carbon concentration increases from 100 to 1000 mg/litre.

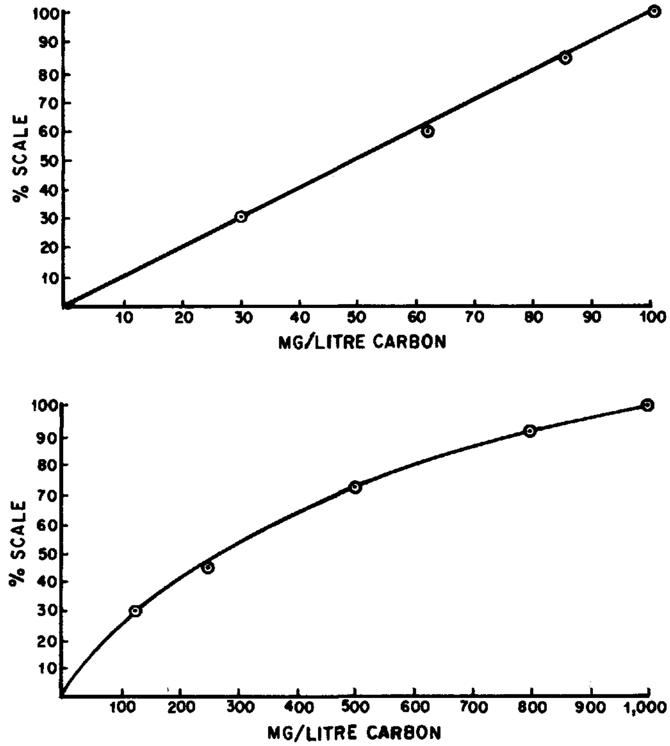

FIG. 3—*Calibration curves (infrared analyzer).*

An example of how a single-stream system, based on volumetric dilution, works is shown in Fig. 4.

Homogenization and Blending—Homogenizers are used primarily to macerate solids and put them into a stable suspension. In order to minimize equipment size and energy consumption, it is preferable to have a batch operation with a small sample. This homogenization procedure should be accomplished just prior to sample analysis, and it is considered a polishing procedure.

Blending is used principally to maintain sample homogeneity. It should be utilized at any stage in sample transfer and preparation where stratification or settling might occur — the most important location being just prior to sample extraction. Blending can be accomplished by mechanical stirring or induced turbulence. In the dilution system just described, efficient blending is obtained by recirculating the diluted sample with a centrifugal pump. The operation is shown in Fig. 5 with a top view of the dilution chamber. Notice the swirling action that is induced as the sample stream is reentering the blending chamber.

Filtration—Although the use of filters is widely accepted in pollution technology, considerable caution should be exercised when choosing a filter. Incorrectly applied filters can do more harm than good. They are comparable to sample probes in being responsible for insufficient sample delivery. In addition to plugging, they can cause serious analyzer errors due to tailing and sample contamination. Filters which absorb materials rather

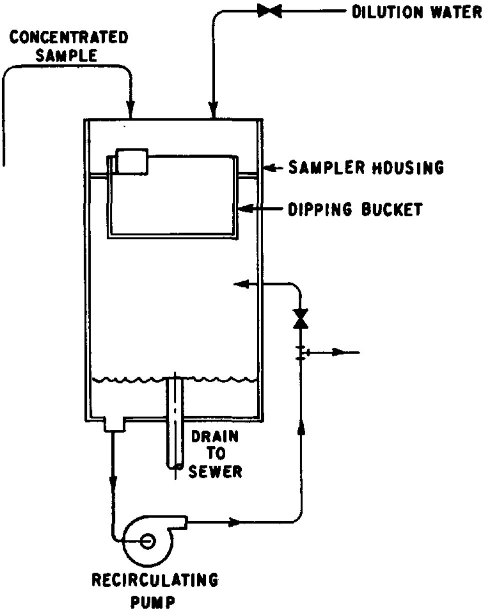

FIG. 4—*Dilution system.*

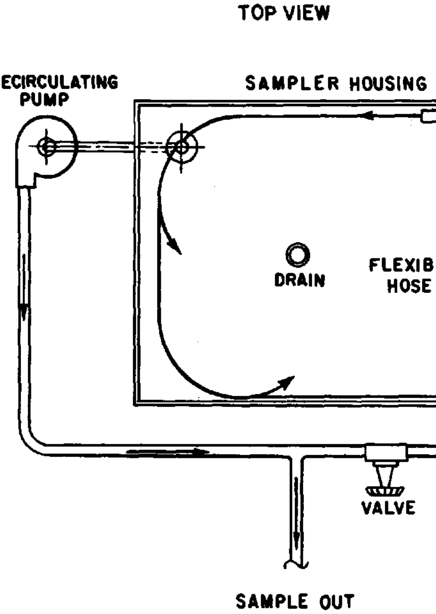

FIG. 5—*Sample blender.*

than separate them should not be used in analytical methods unless the filter is guaranteed selective.

Five different filtering assemblies are shown in Fig. 6. The Cuno Auto-Clean, which utilizes a stack of metal disks, has been reasonably successful in past applications. The second type of Cuno is a cartridge filter, and it offers no mechanism for self-cleaning other than replacing the cartridge. The sand filter has been and is still being used in many locations. If a periodic backflush is employed, it can do a fair job of solids separation, particularly on silty solids. The Swirlklean offers an entirely different approach to filtration from the other ones shown. The sample is injected tangentially into the chamber between the two side membranes. By differential pressure, a certain volume of sample is forced through the filtering membrane. This system can be backflushed by reversing the filtered sample flow through the membrane, permitting the swirling action of the incoming sample to remove the solids from the membrane surface.

The single-pass system is an approach similar to the sketch. By sequencing a filter tape, a small volume of sample, for example, 100 to 500 ml, can be filtered periodically without consuming a large amount of tape. In this system, each sample would be filtered through a clean section of tape. This technique appears frequently in air pollution instrumentation.

No filter can perform indefinitely without some form of maintenance. It must be either cleaned periodically or changed periodically. Dependence on human performance for maintaining a clean system never seems to work satisfactorily. If the cleanup can be automated, by all means do it.

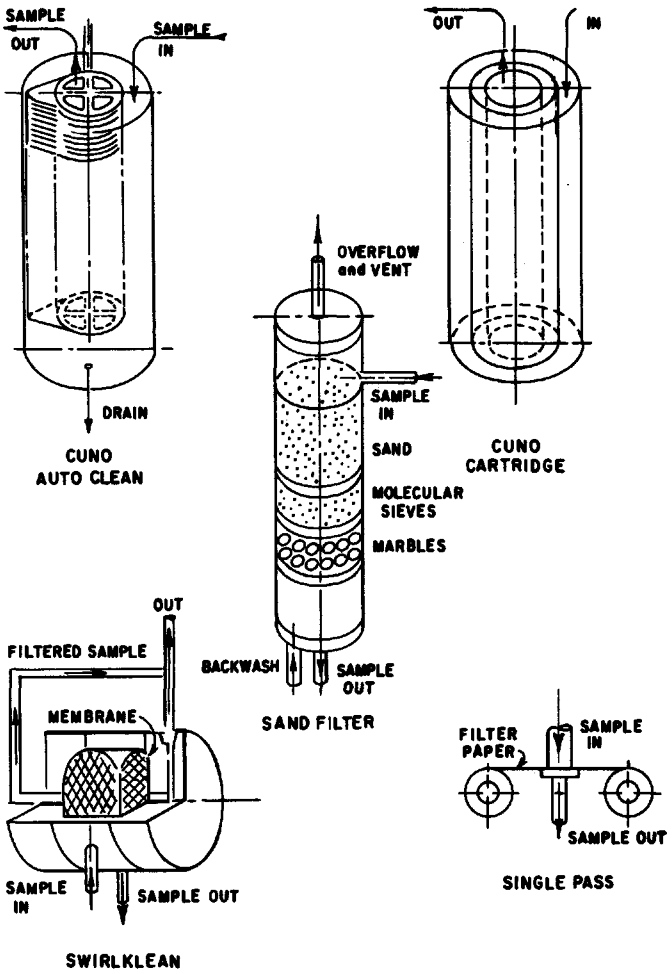

FIG. 6—*Filters.*

Analyzer Interface

Interfacing single or multiple streams into a single analyzer is no problem if two important rules are followed.

(*a*) Never deadhead a stream; keep it flowing all the time.

(*b*) If a manifold is used to gather multiple streams, keep it close to the analyzer. This will reduce the amount of sample required to flush out the previous sample and thereby minimize the chance of cross-contamination.

Both of these points are illustrated in Fig. 7 with a simple three-stream-manifold arrangement. The manifold is short and is mounted vertically to ensure drainage. The valves are always three-way, providing a constant flow all the time.

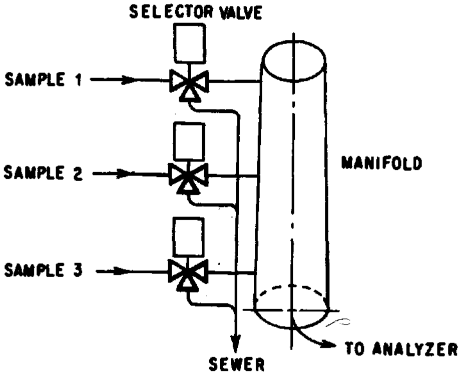

FIG. 7—*Sample manifold.*

Instrument Selection and Installation

It is essential to choose the proper type of monitoring instrument. It must provide the desired measurement with the necessary specificity, sensitivity, accuracy, and precision, plus whatever other specific requirements are essential for a given application. Instrument designs and specifications should be studied to determine the amount of maintenance required for satisfactory operation. The cost and availability of spare parts, and the time required to secure emergency service by factory-trained instrument repairmen, when needed, must be taken into account as essential items when potential maintenance costs are being assessed.

Stream and System Dynamics

The dynamics of the stream to be measured also must be considered. A water supply or process stream that can change characteristics widely within a few minutes cannot be satisfactorily monitored with an instrument that reports results 15 min after a sample is taken. The reverse is also true, since it is not necessary to run analyses on samples of a stable water supply or process every few seconds when the system monitored will not change characteristics over a period of several hours. Under these conditions, a continuously operating monitoring unit may furnish repetitive data of limited value, and, depending upon the instrument type, waste substantial amounts of costly reagents.

Readout Systems

Instrument readout systems are many and varied in concept. They range from simple "Go-No go" lights or the calibrated scale of a thermometer to the typewritten results of a digital computer, as well as to signal outputs and impulses which directly change the parameters of the system being monitored. The basic types of outputs used are analog, digital, alarm, and process control signals.

The analog readout systems involve the indication or recording of a varying signal from the monitoring instruments. A wide variety of indicating meters for monitoring instruments is available. In many cases, indicating meters are built into the instrument, and the buyer has no choice of manufacturer or type. This type of indicating readout can be used only where an operator is available to observe the results.

Analog recording devices are available as an option for most instruments producing some kind of electrical output. Recording furnishes a permanent record of the system being monitored and allows evaluation of the results at any time, without introducing subjective human errors. There is an option and selection of recorder style to be determined by the user, depending on how he plans to evaluate and store the data.

Digital readout systems differ from analog systems in that the readout data are displayed as numbers. Digital indicating instruments also may be supplied with some type of printer or recorder. Digital records vary from the electrically actuated mechanical counter, with embossed digits for stamping numbers on a paper tape, to high-speed magnetic tape systems which store the information in code, to be read out or retrieved by a computer whenever desired. Digital recorders not only have the advantage of numerical display, but also offer the further potential of facilitating data use, in conjunction with a digital computer, for process control or for storage and future evaluation of the data by a computer.

Alarm systems can be built in, as they are in the less-expensive "go-No go" type of instruments. Also, they can be attached to any other kind of readout device to give an audible or visible signal at the instrument or at a remote location when a preset maximum or minimum value is reached.

Surveillance Systems

Surveillance systems in the broadest terms are used for the collection of water-quality data. Automatic monitoring instruments can be used effectively to gather continuous or continual data on water systems under observation, determining short-term discrete changes that are not obtainable by composite sampling and laboratory analysis techniques.

Surveillance systems for data collection on surface waters such as rivers determine changes in stream quality; the nature, location, and degree of change; and pinpoint within monitoring system limits the cause of radical or undesirable changes. Within industrial plants, surveillance systems have been used to detect spills or leaks that would result in losses of expensive product or raw materials. In other applications, monitoring instruments are used to protect costly equipment (such as high-pressure boilers) or processes (waste treatment plants) from harmful waterborne constituents.

Automated monitoring stations have been installed by Government agencies and quasi-government agencies to monitor river quality. The Ohio River Sanitation Commission (ORSANCO) and the U. S. Geological Survey (USGS) have successfully operated systems for many years. The data collected by these and other surveillance systems are available for qualified use from the EPA "STORET" group. The historical data accumulated can present a scorecard on the effectiveness of pollution control efforts.

The most recent thrust of surveillance systems has been to monitor effluent quality and to regulate the amount of waterborne dumping permitted under threat of defined economic levies or fines against the offender. It is here that the automatic monitoring systems will have an important application. When properly designed and operated, these systems provide the flexibility in test parameters and frequency required to detect spills etc. (Fig. 8). More importantly, both the regulating agency and the effluent contributor, be they industrial or municipal groups, can use the same or equivalent testing devices that are readily standardized and will eliminate from test performance the hazards of different sampling techniques, analytical methods, and the human element. In case of litigation, the printed record of the unbiased automatic monitor can be used to provide uniformly acceptable data.

A total network of surface water monitoring systems has been proposed and partially completed. Recorded data from such an automated system would permit the development of inventory maps showing the influence of runoff sources, impoundment, mine water storage, and oxygen depletion, and permit logical evaluation of past water-quality records.

Effluent Systems

Effluent monitoring systems have resulted from the regulations and limits established by the pollution control laws noted early in this chapter. The effluents considered here are the ultimate discharges from industrial or municipal facilities to public watercourses.

The purpose of effluent monitoring is to control contaminant discharges to public watercourses. The monitoring system may be installed for defensive or punitive purposes.

Parameters measured vary with each specific effluent. For some parameters such as total nitrogen or chlorinated hydrocarbons, specific process monitors are not available. In these cases, composite or grab samples must be taken and analyzed in the laboratory with the associated hazards of sampling accepted.

In the case of many parameters, instruments are available for continuous or continual monitoring. These include mercury, chromate, temperature, dissolved oxygen, conductivity, pH, turbidity, total organic carbon, and total oxygen demand.

The monitors are capable of a good degree of reliability with low

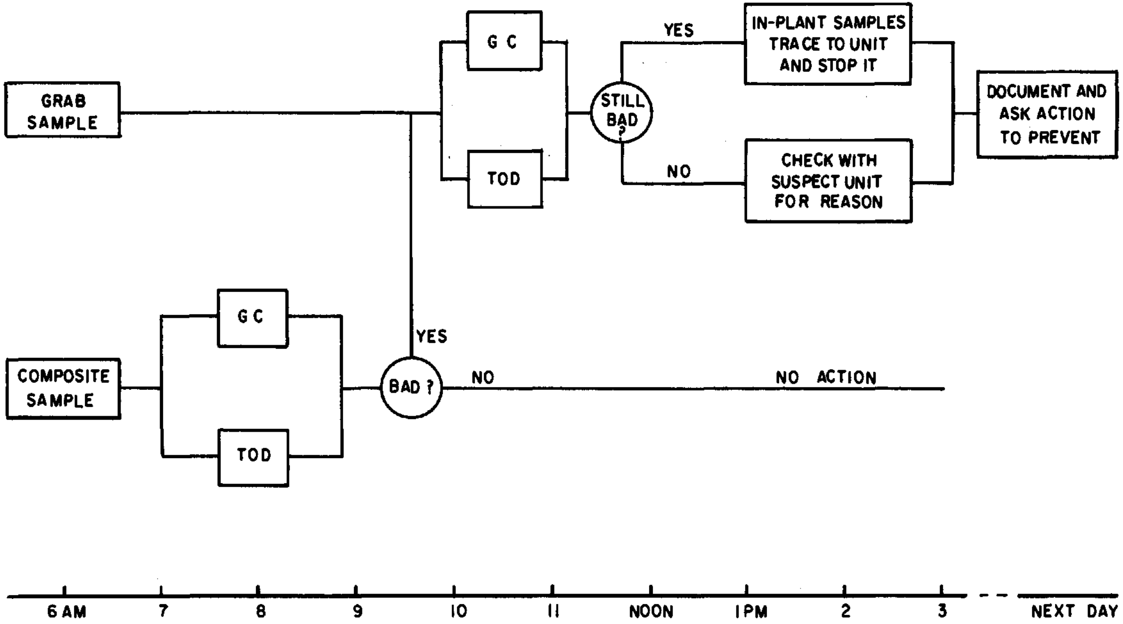

FIG. 8—*Use of TOD-GC system.*

maintenance. Systems employing these measurements include sample preparation and data handling functions. The data signal can be used to activate alarms and control equipment.

The effectiveness of a good effluent monitoring system is shown in Fig. 9. The Dow Chemical Company in Midland, Mich., made a positive commitment to minimize or eliminate plant organic spills by installing a monitoring and control system on waste streams. They installed at total-oxygen-demand (TOD) monitoring network that ultimately operated stream diversion sytems, transferring flow to holding ponds when inevitable spills occurred. The results achieved are dramatic and make the case for continual monitoring. Many of the hazardous spills detected by the system were of too short a duration to be found by grab sampling techniques, and 24-h composite samples would have masked the severity of the spills.

Process Systems

Physical and chemical parameters that are important to the operation and control of industrial processes or to the protection of the process equipment are automatically monitored by many industries. Typical physical parameters include temperature, pressure, flow rate, and liquid level. Chemical parameters are pH, specific anions and cations, along with general and specific organic compounds. Techniques employed in measuring the required parameters include, among others, automatic titrators, selective ion electrodes, chromatography, spectrophotometry, radiography.

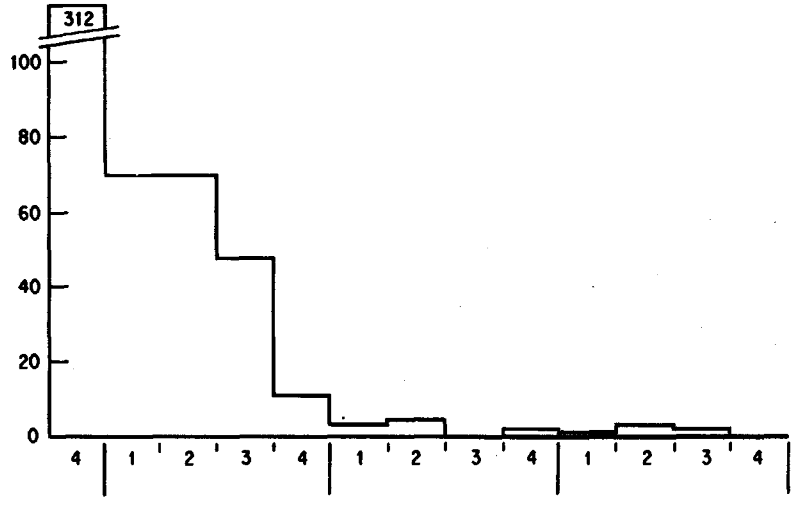

FIG. 9—*TOD monitoring results for clean-water sewers.*

Monitoring systems for power plant water quality was one of the pioneer applications for automated analytical equipment. Several different systems specifically designed for such service have been introduced and are giving excellent service, with minimum maintenance expense and substantial savings in technical manpower costs. Being automated and internally rechecked against standards, and automatically recalibrated at frequent intervals, they produce data free from human bias and subjective errors. Since results are recorded automatically, they are continuously available for inspection to determine causes of observed variations, and are essentially tamperproof. Samples can be analyzed as often as needed, at minimum expense. Moreover, control systems for chemical feed, blowdown, and other adjustments can be tied into the analytical system and used to activate these subsystems whenever necessary, or to adjust feed and blowdown rates in accordance with steam demand and water quality.

Some of the parameters now being monitored by automated systems include silica (in boiler water, steam, and makeup), Fig. 10; hardness, pH, conductivity and silica in demineralizer effluents or evaporator output; phosphate and alkalinity in boiler water; pH, chromate, residual chlorine, phosphate, and zinc in recirculating cooling water; dissolved solids or conductivity of boiler water and cooling water; trace metals in boiler makeup; dissolved oxygen in deaerator effluent and feedwater; hydrazine residual in boiler water; ammonia in condensate; and corrosion rates. Nuclear power plants place even greater emphasis on monitoring, and must add radioactivity detection and measurement to the parameters listed earlier.

Obviously, it would be impractical or too costly to set up such an extensive analytical control program based on manual grab sampling and analysis. Only the availability of rugged, continuous monitoring systems at reasonable cost has permitted the degree of sophistication and control of water analysis currently being employed in modern power plants. The monitoring equipment must perform all the necessary functions, including continuous metering of sample and reagents, mixing, purification (by dialysis, filtration, etc.), heating, digestion, or reaction, measuring, and continuous reporting or recording of results, plus adjustment or control of processes, where indicated. It is a tribute to the skill of those who design and develop monitoring systems that they are able to incorporate the necessary sensitivity, accuracy, and reproducibility in units that are sufficiently rugged and maintenance-free to permit continuous service in severe industrial applications where they are operated by relatively unskilled personnel or technicians with minimum background experience.

Specific process applications in other industries include on-line titration of acidity and iron content in pickling operations to maximize the efficiency of the operation while minimizing acid dumping and associated neutralization costs.

Continuous control of rinse tanks with backflow cycling in multirinse stages reduces water usage and minimizes metal loss and pollution in the electroplating industry.

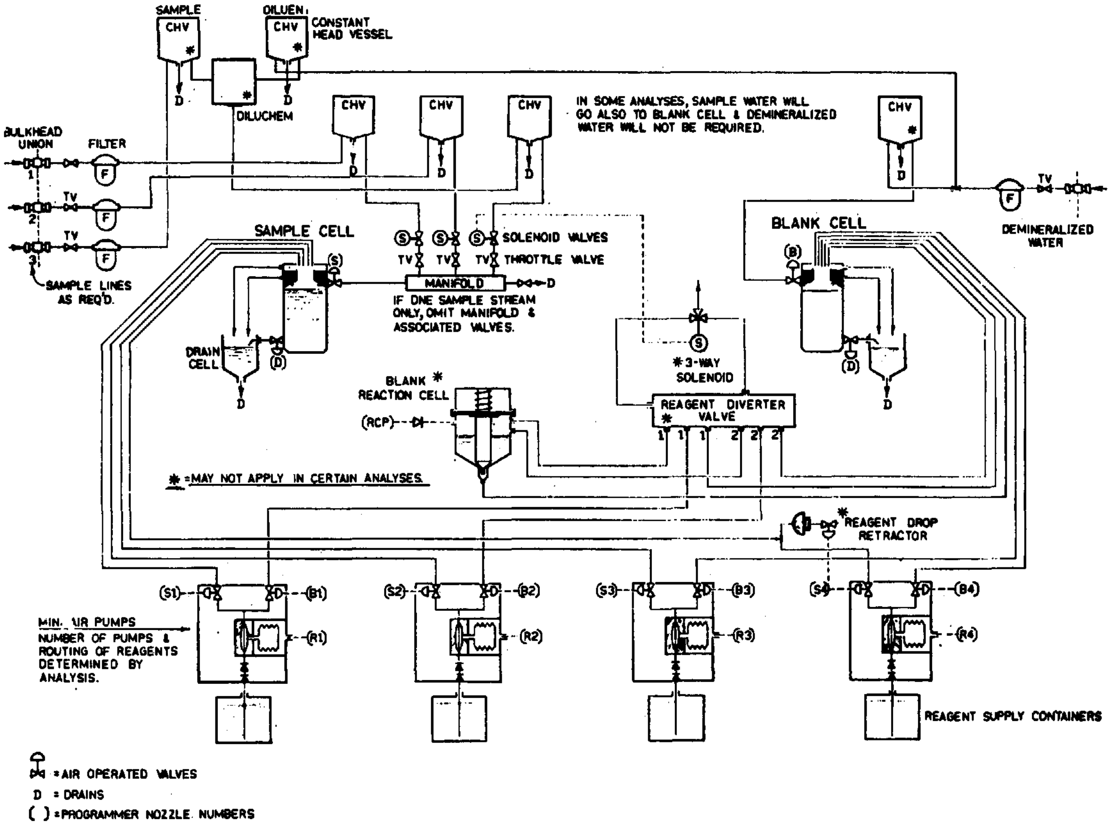

FIG. 10—*Typical flow diagram for automated silica determination on demineralized water supply.*

Leak detection sensors coupled with automatic dump valves in case of leaks allows recirculation of condensate and cooling waters previously used on a once-through basis in many industries

Process losses have been reported where the automatic monitoring system paid for itself in a single day by early detection of the leak of an expensive product.

The industry that is now actively pursuing automatic process control is one of the oldest. Waste treatment plant operation has been brought out of the dark ages by the recent push for pollution control. Efforts to balance plant loading rates, nutrient additions, coagulants, chlorine, dissolved oxygen, and effluent quality, along with early warning of toxic influents, have resulted in many studies and proposals for automatic control systems. Figure 11 shows a good composite of the current measurements available. This plant would feature feedforward or feedback control (Fig. 12) of chemical additions and have holding pond capacity to divert and treat toxic influents.

Instruments Dependent On Physical Measurements

A brief description of some principles of direct-measuring instruments may be of value as a guide in the selection and use of these instruments. It is not within the scope of this chapter to give all details of the principles involved, nor to cover all types of available monitoring instruments. Therefore, the following discussion will survey only the more common instrument types. Also, the several properties will be considered only where pertinent to instruments used to monitor water characteristics.

Temperature

Temperature-measuring instruments probably have been available longer than any other type. The several types of thermometers are well known; they are manufactured in many rugged versions designed for industrial applications. Recording thermometers generally are actuated by expansion or contraction of an enclosed gas or liquid. In deforming its container, the enclosed fluid provides energy to operate a mechanical linkage connected to a pen writing on moving paper driven by a clock motor. The pen also can be actuated by the bending of a bimetallic strip.

Temperature can be measured electrically, or determined by measuring the voltage generated at the junction of two wires of different metals, as in the common thermocouple. Outputs of thermocouples are measured either on millivolt meters or on potentiometric recorders equipped with the proper type of reference junctions. More recent devices in the electrical temperature-measuring field are resistors made of a ceramic material on which electrical resistance varies with temperature. These are called thermistors and, in general, have a much higher sensitivity than other temperature

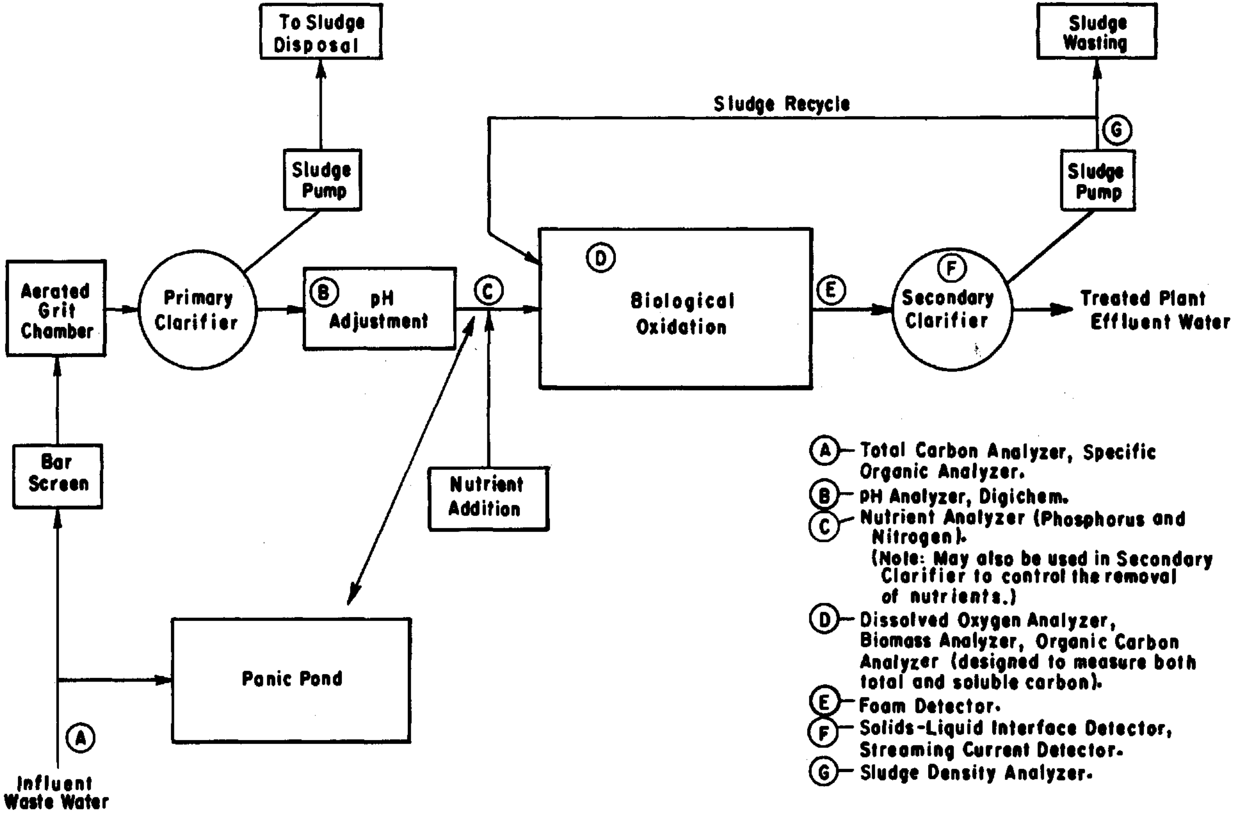

FIG. 11—*Waste treatment plant.*

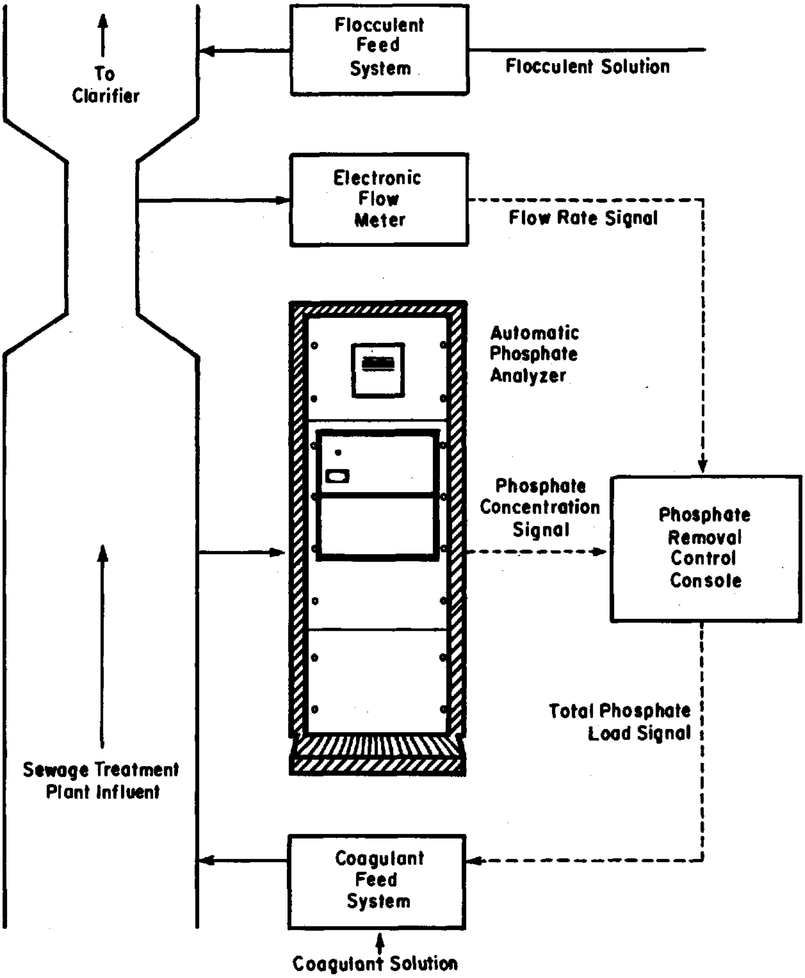

FIG. 12—*Automatic control loop for a typical phosphate removal system in a sewage treatment plant.*

measuring devices. However, they require accurate calibration, a stable electrical power supply, and are limited to temperatures below 300°C.

Conductivity

The conductance of water is another very common direct measurement. It is defined as the reciprocal of the resistance in ohms, measured between opposite faces of a centimetre cube of an aqueous solution at a specified temperature. It is normally expressed in micromhos per centimetre. Pure water has a theoretical minimum conductance of approximately 0.05 μm/cm at 25°C. As ionizable substances are added, the conductance will increase, thus providing a measure of the total ion concentration of a water sample. Since the property of conductance varies with temperature, industrial monitoring instruments should include temperature compensation provisions. The necessary potential is supplied to the conductivity cell by a stable a-c power supply, usually operating at 60 or 1000 Hz, and various methods are used to measure the current flow through the cell.

Recently, electrode-less conductivity instruments have been developed. Here, the solution to be monitored is passed through an electrically insulated tube with inductance coils or capacitor plates around each end, and conductance is measured by inducing a current in the solution. This type of unit is especially useful for monitoring corrosive liquids or those with suspended solids, and which would either attack or deposit an immersed electrode surface. Conductance instruments are very useful in monitoring the total ion content of water, but cannot be used for a specific ion analysis except under special conditions. Useful data on conductivity measurement may be found in the ASTM Tests for Electrical Conductivity of Water (D 1125) [*2*].

Density

The density of water is the basis of direct methods for monitoring the amount of dissolved or suspended solids in water samples. Techniques employed include the use of hydrometer floats in overflow chambers, chain balance float units, liquid purge differential-pressure units, or air bubbler systems. With these basic approaches, electrical position detectors or differential-pressure sensors are used to initiate and transmit signals to indicators or recorders. Since density varies with temperature, industrial monitoring instruments for water density also must have temperature compensation. Careful study of the specifications of available equipments will be necessary to decide upon the type of instrument best suited to a specific application.

Refractive Index

The extent to which fluids of different optical densities will bend or refract light (their index of refraction) is the basis of another monitoring system. Refractive index measurements can be used to monitor water characteristics and to give direct indications of dissolved liquids and solids in water samples. This method applies mainly to binary mixtures of liquids, but also can be used to determine the total impurities in water. The measurement of refractive index is temperature-sensitive, so industrial monitoring devices using this principle must have proper temperature compensation. Various photometric means are used to detect the extent to which the light beam is refracted and to send the appropriate signal to an indicator or recorder.

There are specific applications in which this type of instrument can be very accurate and sensitive.

Surface Tension

Certain organic impurities such as modern detergents have a measurable effect on the surface tension of water, and this effect can be used as the basis for monitoring contamination. Surface tension effects are measured by determining the force necessary to lift a special platinum-iridium ring off a liquid surface. This type of tensiometer device is very sensitive to impurities collecting on the equipment, so the metal ring and vessels must be kept scrupulously clean, and turbid samples must be carefully centrifuged. Information on surface tension measurement may be found in the ASTM Test for Surface Tension of Water and Waste Water (D 1590) [*2*].

Suspended Solids

Suspended solids can be monitored by turbidimetric or nephelometric analyzers, depending upon the sensitivity required. A turbidimeter measures the amount of light passing directly through a sample, while nephelometry is based on light-scattering properties (Tyndall effect) and measures the amount of light scattered by suspended solids at approximately 90 deg from a light beam passing through the sample. Nephelometry is the more accurate procedure, especially in low turbidity ranges. These instruments are affected by variation in particle color and size, but can give accurate results for specific suspended materials. Information on turbidity measurement may be found in the ASTM Tests for Turbidity of Water (D 1889) [*2*].

Color

Flow-type colorimeters can be used to monitor variations in colored components and impurities in water. These instruments are available for measuring the absorption of light rays, from ultraviolet through visible and into the infrared wavelengths. Industrial monitoring colorimetry instruments usually are nondispersive. That is, they do not use a grating or prism to reflect light into its spectrum. Instead they use interference or colored glass filters which allow only the wavelength band of that filter to pass through the sample. Nondispersive infrared instruments also can have filters of standard liquids or gases to isolate wave bands and to compare samples with a reference standard. The wave bands to be passed by given instruments are selected at a wavelength where the colored components of interest absorb the maximum light. The amount of light absorbed at the selected wavelength then will be a function of the concentration of the component of interest in the sample. Photoelectric detectors of various designs are used to sense the amount of light transmitted. A number of different electrical circuits may be used to measure the output of the photodetector and convert it to a useful signal for an indicator or recorder (Fig. 13).

Electrochemical Monitoring Methods

The next three types of monitors to be discussed are different from those listed earlier in that they are based on electrochemical determinations rather than on straightforward physical measurements. The first type of monitoring unit is a pH measuring instrument. pH is a measure of the concentration of hydrogen ions in water, and commonly is defined as the negative logarithm of the hydrogen ion concentration. A number of electrode systems have been developed to measure this property of solutions, but the one that has proven to be the most practical is the glass electrode. It is an electrochemical half cell based on the potential generated across a glass membrane with a fixed hydrogen ion (H+) concentration on one side and the unknown (H+) ion concentration on the other. When used in conjunction with a standard half-cell reference electrode, the glass electrode passes a very-high-impedance potential to a high-impedance amplifier from which the output indicates or records the pH value.

For an industrial pH monitoring instrument, a temperature-sensitive resistance element is immersed in the sample, and connected in the amplifier

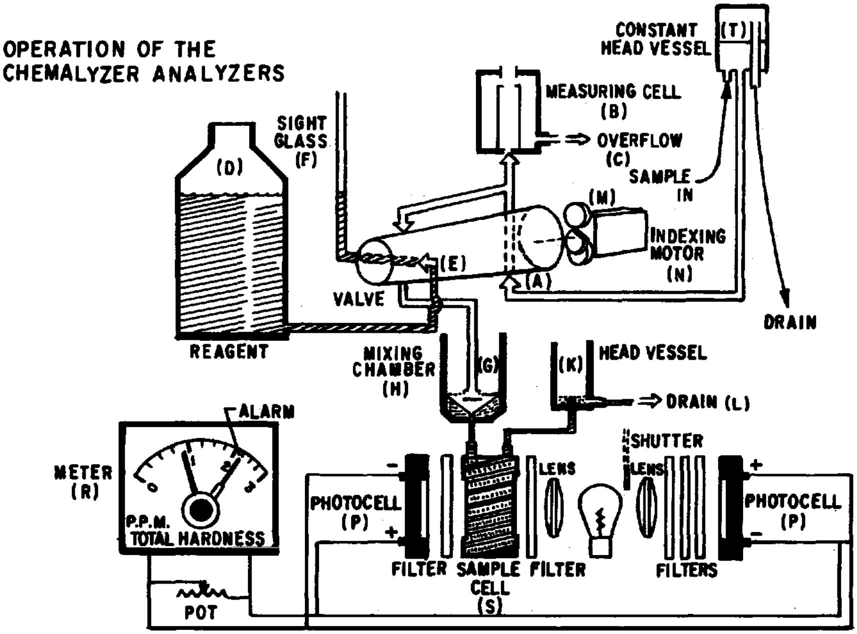

FIG. 13—*Schematic diagram showing components of one indicating-alarm monitoring system for hardness control.*

circuit to compensate for temperature variations. These instruments, when properly installed with suitable flow cells, and continuously maintained, can monitor accurately and reliably the hydrogen ion concentrations of water supplies and other samples. Antimony electrodes have been used in place of standard glass electrodes. While they have a lower impedance, they are attacked by a number of materials found in water; as a result, antimony electrodes do not have widespread application. The ASTM Test for pH of Water and Waste Water (D 1293) [*2*] covers pH measurement by means of the glass electrode.

Oxidation-Reduction Potential

Another electrochemical measurement uses a platinum electrode in conjunction with a standard reference electrode to measure the oxidation-reduction potential of industrial water supplies and aqueous process streams. The readout system is similar to that used for a pH meter except that the scale reading is in millivolts (+ or −). The sign of the potential is important in this case, as it indicates whether the solution has an oxidizing or reducing potential. These monitoring units are classified as direct-measuring instruments and, in general, are simple and maintenance-free. At the same time, they usually cannot provide the specificity necessary to monitor individual components. In other applications, oxidation-reduction systems may comprise the detector section of more complex chemical analysis instruments. The ASTM Test for Oxidation-Reduction Potential of Water (D 1498) [*2*] describes the apparatus and procedures for this measurement.

Specific Ion Electrodes

The third type of electrochemical monitoring unit is the specific ion electrode. Electrodes are available to measure the activity of Na^+, K^+, Ag^+, Cu^{++}, Ca^{++}, Mg^{++}, other divalent ions, F^-, $S^=$,Cl^-, CN^-, and NO_3^- ions, among others. These electrodes measure ion activity, not concentration, so that appropriate corrections must be made (especially at high activity) to get a reading of ion concentration. Various designs are employed in these electrodes. Some are stable and maintenance free, while others are not suitable for industrial monitoring. The specific application must be studied carefully and the manufacturer's suggestions followed.

Chemical Analysis Instruments

Chemical analysis instruments have developed out of a need for specific or sensitive analysis methods for monitoring and controlling water characteristics. Under proper conditions, many components of interest can be made to undergo chemical reactions that produce definite reaction products. Measurement of the amount of reaction products, or the amount of reagent necessary to complete the reaction, is the basis of chemical analysis instruments. In some cases, the function of analytical instrumentation is automation of a laboratory or field test procedure. In other applications, they are the miniaturization of a process reactor. Such analytical instrumentation often is relatively simple compared with other modern types of process control systems. With proper service and maintenance schedules, automatic continuous analytical instruments can provide valuable information that is essential for water monitoring and quality control.

Colorimetric Analyzers

The first of the basic instruments to be described is the colorimetric analyzer. Such units include systems for adding color-forming reagents to the sample. For maximum accuracy, the colorimetric analyzer should incorporate the additional features of a comparison cell, a system for reacting and measuring comparison reagents (or blanks), and an automatic zero or calibration reset. Provisions for necessary pretreatment such as heating, extraction, filtration, digestion, or dialysis can be provided. In many applications, the colorimetric chemical analyzer has the potential of being the most specific and sensitive water-monitoring instrument available (see Fig. 13).

Galvanic and Electrochemical Reactions

Galvanic and electrochemical reactions provide the basis for a number of chemical analysis instruments such as those used to measure hydrazine, or dissolved oxygen and other water-soluble gases which have an effect on electrode reactions when they are added to the electrolyte of a galvanic cell. The physical variations of these instruments are too broad to permit a generalized description of them. Temperature compensation is required for such monitoring units. In dissolved gas analysis, the gas of interest usually is diffused through a plastic membrane to allow long, unattended service. The electrolyte, and in some cases the electrodes, eventually become spent and these must be replaced. Depending upon the physical design, these electrochemical monitoring units often require the least maintenance of any type of chemical analysis instrument.

Coulometric Analyzers

Coulometric instruments are based in principle on Faraday's law, which states that a definite quantity of direct current will cause a valence change in a specific number of ions in a solution. If the amount of current passed is known, then the number of ions changed also is known. Instruments based on this principle have an absolute calibration rather than relative calibration methods based on standards, typical of most other instruments. The generation of the new valence state can be accomplished either directly in the sample solution, or in a separate vessel, in a pure chemical reagent precursor which is then reacted with the sample. The latter allows some freedom from interferences by other ions in the sample which also may undergo a change of valence state when they are near the generating electrodes.

The coulometric instruments include a liquid section containing generating and detecting electrodes which indicate to the circuit that sufficient current is passing to react with the ions in the solution. The readout section includes indicating or recording instruments which measure current sent to the electrodes. The instrument can use either a flow cell or a fixed-volume measuring cell that performs batch-type analysis. The batch type more often are laboratory rather than field monitoring instruments.

Coulometric instruments require periodic cleaning, depending upon the sample stream. In some types, where generating electrodes are the material for the formation of the reacting valence state, the electrodes must be replaced at regular intervals. The electrical generating and measuring circuits require the normal maintenance for circuits of these types, and maintenance problems may vary according to the electrical components used.

Corrosion Measurement

The corrosivity of water is measured by the chemical action of the water on a standard sample of a given material sensitive to the corrosive substances of interest. The amount of chemical reaction occurring in a period of time may be estimated by several different methods, with various instruments. In one case, the current generated by solution of the metal is measured; in another, the change in the resistance of a metal element due to reduction in cross section of the metal probe is measured. The primary maintenance problems with this type of instrument are requirements for periodic replacement of the standard sample units or probes, and leakage, which permits internal resistance changes or short-circuiting of probes.

Titrators

One type of chemical analysis instrument having a broad field of application is the titrator. These units are based on conventional volumetric analysis methods. Such methods are adequately covered in ASTM standards and in many other texts on analytical chemistry, so the details of analytical procedures will not be discussed. The titrator-type instruments include devices for measuring the volume of a standard solution or titrant added to a measured volume of sample, and systems to determine when the added volume of standard solution has provided enough reagent to be equivalent to the component it is reacting within the sample.

The titrator instrument most often is an intermittent or batch type; however, continuous units are available. A continuous titrator instrument usually operates by pumping the sample through the system at a constant rate, and varies the rate of titrant addition so that it will be stoichiometrically equivalent to the component of interest in the sample. Several different approaches are used for measuring and indicating the volume of titrant used. The detecting system to a large extent is dictated by the method of chemical analysis necessary. Detector systems which may be used can be based on pH, redox potential, colorimetric, turbidometric-nephelometric, and conductometric measurements. The maintenance requirements and adaptability of these titrator instruments vary as widely as do their design. The specifications of all such instruments available and economically acceptable should be studied thoroughly to determine which type will perform most effectively in a desired application.

Operation and Maintenance of Monitoring Instrumentation

Because of the great variation in types of monitoring instruments, no attempt will be made here to provide specific operating and maintenance instructions. In most cases, the instrument manufacturers supply specific operating and maintenance information for their equipment, this information being derived both from experience during development and that gained during field operation. Failure to follow the manufacturer's environmental control specifications and operating instructions will lead to unsatisfactory results and equipment malfunction more quickly with monitoring instruments than with any other type of process control equipment.

While many types of monitoring instrumentation are relatively complex, and sometimes challenging to operate and maintain, the data provided are very valuable in defining water characteristics, and justify extra maintenance effort.

The operator's attitude and approach to the operation of monitoring instrumentation, and particularly to its preventive maintenance, must be different than it is to maintenance of control valves, pumps, or other units of process hardware. The monitoring instrument is designed to furnish information about the characteristics of water in the operator's system which can be obtained in no other way. Such instrumentation can be considered as an extension of the human senses and memory which allows the user to extend his natural abilities and technical skills. Through automated instrumentation, more efficient use of manpower can be made, together with accumulation of increased knowledge, leading to more efficient processes and better control of aqueous systems. Monitoring equipment then should receive all the care and attention to operating and maintenance details which it deserves.

For maintaining water-monitoring instruments, a general recommendation is to set up a regular preventive-maintenance program at the time the equipment is installed, and follow up to make sure it is carried out. Any system allowing instruments to operate without scheduled maintenance until a component fails is unsound, and will prove both time-consuming and expensive. Preventive-maintenance programs will vary widely according to the type of instruments used and the nature of their environment. Information needed to establish maintenance programs can be obtained from manufacturer's operating and maintenance manuals, or directly from the nearest manufacturer's service representative.

Obviously, it is not possible in this chapter to explain the detailed functions of every type of water monitoring instrument. The two main reasons are space limitations, and the unusually rapid developments in the monitoring field which soon would make detailed descriptions obsolete. Therefore, for background data, a list of suggested reference texts is appended. In addition, much useful information can be obtained by a survey of the manufacturers' current literature on monitoring systems.

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Chapter 11—Analysis of Water and Waste Water

Water quality is a function of both the source of the water and its intended use. The quality of a given stream can be defined only in terms of the requirements of the system in which it is being received or from which the water is discharged. The waste from one use may well be the water supply for another use. Before one can control water quality for a use, a great deal must be known about both the chemical and physical characterizations of the possible water sources, and the exact requirements for the planned use. Knowing these data, one can set out to develop the proper treatment for the selected water supply. Once the treatment program is started, analytical data are needed to determine its effectiveness. Overtreatment causes unnecessary expense, and undertreatment also will cost money because of equipment inefficiency or failure, plus resulting downtime, maintenance expense, and, potentially, reduced product quality. One may conclude that analytical data are needed for effective planning of the system and for monitoring performance of the system subsequently. The *Annual Book of ASTM Standards*, Part 31 [*1*],[1] presents a wide variety of analytical methods to determine the various constituents and characteristics of significance to water quality evaluation.

This chapter provides the analyst with criteria necessary for the selection of the best method to check for each constituent, and guidance to properly interpret results of the analyses, in relation to the water system under consideration. To accomplish this goal, the chapter discusses (1) the value of a well-defined, systematic program of analysis; (2) sampling methods for various needs; (3) the basis for selection of the test methods to achieve the desired results; (4) the cross-checking of analytical data; and (5) the interpretation of results.

Although the determination of water quality is done to select the proper treatment program, the description of specific treatment methods is beyond the scope of this chapter. (Treatment methods are discussed in Chapter 5.) In selecting sites for new plant construction, where water is required for plant operations and for use in manufacturing products, the quality and quantity

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

of water available, and its analysis, play important parts in the economics of plant operation.

In order to design an effective and comprehensive treatment program, it is necessary to determine all the variables which may be important in the use of the finished water. At first, a complete analysis would be wise, including consideration of seasonal changes; thereafter, perhaps, only selected tests would be necessary on a routine basis to monitor the more important variables and maintain the water treatment program. Variations in certain characteristics often can be predicted on the basis of the source of water. For example, deep well water would not be expected to vary appreciably in organic matter or hardness, while river water may vary rapidly and widely in organic matter, ammonia, and other constituents, depending the nature of water use upstream. Lake water will vary in organic loading depending on depth and size of the lake, changes in temperature, microorganism growth, and pollution factors.

Rivers represent the most commonly used water sources. The impurities encountered can come from diverse sources, including agricultural runoff, municipal wastes, mine drainage, industrial waste, and natural forest runoff. A survey upstream will show several of the specific impurities and often the contributing sources which affect the water quality at the plant site. Treatment required for a river water, depending on the proposed use, may be extensive or minimal as indicated by interpretation of the analytical data. For example, a river water for cooling tower purposes may require as little treatment as a chromate corrosion inhibitor and only minimal control analyses. The same water source used for boiler feedwater may need coagulation, sedimentation, filtration, de-ionizing and de-oxygenation to be sure that corrosion and deposit formation are minimal. Frequent sampling and extensive analysis will be needed for proper operation. A municipal water supply form this same source may require softening filtration, activated carbon treatment, and chlorination to meet the drinking water standards and other end-use criteria.

In many cases, comparisons are made between two or more potential supply sources to determine which source offers the best possibility of efficient and economical operation. A comprehensive analysis of the water from each source is the key to the selection. The economic evaluation must consider all treatment costs, as well as the costs of obtaining and ensuring continued availability of an adequate volume for the needs today and for some time in the future.

Nature and Scope of an Analytical Program

The requirements of the system with respect to the quality of the supply water determines the extent of analysis. The number of tests and accuracy required to maintain control are not the same for all systems. For example, adequate control of water in a low-pressure boiler may require analysis of only four or five items on samples taken once per day or once per shift from a single sampling point, with sensitivity requirements on each analysis falling in the milligram-per-litre range. On the other hand, control of boiler water in a high-pressure steam generator may require eight or ten determinations of items measured in micrograms per litre, on samples taken at various spots throughout the system, every hour or two. The difference in the cost of these two control programs would be substantial. Time and money can be saved by designing the analytical program to collect only essential data. However, the program must be complete enough to ensure protection of expensive equipment from corrosion or deposit formation.

There are several factors to consider when selecting an analytical method, including the sensitivity required, the interferences present, and the variations in precision and accuracy that can be tolerated. Even the background of the analyst to perform the test must be considered, since many procedures are satisfactory only in the hands of a skilled operator. The discussion of water analysis methods in this chapter primarily is designed to assist in the proper selection of individual procedures for specific applications. The test methods described in the latter part of the chapter are grouped according to the constituents for which tests are to be made. For example, all the methods for dissolved oxygen in water are discussed together; so also are methods for iron, and methods for silica. This is done to emphasize the importance of recognizing differences between the various methods available for determining individual constituents, and to illustrate the importance of selecting the proper procedure for a given application. The discussion of methods also includes a brief review of the relative importance of each element in different water treatment and water use situations, to direct the analyst to the selection of the proper method. For example, a series of samples to be analyzed (for hardness, silica, alkalinity, iron, and oil) from a once-through cooling system would be handled differently than similar samples from boiler feedwater. The hardness that can be tolerated in cooling water ordinarily will be high compared with the allowable hardness in boiler feedwater. Thus, one must select a very sensitive hardness test for boiler feedwater, whereas a less sensitive but accurate procedure is adequate for most cooling systems. The amount of silica in a feedwater for a high-pressure boiler ordinarily is kept below 1 mg/litre, and the test method must be very accurate in this low range. Silica in cooling water is not as critical with respect to sensitivity requirements, but the high degree of accuracy still is required for optimum operation. While the test for alkalinity is equally important in both systems, the method used for boiler feedwater may not be applicable to treatment programs used in cooling systems. Cooling water from open recirculating systems often is maintained with pH below 7, and corresponding alkalinity levels, whereas boiler feedwater normally is alkaline.

The concentration range and possible interferences such as highly colored materials present in the sample because of treatment will have to be considered in selecting a method. When iron is found in boiler feedwater, it may mean either that corrosion is taking place, or that suspended iron from reclaimed condensate or the raw source water is not being completely removed. In either case, the iron entering the boiler can contribute to deposits which will cause heat losses and eventual failure of boiler tubes. Feedwater with 10 μg/litre dissolved or suspended iron entering a boiler producing a million pounds of steam per hour can deposit 4.5 kg (10 lb) or more of iron oxides every 1000 h of running time. Thus a few micrograms per litre of iron would indicate potential trouble, and a sensitive test is required. Iron in cooling water is not quite as critical, but it must be controlled in the low milligrams-per-litre range, for it reacts adversely with the treatment chemicals, promotes growth of iron bacteria, and accelerates deposition of fouling layers.

The methods selected for analysis of boiler condensate water will differ from those applicable for untreated water. One would expect boiler condensate to contain extremely small quantities of dissolved or suspended constituents such as calcium, iron, magnesium, and sodium. Thus, test methods for these constituents must be very sensitive. On the other hand, untreated water will contain these same constituents in large quantities, requiring methods with much higher concentration range. The same raw water may contain certain significant constituents such as fluoride or cyanide in very low concentrations, but which may be important in the treatment program. In that case, the raw water will require highly sensitive analytical methods for these constituents, and less sensitive methods for the more standard mineral determinations. Brine or brackish water supplies will require a different analytical approach than freshwater. Brines or brackish waters contain very high concentrations of dissolved salts. A method with a high concentration range and freedom from interferences must be selected. Freshwater samples usually will be lower in dissolved solids; thus a more sensitive test with lower concentration range may be utilized.

Process water supplies will dictate different methods of analysis than will industrial waste-water samples. Process water may contain added water treatment chemicals to control certain elements. The analysis must check on the effectiveness of added treatment chemicals. Certain constituents, when present, are objectionable and must be checked. The presence of objectionable substances may require chemical treatment to be altered, and additional checks made.

Industrial waste control introduces another type of analytical program, since waste solutions are very different from the water received for use. The U. S. Environmental Protection Agency (EPA) and other regulatory bodies have set limits (National Pollutant Discharge Elimination System) (NPDES) for materials which may be discharged into a receiving water. For a given source of waste water, the potential extent of contamination and acceptability of the waste for discharge will depend on the concentration of the particular constituents in the waste water. The appropriate analytical methods are dictated in the regulation, with the option of proving another method equivalent or better. Methods appropriate for the receiving water may not be useful for waste waters, because of concentration differences, interferences, and other factors.

The foregoing discussions show that one must determine not only the specific constituents tests, but also the type of water system being considered, and the required tolerances of the method with respect to precision, accuracy, sensitivity, and interferences.

Planning the Program of Analysis

The planning of a sound program of analysis is the first necessary step if appropriate information is to be realized from the data gathered. This planning is done with the objective of assuring that standards of water quality and treatment established for a particular system are met and continuously maintained. Some care is required in planning. A program that is too extensive, providing unneeded data, causes unnecessary expenditure of time and money. On the other hand, an inadequate program of sampling and analyses can lead to incorrect interpretation of data and improper treatment, with resultant damage to costly equipment or products. The test performed should give the greatest economy of time and motion while still providing the necessary information.

There are four primary considerations in planning a program of analysis: (1) determining what stages of the system need control and, therefore, analysis; (2) determining which constituents at each stage need control and, therefore, how thorough an analysis is required; (3) determining what method will be used in measuring a particular constituent; and (4) determining how frequently the constituent must be measured.

In general, an adequate plan will include provisions for regular analyses of the supply water and any reused water (such as condensates and recirculating cooling waters); analysis of treated waters; analysis of waste-water discharges for compliance with regulatory agency standards; and periodic performance checking of the entire system. Included in the planning must be the sampling procedures and location. Reasonable forethought will result in effective representative sampling.

Selection of the constituents to be measured, and therefore the extent of analysis on a particular sample, will be dictated by the requirements of the system. A complete analysis is required where full knowledge of the various constituents is needed. For example, supply waters initially would require a complete analysis in order to determine the suitability of the supply for a process use. Provisions for determination of substances that will interfere with or damage the process, along with those substances which may interfere with the treatment, are important considerations in a supply water. However, an abbreviated analysis program can be used where only a few constituents are critical. In a treated cooling water, for example, measurement of two or three constituents may suffice for maintaining proper treatment level and water conditions. A combination of an initial complete analysis followed by subsequent abbreviated analyses is common. Variations in a few key constituents may be used to signal the need for further system checking.

In supply waters, an abbreviated analysis may be made once the total constituents are identified. In this case, the constituents measured must be carefully chosen, as surface supplies are subject to seasonal changes and periodic contamination; the constituents measured must reflect these changes. Of considerable aid in determining constituents which must be considered, or are present in troublesome amounts, is the use of qualitative or semiquantitative analytical methods. For example, optical emission techniques can provide rapid analysis of a large number of constituents present in water. In this manner, water supplies can be checked conveniently at regular intervals, to pick up variations which may arise. If emission equipment is not available, it is sometimes profitable to send samples to a consultant laboratory, to supplement other information available for the analytical program.

After the constituents to be measured are determined, the appropriate analytical method must be chosen. The ruling considerations here are the sensitivity, accuracy, and precision desired, the interferences present, and the speed and the cost of the analysis. High-precision methods are used where accuracy and precision are important considerations, and where many interferences must be considered. However, they usually are more complicated and time-consuming than alternative methods, and the accuracy obtained may not justify the time consumed. In many instances, the highprecision methods may not provide the sensitivity needed. Less demanding, simplified methods are appropriate for use where applicable, and can save appreciable time and effort when certain interferences are absent. Also, some analytical methods provide alternative procedures that meet sensitivity requirements. In many instances, accuracy is not the most important consideration.

In the discussion of the various procedures, later in this chapter, other tests mentioned (not included in the *Book of ASTM Standards*, Part 31 [*1*] may be applicable to special cases. In choosing the analytical method, the choice made must be an appropriate balance of the foregoing considerations to meet the needs of the system and the process most effectively, and with maximum economy. An important first step in every analysis is the recording of the sample source and physical appearance. The sample should be labeled appropriately; the analyst must know the type of water, treatment added, if any, and the sampling conditions. The analyst's own description is also important, such as the solution color, turbidity, the presence and color of any solids, and whether magnetic or nonmagnetic, whether the container appears oily or greasy, and the presence of unusual or unexpected odors. All these factors can be used as a check on interpretation of final results, or as a guide to potential analytical difficulties or interferences. In planning analytical methods to use, brief qualitative or semiquantitative tests again can be very helpful. They may be used to indicate the concentration ranges of the constituent sought, or of interferences present, thus guiding the choice of methods.

The fourth consideration in a program of analysis is the frequency of testing, that is, how often a particular analysis is required. The demands for control of a particular system again will determine the choice. Considerations of the type of water needed, the nature of the supply, the methods of treatment, the response time of the control system, and the overall cost of the program are significant to an effective operation. Costs of full protection of equipment and processes must be weighed against the hazard of reduced testing. After a water system and treatment program are fully stabilized, further reduction of the frequency of analysis can be considered. Simplified procedures also may be adopted with periodic checks to verify the accuracy with standardized tests.

Table 1 and associated Tables 2 and 3 suggest an order of application of methods which permits the determination of existing properties and constituents in a logical sequence. The flow diagrams separate the samples affected by air contact from those not affected by air contact. Further divisions are indicated for determinations to be made on flowing samples, separate samples, and special samples. With these considerations in mind, an analytical program can be planned which will conserve time and sample. Often, a simple test for a given constituent or property can be used to detect its presence to determine whether it should be analyzed by the standard method. Such preliminary tests often will save considerable time. One or more constituents can be determined on a single sample by a scheme of successive analyses of filtrates or aliquots, while other constituents require a separate sample and special handling. Many of the tests can be made while others are in progress. With some practice, the analyst will acquire a sense of timing which will permit him to carry out the necessary operations with the greatest possible speed consistent with appropiate accuracy and precision. Furthermore, he will learn to connect the presence of one constituent with the necessary absence of another. For example, ferrous iron would not be present in water that contains residual chlorine.

Special Apparatus for the Laboratory Methods Presented

Advances in analytical instrumentation have made available to the analyst a wide variety of sophisticated apparatus ranging from highly versatile to highly specialized application. The choice of instruments should be governed by the nature and frequency of the analytical information that is desired. Accuracy, sensitivity, and available funds must be considered. Highly precise, sophisticated instruments are expensive; many require special laboratory conditions such as controlled humidity and temperature, and

TABLE 1—*Outline of principal sample groups.*

Sampling procedures shall be in accordance with the applicable ASTM methods.

SAMPLES FOR PROPERTIES AND CONSTITUENTS AFFECTED BY AIR CONTACT

In order to obtain the true concentration of properties and constituents affected by air contact during sampling, or during the interval between sampling and analysis, it is necessary to employ special methods or equipment, or both, for sampling, and, preferably, to carry out the determinations immediately. If determinations are not made immediately in the field, it must be realized that laboratory results reported for these constituents are based on the sample in an as-received condition, and are not necessarily representative of the water sampled, since the laboratory usually has no control over, or knowledge of, the sampling methods used. (Note 1.)

FLOW SAMPLES

(See Table 2)
Flow samples shall be used in determining these properties and constituents at the sample source. This information may be continuously and automatically determined, indicated, and recorded.

SEPARATE SAMPLES

(See Table 3)
Samples for which these properties and constituents are to be determined require that the sample containers be sealed against air contact during the interval between sampling and analysis; or the samples must be chemically fixed immediately after sampling.

SAMPLES FOR PROPERTIES AND CONSTITUENTS UNAFFECTED BY AIR CONTACT

Samples for which these properties and constituents are to be determined may or may not be filtered in the laboratory prior to analysis, depending upon the nature and the amount of undissolved material, the method of analysis used, and the specific information required. If the analysis is to be representative of the sample as collected at the source, the amount and composition of the undissolved material present should be determined. Spectrographic and X-ray diffraction examination of the undissolved material is of value in connection with these procedures. (Note 1.)

SEPARATE PORTIONS OF A SINGLE SAMPLE

Separate portions of a single sample may be used for determining these properties and constituents individually or, in some cases, in a sequence of analyses. The customary precautions against contamination by airborne solids, or too long storage in unsuitable containers (Note 1), must be observed in the case of samples to be analyzed for these constituents.

SEPARATE SAMPLES

Samples for the determination of extractable matter and floating liquids must be collected separately in glass-stoppered flasks of chemically resistant glass. Samples may also be collected in cork-stoppered flasks, provided the stoppers are wrapped in metal foil.

NOTE 1—If the property or constituent to be determined may be affected by reaction of the sample with the sample container, a separate sample should be collected in a special container that will not itself contaminate the sample.

specially trained personnel. It is necessary to consider whether their use will justify initial and continuing costs.

An example will help illustrate some of the factors influencing the choice of instruments. Suppose a particular water is to be analyzed routinely for iron content. A decision is made as to what concentration of iron is significant. ASTM Tests for Iron in Water and Waste Water (D 1068) [*1*] present a colorimetric method applicable to several concentration ranges. If the concentration of interest is greater than 0.1 mg/litre, Nessler tubes can

TABLE 2—*Properties and constituents affected by air contact.*

Flow samples shall be used in determining these properties and constituents at the sample source. This information may be continuously and automatically determined, indicated, and recorded.

Electrical Conductivity: D 1125
Hydrogen: D 1588
Oxygen: D 1589, D 888
pH (Hydrogen Ion): D 1293

be used and the color comparison made visually. If sensitivities down to 0.02 mg/litre are needed, a filter photometer is required. Below 0.02 mg/litre, a spectrophotometer will be required. It will be noted that the greater the sensitivity need, the more costly the instrumentation becomes. However, the instrument also becomes more versatile. The spectrophotometer in this case can be applied to the upper ranges as well, which may be a consideration in other procedures that must be run. Convenience also may be a consideration. In the example just given, when the iron concentration of interest is greater than 0.1 mg/litre it still may be profitable to use photometer instead of visual comparison methods. The frequency of tests required may make it a considerable waste of time and effort to prepare the series of standards needed each time for visual comparison. A photometer, with a standard curve, then can be a timesaving convenience.

The choice between manual and automatic or semiautomatic instrumentation will be governed primarily by the frequency and speed of analysis required. The needs of the analytical program will determine the choices of

TABLE 3—*Properties and constituents affected by air contact.*

Samples for which these properties and constituents are to be determined require that the sample be sealed against air contact during the interval between sampling and analysis; or the samples must be chemically fixed immediately after sampling.

Acidity and Alkalinity: D 1067
Ammonia and Ammonium Ion: D 1426
Calcium and Magnesium Hardness: D 511; D 1126[a]
Carbon Dioxide, Carbonate, Bicarbonate; D 513
Chlorine Residual: D 1253, D 1427
Chlorine Requirement: D 1291
Hydrazine: D 1385
Hydroxide Ion: D 514
Iron: D 1068
Nitrite Ion: D 1254
Dissolved Oxygen: D 888, D 1589
pH: D 1293[b]
Phenolic-Type Compounds: D 1783, D 2580
Sulfides and Hydrogen Sulfide: D 1255[b]
Sulfur Dioxide, Sulfite, and Bisulfite: D 1339[b]

[a] These properties and constituents are usually determined on separate portions of a single sample that has not been sealed against air contact, because, in most instances, it is not justified to obtain separate, sealed, or chemically fixed samples for these determinations. When these determinations are requested on samples, a note should be made qualifying the analytical results in this regard.

[b] In order to calculate these constituents correctly, the pH value of the sample must be noted simultaneously with the sampling. The truest pH value would be in the flowing source.

instrumentation. A time-and-cost evaluation may become necessary when considering instrumentation selection. Of course, any fairly extensive analytical program will require the usual laboratory facilities. The quantity and types of analytical balances, fume hoods, steam tables, ovens, laboratory bench space, sample storage, and a host of ancillary equipment must fit the analytical program. Certain analyses will require special sampling apparatus; this too must be considered.

Not to be overlooked is safety of the laboratory or testing area. Control measures for toxic gas, fire, and explosion hazards must be planned. Flammable compounds must be safely stored. Personnel safety involves mandatory use of protective clothing, safety shields and glasses, a knowledge of the chemicals and reactions involved, and an aggressive laboratory safety education program.

Laboratory Practices

To help ensure the success of an analytical program, certain practices should be observed in the laboratory and become part of the accepted routine. Analytical methods may represent sound scientific principles and years of development, but if they are misused or abused, the effort is wasted. Similarly, the most modern facilities and equipment must be properly used in order to yield meaningful information. A review of some of these factors should be helpful.

Sample and reagent containers must be selected with care. The choice of clear or colored storage containers, soft or borosilicate glassware, plastic containers, and the type of stoppers or caps used can influence accuracy. Generally, a method or sampling procedure will indicate the type of container required; these requirements should be adhered to rigidly. Cleanliness of glassware and containers is of the utmost importance in water analysis. Since concentrations of some constituents may be sought in the micrograms-per-litre range, even slight traces of extraneous material can cause appreciable error. Glassware may be segregated for specific uses, but it is better to treat the entire lot for the severest case.

To eliminate or recognize errors traceable to reagent variations, operator habits, and similar factors, blank determinations should be run. Spot checks on the reagent water [see ASTM Specifications for Reagent Water (D 1193)] [*1*] should be made, and the there should also be occasional checks on known samples to establish relative accuracy among analysts in the laboratory and between laboratories.

To eliminate other potential sources of error, periodic checks on calibration or standardization of analytical equipment or solutions must be made. With equipment such as spectrophotometers, standard curves should be checked frequently. New dye lots should always be checked because batch-to-batch variations may shift calibration curves. pH meters must be calibrated frequently. Even thermometers should not be assumed to be correct, but should be compared with one known to be accurate.

Another important aspect of laboratory practice is the quest for new and improved methods. The analyst should not cease to search once he has found a satisfactory one. Methods offering greater specificity and reliability are continually being developed. He should be aware of these, evaluate them, and introduce them, if they are improvements over existing procedures.

Since the analyst is an important part of any method, safety must be considered in laboratory practices. Knowledge of potentially dangerous reactions and conditions is essential, and due precautions should be part of the laboratory routine.

Analytical Sampling

The best analytical methods are of no value if poor sampling techniques are employed. The sample must be representative of the water to be examined, and the concentration of the constituent of interest must remain the same until the analytical tests are made. The technique of sampling varies, depending on the type of water and its use.

After the program of analysis is planned, consideration must be given to obtaining representative samples. In this respect, the proper location of sampling points and auxiliary equipment such as cooling coils or degassers is important. Several methods in the *Annual Book of ASTM Standards*, Part 31, cover the equipment and general techniques of sampling:

D 1192, Specifications for Equipment for Sampling Water and Steam.
D 1066, Sampling Steam.
D 887, Field Sampling of Water-Formed Deposits.
D 3370, Practices for Sampling Water.

These range from the selection of valves, fittings, and equipment to the methods of sampling of specific waters, such as steam and boiler waters. Method D 3370 discusses the sampling of water and includes a list of sample volumes required for various determinations. All of these methods should be consulted when setting up the sampling procedures and locations, and the appropriate method consulted when sampling. A complete discussion of sampling principles is presented in Chapter 9.

Many samples require special techniques and containers. For example, trace iron or copper analysis requires specially cleaned containers and acidification; samples for silica analysis should be taken in plastic bottles; each sample for dissolved oxygen must be flushed through the bottle with at least ten times its volume of sample and then carefully stoppered to prevent air entrapment. Each ASTM method will specify the technique of sampling required and should be followed accurately to ensure meaningful analytical results.

Discussion of Methods

A variety of methods is generally available for each determination. In addition to the use to be made of the results, the choice of procedures is governed by the probable range of concentrations, the accuracy required, the presence of interfering substances, the skill of the analyst, and the apparatus available.

This chapter is intended as an aid in making the best compromise between speed on the one hand and completeness and accuracy on the other. Therefore, the discussion of each constituent indicates, in most cases, several available methods for determining that constituent and provides some basis for making choices in specific cases.

The discussion of methods in this chapter is presented in alphabetical order by constituent or property in each of the following categories, of which Table 4*a*–*e* gives a complete listing:

Organic constituents (Table 4*a*)
General properties (Table 4*b*)
Radioactivity (Table 4*c*)
Bacteriological (Table 4*d*)
Inorganic constituents (Table 4*e*)

TABLE 4—*Categorical listings of ASTM methods discussed in this chapter.*

(*a*) ORGANIC CONSTITUENTS

Concentration Methods	
D 2910 - 75	Organic Matter, Removal of, by Activated Carbon Adsorption
D 2778 - 70 (1974)	Organic Matter, Solvent Extraction of
General Methods	
D 2579 - 74	Carbon, Total and Organic, by Combustion Infrared
D 2908 - 74	Organic Matter, Volatile, by Gas Chromatography
D 1252 - 67 (1974)	Oxygen Demand, Chemical (Dichromate)
D 3250 - 77	Oxygen Demand, Total, by Combustion
D 3560 - 77	Oxygen Demand, by Combustion-Infrared Analysis
Specific Constituents	
	Adenosine Triphosphate (ATP) Content of Microorganisms, proposed
D 2327 - 68 (1974)	Amines, Primary and Secondary; Octadecyl- and Dioctadecylamine
D 2330 - 68 (1974)	Alkyl Benzene Sulfonate
	A. Direct Methylene Blue Colorimetric
	B. Interference Limited Methylene Blue Colorimetric
D 2036 - 75	Cyanides
	A. Total, After Distillation
	B. Amenable to Chlorination
	C. Amenable to Chlorination Without Distillation
	D. Cyanogen Chloride
	E. Spot Test for Sample Screening
D 2036 - 75	Cyanogen Chloride
D 2909 - 74	Cyclohexylamine, Colorimetric with Diazotized *p*-Nitroaniline
D 3113 - 75	EDTA, Tetrasodium Salt of,
	A. Total (Chelated and Unchelated)
	B. Unchelated
D 3478 - 75 T	Herbicides, Chlorinated Phenoxy Acid, by Gas Chromatography

TABLE 4—*Continued.*

(*a*) ORGANIC CONSTITUENTS (*continued*)

Specific Constituents *Continued*	
D 1942 - 74	Morpholine, Colorimetric by Thiocarbamate
D 3371 - 74 T	Nitriles, by Gas-Liquid Chromatography
D 3086 - 72 T	Pesticides, Organochlorine
D 1783 - 70 (1974)	Phenolic Compounds A. Chloroform Extraction B. Direct Colorimetric
D 2580 - 68 (1974)	Phenols, by Gas-Liquid Chromatography
D 3534 - 76 T	Test for Polychlorinated Biphenyls (PCB's) in Water
Waterborne Oils	
D 3415 - 75 T	Identification
D 3325 - 74 T	Preservation of Samples
D 3326 - 74 T	Preparation of Sample for Identification
D 3327 - 74 T	Analysis for Selected Elements A. Nitrogen B. Sulfur C. Nickel and Vanadium
D 3328 - 74a T	Petroleum Oils, Comparison of, by Gas Chromatography
D 3414 - 75 T	Infrared Analysis

(*b*) GENERAL PROPERTIES

D 1067 - 70	Acidity or Alkalinity A. Electrometric Titration B. Electrometric or Color-Change Titration C. Color-Comparison Titration D. Color-Change Titration after Boiling E. Color-Change Titration after H_2O_2 and Boiling
D 1291 - 75	Chlorine Requirement
D 2035 - 74	Coagulation-Flocculation Jar Test
D 1125 - 77	Conductivity, Electrical A. Laboratory B. Field C. Saline Waters by Electrodeless Method
D 2776 - 72	Corrosivity, in Absence of Heat Transfer (Electrical Methods) A. Electrical Resistance B. Linear Polarization
D 807 - 52 (1976)	Corrosivity, Embrittlement Detector Method
D 2688 - 70	Corrosivity, in Absence of Heat Transfer (Weight Loss Methods) A. Steam Condensate (NDHA) B. Cooling Water (Coupon) C. Cooling and Distribution Water (ISWS) D. Steam Condensate (USBM)
D 1126 - 67 (1974)	Hardness A. Gravimetric B. Titrimetric
D 1888 - 67 (1974)	Matter, Particulate and Dissolved A. More than 25 ppm B. 25 ppm or Less (Automatic Evaporation)
D 1292 - 65 (1975)	Odor

Continued.

TABLE 4—*Continued.*

(*b*) GENERAL PROPERTIES (*continued*)

D 1498 - 76	Oxidation-Reduction Potential
D 1252 - 67 (1974)	Oxygen Demand, Chemical (Dichromate)
D 3250 - 77	Oxygen Demand, Total, by Combustion
D 1293 - 65 (1970)	pH
	Solids (see Matter, Particulate and Dissolved)
D 1429 - 76	Specific Gravity
	A. Pycnometer Method
	B. Erlenmeyer Flask Method
D 1590 - 60 (1972)	Surface Tension
D 1345 - 59 (1977)	Toxicity, Freshwater Fishes
D 2037 - 68 (1973)	Toxicity, Inhibitory, to Diatoms
D 1889 - 71 (1976)	Turbidity
	A. Jackson Candle
	B. Nephelometric
	C. Absolute

(*c*) RADIOACTIVITY

Measurement of Radioactivity	
D 3085 - 75	Activity, Low-Level
*D 1943 - 66 (1971)	Alpha Particle Radioactivity
D 3084 - 75	Alpha Spectrometry
*D 1890 - 66 (1971)	Beta Particle Radioactivity
*D 1690 - 73	Gamma Radioactivity
*D 2459 - 72	Gamma Spectrometry
*D 2470 - 70 (1975)	Neutron-Emitting Fission Products
Specific Radionuclides	
*D 2038 - 74	Barium
*D 2577 - 72	Cesium
*D 2334 - 73	Iodine
	A. Heterogeneous Exchange
	B. Distillation
	C. Extraction
*D 2461 - 69 (1975)	Iron-59
*D 2039 - 74	Manganese
D 3357 - 74 T	Nickel
D 2460 - 70 (1975)	Radium, Radionuclides of
D 3454 - 75 T	Radium-226
*D 2476 - 75	Tritium
E 318 - 69 (1975)	Uranium, Colorimetric
D 2907 - 75	Uranium
	A. Direct Fluorometric
	B. Extraction
D 3315 - 73 T	Zirconium
Heavy Water	
*D 2032 - 68 (1975)	Deuterium Oxide
*D 2033 - 73	Deuterium Oxide, Permanganate Consumption by Impurities in
*D 2184 - 72	Deuterium Oxide, Testing

TABLE 4—*Continued.*

(*d*) Bacteriological

	Adenosine Triphosphate (ATP) Content of Microorganisms, proposed
D 3508 - 76 T	Fecal Coliform Recovery, Evaluation of Membrane Filters
D 1128 - 60 (1974)	Microorganisms, Microscopic Matter, Identification of
F 60 - 68 (1973)	Microbiological Contaminants, Detection and Enumeration
D 932 - 72	Iron Bacteria
D 993 - 58 (1976)	Sulfate-Reducing Bacteria
	A. Iodimetric
	B. Lead Acetate Paper

(*e*) Inorganic constituents

D 857 - 69 (1976)	Aluminum
	A. Fluorometric
	B. Spectrophotometric with 8-Quinolinol
	C. Spectrophotometric with Ferron
D 1426 - 74	Ammonia Nitrogen
	A. Distillation
	B. Direct Nesslerization
	Arsenic by Differential Pulse Polarography, proposed
D 2972 - 74	Arsenic, Spectrophotometric with Silver Diethyldithiocarbamate
D 513 - 71	Bicarbonate and Carbonate, Carbon Dioxide
	A. Precise CO_2 Evolution
	B. Abridged CO_2 Evolution
	C. Bicarbonate Titration
	D. Differential Titration
	E. Direct Titration of Free CO_2
D 3082 - 74	Boron
	A. Carminic Acid Colorimetric
	B. Mannitol Potentiometric
D 1246 - 77	Bromide and Iodide
	A. Iodide, Colorimetric-Catalytic
	B. Bromide, Colorimetric-Catalytic
	C. Iodide and Bromide, Titrimetric
D 2576 - 70 (1976)	Cadmium by Atomic Absorption Spectrophotometry
	Cadmium and Lead by Differential Pulse Anodic Stripping Voltammetry, proposed
D 2576 - 70 (1976)	Calcium by Atomic Absorption Spectrophotometry
D 3557 - 77	Cadmium by Atomic Absorption Spectrophotometry
	A. Atomic Absorption, Direct
	B. Atomic Absorption, Chelation Extraction
D 511 - 76	Calcium and Magnesium
	A. Gravimetric
	B. Complexometric Titration
	C. Atomic Absorption Spectrophotometric
D 1126 - 67 (1974)	Calcium and Magnesium Hardness
	A. Gravimetric
	B. Titrimetric
D 513 - 71	Carbon Dioxide, Bicarbonate, Carbonate
	A. Precise CO_2 Evolution
	B. Abridged CO_2 Evolution
	C. Bicarbonate Titration
	D. Differential Titration
	E. Direct Titration of Free CO_2

Continued.

TABLE 4—*Continued.*

(*e*) INORGANIC CONSTITUENTS (*continued*)

D 512 - 67 (1974)	Chloride
	A. Mercurimetric Titration
	B. Silver Nitrate Titration
	C. Colorimetric with Ferric Thiocyanate
D 1253 - 76	Chlorine, Residual, in Water
	A. Direct Amperometric Titration
	B. Starch-Iodide Titration (Direct and Back Titration)
	C. Amperometric Back Titration
D 1427 - 68 (1974)	Chlorine, Residual, in Waste Water
	A. Starch-Iodide Titration
	B. Amperometric Titration
D 1687 - 77	Chromium, Total
	A. Permanganate Oxidation
	B. Hypobromite Oxidation
	C. Alkaline-Persulfate Oxidation
	D. Atomic Absorption
D 2576 - 70 (1976)	Chromium by Atomic Absorption Spectrophotometry
D 2576 - 70 (1976)	Cobalt by Atomic Absorption Spectrophotometry
D 3558 - 77	Cobalt by Atomic Absorption Spectrophotometry
	A. Atomic Absorption, Direct
	B. Atomic Absorption, Chelation Extraction
D 1688 - 77	Copper
	A. Colorimetric with Neocuproine (High Range)
	B. Colorimetric with Neocuproine (Low Range)
	C. Colorimetric with Cuprethol
	D. Atomic Absorption, Direct
	E. Atomic Absorption, Chelation Extraction
D 2576 - 70 (1976)	Copper by Atomic Absorption Spectrophotometry
F 57 - 68 (1973)	Copper in High-Purity Water
D 1179 - 72	Fluoride
	A. Photometric SPADNS
	B. Ion Selective Probe
D 1385 - 67 (1972)	Hydrazine, Colorimetric with *p*-Dimethylaminobenzaldehyde
D 1588 - 60 (1974)	Hydrogen, Dissolved and Gaseous
	A. Thermal Conductivity
	B. Volumetric
D 514 - 67 (1974)	Hydroxide, Titrimetric
D 1246 - 77	Iodide and Bromide
	A. Iodide, Chlorimetric-Catalytic
	B. Bromide, Colorimetric-Catalytic
	C. Iodide and Bromide, Volumetric
D 1068 - 77	Iron
	A. Photometric, Orthophenanthroline
	B. Photometric, Bathophenanthroline
	C. Atomic Absorption, Direct
	D. Atomic Absorption, Chelation Extraction
D 2576 - 70 (1976)	Iron by Atomic Absorption Spectrophotometry
D 2576 - 70 (1976)	Lead by Atomic Absorption Spectrophotometry
D 3559 - 77	Lead by Atomic Absorption Spectrophotometry
	A. Atomic Absorption, Direct
	B. Atomic Absorption, Chelation Extraction
	Lead and Cadmium by Atomic Spectrophotometry, proposed
D 3561 - 77	Lithium, Potassium, and Sodium in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry
D 2576 - 70 (1976)	Magnesium by Atomic Absorption Spectrophotometry
D 511 - 76	Magnesium and Calcium
	A. Gravimetric

TABLE 4—*Continued.*

(*e*) INORGANIC CONSTITUENTS (*continued*)

	B. Complexometric Titration
	C. Atomic Absorption Spectrophotometric
D 858-77	Manganese, Colorimetric as Permanganate
	A. Colorimetric
	B. Atomic Absorption, Direct
	C. Atomic Absorption, Chelation Extraction
D 2576-70 (1976)	Manganese by Atomic Absorption Spectrophotometry
D 3223-73	Mercury by Cold Vapor Atomic Absorption Spectrophotometry
D 2576-70 (1976)	Metals by Atomic Absorption Spectrophotometry
D 2576-70 (1976)	Metals by Atomic Absorption Spectrophotometry
	A. Cadmium, 0.05 to 5 mg/litre
	B. Calcium, 0.3 to 15 mg/litre
	C. Chromium, 0.2 to 20 mg/litre
	D. Cobalt, 0.25 to 50 mg/litre
	E. Copper, 0.1 to 20 mg/litre
	F. Iron, 0.1 to 20 mg/litre
	G. Lead, 0.34 to 40 mg/litre
	H. Magnesium, 0.05 to 3.5 mg/litre
	I. Manganese, 0.04 to 10 mg/litre
	J. Nickel, 0.08 to 20 mg/litre
	K. Zinc, 0.02 to 3 mg/litre
D 3372-75	Molybdenum by Atomic Absorption Spectrophotometry
D 1886-77	Nickel
	A. Photometric, Carbamate
	B. Photometric, Glyoxime
	C. Atomic Absorption, Direct
	D. Atomic Absorption, Chelation Extraction
D 2576-70 (1976)	Nickel by Atomic Absorption Spectrophotometry
D 992-71	Nitrate, Colorimetric with Brucine-Sulfanilic Acid
D 1254-67 (1974)	Nitrate
	A. Colorimetric by Diazotization
	B. Volumetric with Permanganate
D 1589-60 (1974)	Oxygen, Dissolved in Waste Water
	A. Alsterberg (Azide)
	B. Rideal-Stewart
	C. Pomeroy-Kirshman-Alsterberg
	D. Polarographic
D 888-66 (1977)	Oxygen, Dissolved in Water
	A. Colorimetric-Indigo Carmine
	B. Dead-Stop End Point
	C. Potentiometric End Point
	D. Thiosulfate Titration
	E. Thiosulfate Titration-Starch Indicator
D 515-72	Phosphorus
	A. Colorimetric, Ascorbic Acid Reduction
	B. Colorimetric, Amino Reduction
	C. Colorimetric, Molybdovanadophosphate
D 3561-77	Potassium, Sodium, and Lithium in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry
D 1428-64 (1971)	Potassium and Sodium by Flame Photometry
	A. Analysis of Water
	B. Trace Amounts of Sodium in Low-Solids Water
	C. Analysis of Water-Formed Deposits
D 3081-72 T	Selenium, Colorimetric with Diaminobenzidine

Continued.

TABLE 4—*Continued.*

(*e*) INORGANIC CONSTITUENTS (*continued*)

D 859 - 68 (1974)	Silica
	A. Gravimetric
	B. Colorimetric as Molybdenum Blue
	C. Colorimetric as Molybdenum Yellow or Blue
	D. Colorimetric, Sulfite Reduction
	Spectrochemical Analysis by Rotating Desk Technique Using An Optical Emission Spectrometer, proposed
D 3561 - 77	Sodium, Potassium, and Lithium in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry
D 1428 - 64 (1971)	Sodium and Potassium by Flame Photometry
	A. Analysis of Water
	B. Trace Amounts of Sodium in Low-Solids Water
	C. Analysis of Water-Formed Deposits
D 2791 - 77	Sodium, Continuous Determination by Ion Selective Electrode
	A. Sodium Ion-Electrode
	B. Flame Photometry
D 3352 - 74	Strontium, in Brackish Water, Seawater, and Brines
D 516 - 68 (1974)	Sulfate
	A. Gravimetric
	B. Turbidimetric
	C. Volumetric
D 1339 - 72	Sulfite, Volumetric
	A. 0.1 to 6 mg/litre Na_2SO_3
	B. 6 mg/litre Na_2SO_3 or higher
	C. 3 mg/litre Na_2SO_3 or higher
D 2333 - 68 (1974)	Thorium, Colorimetric with 1-(*o*-Arsonophenylazo)-2-Naphthol-3,6-Disulfonic acid
D 2907 - 75	Uranium
	A. Direct Fluorometric
	B. Extraction
D 3373 - 75	Vanadium, Colorimetric-Catalytic
D 1691 - 77	Zinc
	A. Colorimetric with Zincon, High Range
	B. Colorimetric with Zincon, Low Range
	C. Atomic Absorption, Direct
	D. Atomic Absorption, Chelation Extraction
D 2576 - 70 (1976)	Zinc by Atomic Absorption Spectrophotometry

Analysis of Organic Constituents in Water

The ever-increasing number of organic constituents which have been detected in water supplies has become a significant concern and problem in determining water quality. The usual methods of analysis and control are not sensitive enough to monitor the concentrations of these organic contaminants. Such substances as insecticides, herbicides, and other organics in the micrograms-per-litre concentration range may impair water quality for several important intended uses. Drinking water use may be impaired by deteriorated taste and odor of the water. Toxicity to aquatic organisms, including food-fish, may destroy or seriously limit this natural-resource use. However, the long-term effects of such organic contaminants are largely unknown.

New techniques which are required for analysis are being developed and standardized rapidly. Chromatography methods are being used to separate the constituents for identification by infrared, ultraviolet, and mass spectroscopy. Solvent extraction and activated carbon adsorption have been used to separate and concentrate the organic substances from water. Thin-layer and paper chromatography are helpful in separating the organics that cannot be separated by gas-liquid chromatography. Identification of specific organic compounds is limited to the compounds for which there are pure standards to compare elution times in gas and liquid chromatography. Even these identifications must be considered only tentative until confirmed by at least two other columns or, in liquid chromatography, two different developing conditions. It is advisable to further confirm the organic structure by spectroscopy. Fluorescent spectroscopy has been used as a detector with paper and thin-layer chromatography. The chromatographed spots are caused to fluoresce by ultraviolet light excitation, and the spectrum of the fluorescent emission is used to identify the compound. The intensity of the fluorescence can be related to the concentration of the compound present in the spot.

Analysis of organic contaminants in water in nanogram- and picogram-per-litre concentrations is receiving much attention, and new techniques are being developed. Table 4*a* shows the methods published in the *Annual Book of ASTM Standards*, Part 31, for organic constituents of water and waste water.

Chemical Oxygen Demand

Chemical oxygen demand (COD) is defined as the amount of oxygen, expressed in milligrams per litre, consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter in waste water, corrected for the influence of chlorides. In itself, the chemical oxygen demand is not a reliable index as to the quality or quantity of pollution, yet its determination can give worthwhile information when compared with previous results for the same water, or when considered in the light of other knowledge about the constituents of the water. Not all organic substances are oxidized completely or at the same rate; therefore, use of precisely reproducible techniques is important when comparisons are needed.

ASTM Method D 1252 uses a standard potassium dichromate solution in 50 volume percent sulfuric acid to oxidize organic and oxidizable inorganic material. The excess dichromate is then titrated with a standard ferrous ammonium sulfate solution, using *o*-phenanthroline ferrous complex as an internal indicator. Silver sulfate can be added as a catalyst to facilitate the oxidation of straight chain organic acids and alcohols.

Other oxidizing agents such as potassium permanganate and potassium iodate have been used to determine COD, but the dichromate method is more reproducible and generally superior. On relatively pure waters, however, the permanganate COD may be preferable because much more dilute solutions can be used.

General Properties of Water

Properties of water not usually measured in the laboratory are not included in Table 4*b*. Of these, temperature is probably the most important.

Acidity and Basicity (Alkalinity) [2][2]

Acidity and basicity (alkalinity) are defined as the quantitative capacity of aqueous media to react with hydroxyl or hydrogen ions, respectively, as distanct from pH, which is an intensity factor. Acidity or basicity in water is the result of dissociation or hydrolysis of its solutes. The strength of the acidity or basicity gives a good indication of the potential corrosiveness of the water and also furnishes a further guide in choosing appropriate treatment of either raw water or plant effluents.

Alkalinity in water may be reported in terms of equivalent titratable amounts of bicarbonate, carbonate, or hydroxide ions, or in terms of equivalent amounts of calcium carbonate. The term *alkalinity* as used in water analyses is not in full accord with generally accepted chemical terminology. In the discussion of pH, 7.0 is considered to be the neutral point. In water analysis about 4.5 is the end point for titration of alkalinity. Thus, a water with a pH of 6 could be called *acid* on the basis of the pH, but might still have titratable *alkalinity*. Some water chemists prefer to avoid the general term *alkalinity*, and speak of carbonate, bicarbonate, and hydroxide instead. The determination of these ions, however, is an acid-base titration and does not differentiate the ions that enter the reaction.

Sources of Alkalinity

The anions that may contribute to alkalinity are those which form acids that are only weakly dissociated in solution, and which thus enter into hydrolysis reactions. Chloride, sulfate, and nitrate ions do not affect the alkalinity. Cations that form weakly dissociated bases take part in hydrolysis reactions which tend to produce acidity rather than alkalinity. The presence of certain organic materials may have a considerable effect upon the alkalinity determination.

Because of the relative abundance of carbonate minerals and because carbon dioxide, which enters into equilibria with them in water solution, is readily available, bicarbonate and carbonate are to be expected in most waters. The presence of hydroxide ions in natural water in amounts sufficient to affect the alkalinity determination directly is very rare, unless artificial contamination has occurred.

[2] Much of the following discussion is taken from Ref *2*.

Hydroxide may occur in water that has been softened by the lime or lime-soda process. Water in contact with fresh concrete may have an excessively high pH and apparent hydroxide alkalinity, due in part to silicates. Concrete may be a source of hydroxide alkalinity in samples from wells that are under construction.

Under any system of reporting titrated alkalinity now in use, all the effects of the anions entering into hydrolysis reactions are lumped together and reported as an equivalent amount of a single substance, or as two more or less postulated ions. Thus, although alkalinity data may suggest the presence of definite amounts of carbonate, bicarbonate, or hydroxide, the ions have not been directly determined as such and the results may include the equivalent of all or part of such other anions as may tend to hydrolize. These ions include silicate, phosphate, borate, and possibly fluoride. Some other ions not ordinarily found in natural water, such as arsenate, aluminate, and certain organic anions which may occur in colored waters, also could increase the alkalinity.

Chemistry of Alkalinity Determination

The alkalinity of water is determined in the laboratory by titration with standard acid to a definite pH. In the titration, conversion of dissociated carbonate ions (CO_3^-) to undissociated carbonic acid takes place in two steps. In the first step, the carbonate ions in solution each take up one hydrogen ion and become bicarbonate ions (HCO_3^-). The hydrogen ions needed are supplied by the acid added in the titration. As the titration proceeds, the amount of unchanged carbonate decreases until the carbonate ions are nearly changed over. At this point in the titration, a small addition of acid will produce a comparatively large reduction in pH, indicating the essential completion of the first step. This end point usually is considered to be at a pH of 8.2 and can be observed either with a pH measuring device or an indicator that changes color in this range, such as phenolphthalein. Theoretically, at this pH level, the ratio of HCO_3^- ions to CO_3^- ions is more than 100 to 1, as computed from dissociation constants for water and carbonic acid.

In the second step, each of the bicarbonate ions takes up one hydrogen ion to form molecules of undissociated carbonic acid. This requires additional quantities of acid. When nearly all the HCO_3^- ions have been taken care of, the addition of a small amount of acid again causes a large decrease in pH. At a pH of 4.5, the ratio of H_2CO_3 molecules to HCO_3^- ions is theoretically more than 100 to 1, and this is chosen as the end point. It can be detected by a pH measuring device or by a suitable indicator such as methyl orange or methyl red.

In the interpretation of the titration, it is assumed that all alkalinity present in the water was in the forms of HCO_3^-, CO_3^-, and OH^-. If no OH^- is present, the acid required to complete Step 1 is a measure of the CO_3^-

content. The amount required for Step 2, when corrected for any HCO_3^- produced in the carrying out of Step 1, is a measure of the original HCO_3^- content. Waters containing OH^- require more acid for Step 1 than for Step 2 and the magnitude of this difference is a measure of the OH^- concentration. It is assumed throughout that OH^- and HCO_3^- cannot exist in the same solution.

No matter what ions may be involved, if they are titrated stoichiometrically by lowering the pH to 4.5, alkalinity values in equivalents per million (epm) which give a cation-anion balance are obtained. Silicate in the form SiO_3^- should not be present in waters in measurable amounts unless the pH is at least 11. The $HSiO_3^-$ form, however, might represent about half the silica present at a pH of 9 and about a tenth of it at pH 8.

Dissociated silica can contribute to titrated alkalinity between pH values of 8 and 9, but the magnitude of the effect in this range is uncertain. Silicate ions in either of the foregoing forms would be fully titrated in the regular alkalinity determinations. They would then be reported in terms of equivalent quantities of bicarbonate or carbonate. Other types of silicate ions also might affect the alkalinity.

Orthophosphate may occur in water in three forms, $PO_4^{=}$, $HPO_4^{=}$, and $H_2PO_4^-$. The trivalent form is present in appreciable amounts only above a pH of 10. The $HPO_4^{=}$ ion predominates from a pH of 7 to a pH of 2. The phosphate ions are not fully converted to orthophosphoric acid even at a pH of 1, but practically all the $HPO_4^{=}$ ions would be converted to $H_2PO_4^-$ ions in an alkalinity titration stopped at a pH of 4.5. Waters that contain enough phosphate to affect the alkalinity appreciably are rare in nature. If such a water were titrated for alkalinity in the usual way, a part of the phosphate (about a third) would appear as an equivalent amount of bicarbonate or carbonate.

Borate ions also hydrolyze in water to affect the pH. Theoretically these ions should all be converted to boric acid in the regular alkalinity titration. The form of such ions in solution in natural waters is not certain, however, and the effect of borates on alkalinity titration is difficult to evaluate fully. Waters are seldom found in which measurable alkalinity is contributed by borate ions, because boron concentrations in water are normally very low. Borate in the dihydrogen form ($H_2BO_3^-$) is theoretically possible in the ratio of 1 part to about 17 parts of the undissociated acid at a pH of 8. At a pH of 7 and lower, dissociated ions are essentially absent.

Fluoride ions hydrolyze, but weakly, and probably they are rarely present in large enough amounts to affect the alkalinity.

The values given for dissociation constants in the literature hold for dilute solutions of single salts. Natural waters are not so simple, and exact conformance with theoretical behavior, therefore, is not to be expected. The computations, however, do give useful indications of the behavior of various ions that can take part in hydrolysis and contribute to alkalinity.

Relation to pH

Many users of chemical analyses are confused by the distinction between pH value and titratable alkalinity (because the titration for alkalinity is carried to a pH of 4.5, whereas at the same time a pH of 7 is stated to be the neutral point).

If all the hydrolysis in a water is assumed to be due to the system $CO_3^{=} \overset{H^+}{\rightleftharpoons} HCO_3 \overset{H^+}{\rightleftharpoons} H_2CO_3$, the pH provides a means of deciding how far to the left the reaction is displaced. A pH below 8.2 indicates the absence of the normal carbonate phase and a pH below 4.5 indicates the absence of both the normal carbonate and bicarbonate phases, but otherwise the pH is only qualitative. By titration of the system with acid, a quantitative determination of the amount of each phase can be made, if the original assumption as to the ions present is correct. To complete this determination the equilibrium must be shifted all the way to the right and the pH lowered to 4.5. In pure water at neutrality the pH is 7, but this represents an absence of ions that would take part in hydrolysis and is an entirely different condition.

Range of Concentration

Alkalinity reported as hydroxide is ordinarily absent from uncontaminated natural water. Alkalinities reported as carbonate are common, particularly in groundwaters, or concentrated surface waters that have a large amount of sodium in proportion to calcium and magnesium. The usual stream water has no apparent carbonate alkalinity and should have a pH below 8.2 if it contains an appreciable amount of calcium. Some surface waters have a pH greater than 8.2, either from $CO_3^{=}$ or as a result of silicates or other anions in solution.

Alkalinity reported as carbonate usually is present in small amounts, generally less than 10 mg/litre. In waters high in sodium, higher values are sometimes encountered, but concentrations over 50 mg/litre are extremely unusual.

In acid waters, there is no bicarbonate alkalinity. In alkaline waters (all those whose pH is 4.5 or over), the range in alkalinity reported as bicarbonate is from zero up to more than 1000 mg/litre, although concentrations much higher than 500 mg/litre are unusual. Waters highly charged with carbon dioxide may contain large amounts of alkalinity as bicarbonate. The reduction of sulfate to sulfide with the assistance of certain types of bacteria produces carbon dioxide as a by-product, and may cause high bicarbonate concentrations in waters associated with petroleum.

Acidity

As a corollary to the property of alkalinity, there is the opposite property of *acidity* which is found in some natural waters. If the usual *alkalinity* end point is used, a water would not be reported as having acidity unless its pH is below 4.5.

Sources of Natural Water Acidity

Free acids such as HCl or gases like SO_2 combine with water to form acid. Certain hot springs yield strongly acid water that has dissolved these substances. Free acids may also be added to streams or groundwaters through waste disposal, or through oxidation of sulfides. The latter source is an important one in mining districts. Drainage from mines in areas where pyrite or other metallic sulfides occur in the ore, or in associated strata, may be strongly acid, containing not only free sulfuric acid but also iron and aluminum. This effect is especially noticeable in coal mining areas.

The oxidation of pyrite in air, which may be aided by some types of bacteria, produces ferrous sulfate and sulfuric acid. The ferrous sulfate may be further oxidized to ferric sulfate, and eventually precipitates as ferric hydroxide. The hydroxide ions thus are removed from solution and the water becomes more acid through the process of hydrolysis. Aluminum cations in water also hydrolyze to give an acid reaction. A considerable oxygen supply is required for oxidation of pyrite, and ordinarily it would not take place very far below the water table, or in other situations where oxygen is deficient. Ferrous and ferric salts are added to surface streams in some types of industrial wastes.

Ammonium ions occasionally occur in natural waters. These ions are capable of hydrolysis, contributing to the acidity of samples.

Chemistry of Acidity Determination

In those waters which have a pH below 4.5, the presence of acidity is reported. The acidity may be the result of actual free acids such as sulfuric or hydrochloric in solution. It can also be the result of the hydrolysis of certain cations in solution. The free-mineral-acid determination usually is accomplished by titration with standard alkali to a pH of about 4.5 in the cold solution. An approximation of acidity can be obtained also by means of a calculation based on the pH. These two procedures give meaningful results only in the absence or near absence of iron and any other cations that might cause hydrolysis.

Total acidity generally has been determined by titration to the phenolphthalein end point (pH 8.2) at the boiling temperature. This supposedly gives the net effect of hydrolysis as well as the free-acid content. Actually the end point is somewhat arbitrary and may not be stoichiometric for all forms of iron or other cations involved in hydrolysis. No method for accurate determination of free acid in the presence of salts which hydrolyze to lower pH has yet been described, and lack of cation-anion balance is to be expected in waters where these conditions exist.

Range of Concentration

Acidity can range from zero at the pH level that is taken as neutrality to several hundred milligrams per litre for pH levels around 2.5. Springs and waters strongly affected by mine drainage or industrial wastes may at times have lower pH values. The total acidity has some significance in terms of treatment needed, but is of less value in the representation of actual conditions in the water than reporting of alkalinity as carbonate and bicarbonate is for alkaline water.

Methods

In ASTM Methods D 1067, the high-precision procedure involves electrometric titration with 0.02 *N* hydrochloric acid or sodium hydroxide either to specific pH end points, or by developing a titration curve for the sample and noting the pH values at the inflection points of the curve. The latter procedure is used for evaluation of the buffering capacity of water if the buffering salts are other than carbonates and bicarbonates.

Three routine procedures were included in Methods D 1067. Method A involves titration to a predesignated pH, the end point being determined electrometrically or by color change of an internal indicator. In Method B, the end point is determined by comparison of the color developed by an added indicator with the color of a standard buffer solution containing the same added indicator. In routine Method C, particularly applicable to acid waste waters, the sample is boiled to attain equilibrium, then titrated to a designated pH, the end point being determined by color change of an internal indicator. The latter procedure is applicable for waters highly polluted with acid industrial wastes, containing slowly hydrolyzable or buffering materials, or materials that will interfere by reason of color, precipitation, and other factors.

Alkalinity or acidity in the intermediate range between pH 3.5 and pH 9 is arbitrarily regarded as resulting from the presence of weak bases or weak acids. Alkalinity above this range, or acidity below it, is considered to be due to the presence of relatively strong bases or strong acids, respectively.

Special procedures said to be sensitive and accurate to 0.05 mg/litre have been developed for measuring extremely low alkalinities [*3*].

Accuracy and Reproducibility of Results

It is evident from the foregoing that for some waters, at least, alkalinity data are largely empirical. Relative amounts of the different forms of alkalinity reported by analyses should not always be considered significant, as changes can occur from the time the sample is collected until the bottle is opened and the alkalinity titration is made. The *total alkalinity* of a sample should be a reproducible figure, provided that similar conditions of sample treatment are followed. Agreement much closer than 2 to 5 percent, however, cannot be expected on duplicate samples, and differences this size should not be considered significant in making interpretations.

Because of the uncertainty regarding chemistry of acid waters, and their tendency to change in storage, the data on acidity also should be interpreted cautiously.

Chlorine Requirement

Often it is desirable to establish the quantity of chlorine required to achieve a specific objective in the treatment of a water by chlorination. This objective might be elimination of tastes and odors; reduction of biochemical oxygen demand by destroying or modifying decomposable organic substances; separation of grease in waste water; or destruction or modification of oxidizable constituents in waste water.

ASTM Method D 1291 provides a procedure for finding the chlorine requirement of process water and waste water. It involves adding a chlorine solution of known strength, in increasing increments of chlorine concentrations, to different portions of the sample water. The contact time and pH are maintained as specified for the particular object of chlorination. The chlorine requirement of the water is found by interpolation of a plotted curve of chlorine dosages against the results of chlorine residual tests or other tests which determine whether the specific object of the chlorination has been reached in the different sample portions. The chlorine requirement is the amount of chlorine, expressed in parts per million, required to achieve the objectives of chlorination.

Color

Color is a common constituent of many natural waters. It generally results from natural metallic ions, and from lignins, humic acids, and other vegetation products thought to be in colloidal suspension. In drinking water, color is objectionable for aesthetic reasons, but in several manufacturing processes, virtually colorless waters are required. Occasionally, pollution by industrial wastes will impart unusual or unnatural colors to water supplies.

Artificial color scales, using standards prepared from potassium chloroplatinate and cobaltous chloride solutions, are often used to measure natural color in water [*4*]. Suspended matter must be removed by centrifuging before the comparisons are made. Addition of calcium chloride [*5*] to assist in centrifuging is desirable with some types of turbidity. Spectrophotometric and photometric methods have been developed [*6*], some especially for industrial waste water [*4*].

Continuous measurement of color has been practiced to a very limited extent. Methods for measuring color, with particular emphasis on photometric methods which offer greatest promise for continuous analysis, are discussed by Staats [*7*].

Electrical Conductivity

Electrical conductivity has special significance because it is a quick and convenient method for measuring electrolyte concentration. The specific conductance of a dilute solution of an electrolyte is almost directly proportional to the ionic concentration of the electrolyte, and the total conductivity of a given water is equal to the sum of the several conductivities resulting from the electrolytes present. Because of the unusually high conductance per weight unit of the hydrogen or hydroxide ion, samples frequently are neutralized before the electrical conductivity is measured. Conductivity measurements can therefore be related to dissolved solids concentration. Also, they sometimes are required for special investigations of corrosion in water.

ASTM Method D 1125 describes the apparatus and procedures for determining electrical conductivity of industrial waters. The high-precision procedure included requires careful control of temperature, all measurements being made at 25° C. The procedure designed for more routine use incorporates a temperature correction chart.

Conductivity is a useful guide to the purity of distilled water and is much used for evaluation of steam purity in the power industry. It is important to note, however, that dissolved gases (particularly carbon dioxide and ammonia) have an important effect on conductivity. When determining steam purity by this method, it is generally necessary to reduce the concentration of these gases and to correct for the residuals present [*8*, *9*]. Special apparatus is available for removing gases from the water before the conductivity determination is made [*10*,*11*]. A good approximation of the dissolved solids in distilled water and condensate can be made by boiling a sample down to less than half the original volume to drive off the dissolved gases, determining the conductivity of the cooled remainder, and by correcting this value for the reduction in volume [*12*,*13*].

Electrical conductivity cannot be precisely related to dissolved solids because some dissolved substances such as silica and certain types of organic matter contribute little or nothing to the conductivity.

Continuous measurement of conductivity of flowing samples is often used for monitoring process waters [*14*], and is essential in monitoring quality of high-purity supplies, such as demineralized water.

Hardness

Hardness is now generally accepted as representing the total concentration of calcium and magnesium ions. Originally hardness was understood to be the capacity of a water for precipitating soap. It was measured by the amount of a standard soap solution required to produce a stable lather. Therefore, other polyvalent ions (in addition to calcium and magnesium) capable of precipitating the soap were included as part of the hardness.

Hardness has traditionally been classified as two types: *temporary hardness* and *permanent hardness*. That portion of hardness which disappears upon boiling is referred to as *temporary hardness*, and is essentially the bicarbonates of calcium and magnesium which are precipitated as carbonates by the loss of carbon dioxide in heating. The hardness remaining after boiling is *permanent hardness*, including sulfates, chlorides, and nitrates of calcium and magnesium. Most often the total hardness concentration is the primary interest. Most analytical methods do not differentiate between the foregoing hardness classifications, but determine only total hardness, with provisions for determining the individual calcium and magnesium concentrations. The various properties and effects of hardness in industrial water are discussed under *Calcium* and *Magnesium* in this chapter.

ASTM Methods D 1126 provide two methods for determining total hardness. The more precise procedure is a gravimetric method that is cumbersome but dependable with waters of unknown composition. Calcium is determined by precipitation as the oxalate, which is then ignited to calcium oxide. Magnesium is determined by the precipitation of magnesium ammonium orthophosphate, which is then ignited to magnesium pyrophosphate. Total hardness is calculated from the sum of calcium and magnesium in the ignited residues.

The more rapid method is a volumetric titration in which a buffered water sample is titrated with an organic sequestering agent, sodium ethylenediamine tetraacetate, in the presence of an indicator dye. By titrating a second aliquot of the sample in the presence of a different indicator and buffer, a separate determination is made for calcium, thus differentiating between the calcium and magnesium. If interferences to not exceed the specified limits, the volumetric method is as accurate as the gravimetric method.

Odor

Odor is a characteristic of many natural waters and can be the result of many contributing factors. Among these are pollution by sewage and trade wastes, the presence of living matter (bacteria, fungi, algae, and animal life), the decomposition of various forms of living matter, and the presence of colloidal vegetable or earthy matter.

Odor tests can be useful in many respects. For example, they may be used in checking the quality of raw and treated waters, in determining the effectiveness of deodorizing procedures, and as a method of tracking sources of contamination or leaks in industrial processes. Odor is difficult to measure quantitatively.

ASTM Method D 1292 is a method for measuring odor in waters for comparative or control purposes. The threshold odor number of water is determined by using the sense of smell and a series of dilutions of the sample with odor-free water. The odor threshold of a sample represents the number of volumes of dilution water required to yield the minimum definitely perceptible odor. Psychological influences are eliminated as much as possible by having one person dilute the sample and label the flasks in code, and other persons conduct the odor tests, examining dilutions in random order. The average results of two or more odor testers is suggested. ASTM Method D 1292 also includes a table for classifying odors by chemical types. Chapter 12 of this manual presents a comprehensive discussion on odor testing and other sensory examination methods.

Oxidation-Reduction Potential

The oxidation-reduction potential of a solution is defined as the electromotive force (emf) developed by a platinum electrode immersed in the water, referred to the standard hydrogen electrode. Every oxidation-reduction reaction involves an exchange of electrons; the emf necessary to oppose this flow of electrons gives a measure of the oxidation-reduction potential. ASTM Method D 1498 describes the apparatus and procedure for measuring the oxidation-reduction potential of all types of industrial waters. It does not deal with the interpretation or application of the results. Empirical testing is necessary to adapt this method of measurement to specific ions in a particular application.

Some of the applications of oxidation reduction potential measurements in water have been summarized by Rosenthal. In one stage of the seawater bromine process, the concentration of free bromine in acidified seawater treated with chlorine is obtained by measuring the oxidation-reduction potential. A similar measurement on a plating plant waste is used as a gage of dichromate ion concentration for controlling the addition of a reducing agent. Continuous measurement of low chlorine concentrations is possible by this method.

Specific Gravity

Specific gravity is the ratio of weight of a given volume of sample to the weight of an equal volume of water, under a fixed set of conditions. It is rarely an important property of industrial supply or process waters, but may be significant in waste analysis. It can be used to estimate the concentration of certain solutions used in industrial processes such as caustic or brines, and the concentration of dissolved solids in waters by evaporation.

ASTM Method D 1429 covers an accurate gravimetric determination using a specific-gravity bottle (pycnometer) in which a known volume of water is weighed at a temperature of 15.5° C (60° F). This method has an accuracy of ±0.0005. A less-precise method is included for determining the specific gravity of sludges and muds. This is done by weighing an Erlenmeyer flask filled first with water and then with the sample, and comparing the two net weights.

Specific gravity also has been determined to the fourth decimal place with a balance of the Westphal type which measures buoyancy of the water on a totally immersed plummet. Specific gravity of concentrated brines and caustic solutions can be measured with appropriate hydrometers with sufficient accuracy for control purposes. A quick approximation of the specific gravity of any water solution can be made by weighing a pipetted sample and comparing it with the weight of the same volume of distilled water at the working temperature.

Surface Tension

Surface tension is a little-used property in the investigation and control analyses of industrial waters. Occasionally, it is used to indicate contamination by some water-soluble organic solvent or as an indication of the presence of surfactants. This can be helpful, for example, in locating a possible cause of boiler water foaming.

ASTM Method D 1590 uses a ring tensiometer to measure the surface tension of a liquid. It measures the amount of force required to lift a standard platinum-iridium wire ring from the surface of the sample. The method does not disclose any direct relationship between the surface tension and the concentration of surfactant solutions.

A rough indication of surface tension can be obtained with a slender glass-stoppered glass tube which is filled to a standard mark with the sample. The tube is stoppered and placed in a horizontal position, and the length of the air bubble is compared with the length of the air bubble when distilled water is used in place of the sample. With samples of lowered surface tension, the bubble is longer than that obtained with distilled water. The tube is calibrated by filling to the standard mark with distilled water, stoppering, placing a horizontal position, and marking the tube at the two ends of the air bubble.

Suspended and Dissolved Matter

Suspended solids in supply and process waters are an important consideration in water treatment. They add to deposition and fouling problems, and in high-velocity water contribute to the erosion of metallic surfaces. The determination of suspended solids often is used as a guide to the satisfactory operation of plant processes and to the final disposition of industrial wastes.

The amount of dissolved solids present in an industrial water is one of its more important properties, since it is one of the factors that determine use and reuse of the water. In boiler wasters, there is a dissolved solids limit above which carry-over and steam contamination sharply increase. The test is useful in complete analysis because the result compared with the sum of individual constituents can be used as a check on the analysis.

Methods for determining suspended and dissolved matter in water are presented in ASTM Method D 1888. Method B of D 1888 is intended for waters containing less than 25 mg/litre solids. In Method B, more than 4 litres of sample are required and the evaporation is done slowly, with special precautions to exclude contaminants. This method requires special equipment, including an automatic evaporation feature which may not be available in most laboratories. As an alternative procedure, it is possible to obtain an approximate measure of dissolved solids in high-purity waters by measuring the electrical conductivity (see discussion under *Electrical Conductivity*).

Method A of D 1888 is applicable for waters with a dissolved solids content of 25 mg/litre or more. It involves evaporating sufficient sample to yield at least 25 mg of residue, which is dried and weighed. Provisions also are made for determining volatile solids and fixed solids.

Turbidity

Turbidity in waters is due to the presence of suspended solids dispersed throughout the water, resulting in a reduction of its transparency. Measurement of turbidity is therefore a measure of opacity or light-scattering by suspended solids, and is reported in arbitrary units. ASTM Method D 1889 covers the determination of the turbidity in industrial water and industrial waste water. Three procedures are presented, the Jackson candle, nephelometric, and absolute turbidity methods.

A Jackson candle turbidimeter consists of a graduated glass tube, a standard candle, and a support for the candle and tube. The water being tested is poured into the tube until the image of the candle flame just disappears. The depth of water at this point is related to turbidity values by standardization of the apparatus; usually it is converted directly into turbidity values by reference to tables supplied with the instrument. Waters of high turbidity, more than Jackson turbidity number 1000, are diluted before the test is made.

When turbidity is lower than Jackson turbidity number 25, it is desirable to use a relative turbidity method such as nephelometry. This is based on the light-scattering properties (Tyndall effect) of the suspended solids. Nephelometers are available commercially, and most of these instruments measure light scattered at approximately 90 deg, or at 90 and 270 deg. Turbidity standards have been prepared by thoroughly mixing suitable amounts of finely divided titanium dioxide into partially polymerized polystyrene. Calibrated commercial standards in sealed tubes can be purchased. Results are reported in terms of turbidity units.

Neither of the preceding methods measures absolute turbidity. Instruments are commercially available for measuring absolute turbidity and are based on an integrating sphere which sums up most of the source light that has been scattered by the sample. This method is not subject to particle size limitations. Absolute turbidity is defined as the fractional decrease of incident monochromatic light intensity, due to scattering, in traversing 1 cm of fluid.

In some industrial research and control applications, it is desirable to know the dissymmetry of the light-scattering at various angles in order to determine the average linear dimensions of the suspended particles. A goniophotometer can be used to obtain the geometric light-scattering pattern for this purpose.

Radioactivity (Table 4c)

Radioactivity measurements are becoming increasingly important as the "Nuclear Age" progresses. Instrumental methods are used which may indicate only the intensity of radiation for safety purposes, or which may provide information on the nature of the radiation, the intensity, and the half-life to permit quantitative determination of individual isotropic species.

These measurements may be important to industrial water analysis from two standpoints: (1) analysis for nonradioactive constituents by radioactivation methods; and (2) analysis to detect radioactive contamination of supply, process, or waste waters, or the concentration of radioactive isotopes that have been added as tracers. There are three methods for measuring the separate types of radioactive emission: ASTM Methods D 1943 , D 1890, and D 1690. ASTM Methods D 2459, D 2470, D 3084, and D 3085 are additional radioactivity measurements. Specific radionuclides are determined by ASTM methods as shown in Table 4*c*. Trace quantities of some nonradioactive elements can be determined by the neutron activation method. The sample is exposed to neutron radiation in a nuclear reactor or an accelerator to produce a radioactive isotope of the element to be determined. Since this radioisotope has its own characteristic radiations and mode of decay, its concentration can be determined. Some laboratories equipped with the extensive and expensive equipment required will perform this type of analysis on a fee basis. This analysis can determine only the elemental concentrations and not the chemical form of the element. Chapters 16, 17, and 18 should be consulted for more information on the subject.

Biological or Other Tests (Table 4*d* and *e*)

Iron Bacteria

Iron bacteria is a general classification for microorganisms that utilize ferrous iron as a source of energy and are characterized by the deposition of ferric hydroxide in their mucilaginous sheaths. The process is continuous with these growths, and over a period of time large accumulations of slimy brown deposits can occur. Iron bacteria may clog water lines, reduce heat transfer, and cause staining; objectionable odors may arise following death of the bacteria. The organic matter in the water is consequently increased, and this in turn favors the multiplication of other bacteria.

ASTM Method D 932 describes the procedure for the detection and identification of iron bacteria by examination under a microscope. Several genera are characterized, and photographs are provided to aid in their identification.

Microorganisms

An examination of a water supply for microorganisms is done for one or more of the following reasons: to detect contamination; to identify and estimate the amount of algae, bacteria, mold, protozoa, and other plankton; to elucidate the results of chemical examination and microbicidal treatment; and to ascertain the causes of undesired odor, color, or turbidity. Chapter 5, Treatment of Process Water and Waste Water, mentions the effects of, and treatment for, various microorganisms occurring in water.

ASTM Method D 1128 covers the identification, by microscopic examination, of bacterial cells, mold filaments, algae, protozoa, and other small animals, and such particles of inert material as may be found in process water and waste water.

Sulfate-Reducing Bacteria

Sulfate-reducing bacteria are microorganisms capable of reducing sulfate, or other forms of oxidized sulfur, to hydrogen sulfide. This reaction takes place only under anaerobic conditions; thus, the bacteria may be found in quantity in anaerobic deep wells, lake or marsh bottoms, reservoir bottoms, in the soil, and beneath deposits or other bacterial growth in aerated systems. Their proliferation and the amount of hydrogen sulfide produced depend upon the sulfate concentration. Because of the production of hydrogen sulfide, these bacteria cause corrosion of metals and deposition problems.

ASTM Methods D 993 include a procedure for identification and estimation of sulfate-reducing bacteria, based on iodometric determination of the hydrogen sulfide produced by the bacteria in a suitable medium under anaerobic conditions. A simplified procedure provides for qualitative determination based on the use of lead acetate paper to detect the hydrogen sulfide produced.

Toxicity to Freshwater Fishes

With an ever-increasing variety of manufacturing processes using chemicals and discharging waste products to rivers and streams, the protection of fish life from deleterious pollution is an important consideration. ASTM Method D 1345 is a bioassay procedure applicable for use as a guide in evaluating *acute toxicity* of wastes to freshwater fishes, and in estimating safe concentrations of such industrial waste discharges. It is a batch method which evaluates the acute toxicity of industrial wastes and other water pollutants, and can be applied to the determination of the toxicity of pure chemical compounds in water solution as well. Acute toxicity is defined as any direct lethal action of pollution to freshwater fishes that is demonstrable within 96 h or less. Test fish are exposed to dilutions of the sample being evaluated for specified periods, and median tolerance limits are calculated. This test does not evaluate long-range toxic effects such as substances that may interfere seriously with growth and reproduction.

Aluminum

The control of aluminum in industrial waters is desirable because of its potential scale- and sludge-forming characteristics. Its presence may be due to suspended clays which are present in the raw water or from coagulants used in the pretreatment of raw waters. Corrosion and erosion of aluminum tubing in condensers and feedwater heaters also can be a source of aluminum. While the corrosion-erosion rate of these tubes is low, the large surface area involved eventually can lead to sizeable concentrations in boilers.

Aluminum in the form of *alumina* or the aluminum ion can be troublesome in boilers. If hardness treatment of the feedwater is not properly controlled and maintained, scale deposits of calcium and magnesium aluminate may form. Also, in carbonate- or phosphate-treated feedwaters, the presence of aluminum in excess may cause hard adherent aluminum-silica complex deposits in the boiler. This sodium aluminum silicate scale called *analcite* sharply reduces the heat-transfer ability of boiler tubes. Thin films of analcite deposits can lead to several overheating and metal failure.

Alumina can be troublesome in cooling waters, because it precipitates at pH levels usually maintained. Alumina may be present because of carry-over from coagulation and clarification procedures. Dissolved aluminum may also react with cooling water treatment chemicals, such as phosphates, to form precipitates.

When analyzing raw waters for aluminum, attention should be given to the presence of insoluble clays and other aluminum-containing suspended matter. In boilers, these clays will become soluble forms of alumina at normal operating levels of alkalinity and temperature, and so will become available to contribute to deposition.

Fluorometric and spectrophotometric techniques both offer extreme sensitivity for determining trace amounts of aluminum. One rapid method [*15*] based on the fluorescence of aluminum 8-hydroxyquinolate in chloroform solution is capable of detecting 5μg of aluminum per litre of water solution. Another micrograms-per-litre range test [*16*] for aluminum in high-purity waters uses morin reagent. In this test for aluminum concentrations of 0.25 to 2.0 μg/litre, the standard deviation ranges from 0.09 to 0.06. These two methods now are included in ASTM Methods D 857, Methods B and A, respectively, Spectrophotometric Method C using Ferron (8-hydroxy-7-

iodo-5-quinoline sulfonic acid) determines only soluble aluminum in the concentration range of 0 to 2.0 mg/litre.

Several other reagents exist for the colorimetric determination of aluminum. Among these, aluminon (aurin tricarboxylic acid) probably is the most widely used. Improvements in the aluminon test in recent years have increased its reliability and sensitivity [*17*], and some authors believe it to be superior to other colorimetric tests, including hematoxylin [*18*,*19*]. Methods using aluminon reagents [*17*] have a limit of detection of 0.02 mg/litre.

Another test [*20*] for aluminum using Solochrome Cyanine R is purportedly capable of detecting 0.004 mg/litre aluminum. It is relatively simple and reliable, but fluoride and large amounts of orthophosphate, pyrophosphate, and hexametaphosphate interfere. Ascorbic acid is used to eliminate ferric iron interference.

Ammonia and Ammonium

Ammonia is a gas which is highly soluble in water and is found in many surface and groundwaters. In mineral waters, it is mostly the result of percolation through strata which contain ammoniacal salts; however, ammonia can be the result of reduction of nitrate in waters by prolonged contact with metallic piping and tanks, or percolation through some reducing media such as ferruginous sand. Ammonia in water is sometimes derived from decomposition of sewage, and from agricultural runoff. This ammonia is readily oxidized to nitrate by certain organisms. The presence of ammonia is often regarded as indicative of fresh pollution by nitrogenous wastes.

Concentrations of ammonium ion, as distinct from total ammonia content, can be calculated readily from the latter value if sufficient information is available. The total ammonium content is distributed among ammonium ion, free ammonia (ammonium hydroxide), and other un-ionized ammonium compounds. When the last can be neglected, the concentration of ammonium ion at any given temperature depends on the pH of the water.

Generally speaking, the value is useful only for estimating the effect of small concentrations of ammonia on the conductivity of steam condensate. For this purpose, distribution may be obtained from a table in which percentages of ionized and un-ionized ammonia are given for the pH range from 1 to 13. The difference between total ammonia and ammonium ion also has some significance in the prediction of losses of ammonia at vents.

Ammonia is often used in water treatment to control or adjust pH. For example, in condensate systems, ammonia can be fed to control corrosion by carbonic acid. In this respect, ammonia may be objectionable if the condensate is to be used as boiler feedwater. Ammonia, especially in the presence of oxygen, can be corrosive to the copper and copper alloy equipment in steam condensing and preboiler systems. In cooling waters, ammonia can be a nutrient for microorganisms, giving rise to objectionable amounts of microbiological growth. Also, the conversion of ammonia to nitrates by certain microorganisms can cause a reduction in the pH of the water.

The two procedures of ASTM Method D 1426 cover the determination of ammonia and ammonium ions. The high-precision procedure is applicable to all types of industrial waters. It involves buffering the sample with a mixture of phosphates to pH 7.4 to inhibit hydrolysis of organic nitrogen compounds, and distilling it into a boric acid solution. Ammonia nitrogen is measured in the distillate by Nesslerization or by titrating with standard sulfuric acid. The routine procedure uses direct Nesslerization (without distillation) for rapid, routine determination of ammonia nitrogen. Interferences in both procedures are discussed in the method cited. Determinations should be carried out at room temperature (25 to 30°C).

Nessler reagent is a strongly alkaline solution containing a complex iodide of mercury which reacts with ammonia to form a brownish complex amine. The reaction is so sensitive that less than 0.1 mg/litre of ammonia can be measured easily. Color comparisons with standards can be made roughly in bottles, but more exactly in Nessler tubes. Color comparators or colorimeters are also used. Standards can be made from known concentrations of ammonia, or permanent standards may be prepared in Nessler tubes from solutions of potassium chloroplatinate and cobaltous chloride. Samples containing colored or turbidity-forming impurities frequently can be diluted with ammonia-free water until they no longer interfere with the determination. Barium, calcium, magnesium, and other metals that produce turbidity can first be precipitated in the water sample and the supernatant used for ammonia analysis. Cloudiness due to the formation of magnesium hydroxide and calcium carbonate can be prevented by using Rochelle salts or glassy polyphosphates to sequester the alkaline-earth ions.

The sodium phenolate method [*21*] is reportedly free from the annoyance caused by turbidity when determining low concentrations of ammonia colorimetrically. This procedure is based on photometric measurement of the intensity of the blue color formed when sodium hypochlorite is added to a sample containing a low concentration of ammonia plus sodium phenolate solution. It has been reported that the presence of amines does not interfere with this method.

The total nitrogen content of a water includes nitrate, nitrite, organic, and ammonia nitrogen. The latter two comprise what is regarded as the total Kjeldahl nitrogen. A Kjeldahl nitrogen involves a digestion step in which the organic nitrogen present is converted to ammonium bisulfate by the action of sulfuric acid and a catalyst. Nitrate and nitrite are not included by this procedure, but can be determined as ammonia if a reduction method is used [*22*].

Organic nitrogen compounds are produced by biological processes; hence, an increase in the organic nitrogen content of a water may indicate increased pollution. The organic nitrogen can be determined directly with the Kjeldahl method if any ammonia present is first removed by distillation from a buffered sample.

In all of the foregoing procedures, after digestion, the resulting ammonia is distilled from an alkaline medium and can be measured as given in ASTM Test of Ammonia on Industrial Water and Industrial Waste Water (D 1426), or titrated if the amount is large.

Barium and Strontium

Barium and strontium are usually negligible and, therefore, unimportant in most industrial waters. However, water supplies in occasional geographic locations may contain significant quantities. Barium and strontium may be introduced into the water system as minor impurities in chemicals used in the softening and pretreatment of water supplies. The reactions of barium and strontium in boiler waters and cooling waters are similar to those of calcium and magnesium and, therefore, seldom cause problems in industrial systems.

Both strontium [*23*] and barium [*24*] have been determined by precipitation with chromate. The precipitate is separated, redissolved, and the chromate determined colorimetrically. The sample should contain at least 10 mg of the constituent sought, and suitable precautions must be taken to effect its quantitative precipitation as the chromate.

Barium of the order of 50 mg/litre can be determined quickly by titration with sodium sulfate [*25*] in the presence of a suitable indicator. However, when special accuracy is required, the gravimetric method, in which barium sulfate is precipitated and weighed, is recommended. A more rapid method is the estimation of barium from turbidity formed upon the addition of a small quantity of sulfuric acid to the water, in comparison with similarly prepared standards. Small quantities of barium in natural waters contaminated by industrial wastes were determined by Dzhaparidze [*26*] in this manner. One milligram per litre of barium could be detected.

For an accurate determination of strontium, it is essential that it be separated from calcium. When strontium is present, the standard gravimetric oxalate method determines calcium and strontium oxides together. The oxides are dissolved in nitric acid and the solution is evaporated to dryness. The residue is then heated to 160°C for 2 h, cooled, and a mixture of equal parts of absolute alcohol and ether is added to dissolve calcium nitrate. Evaporation, heating, and extraction are repeated on the strontium nitrate residue until extraction of calcium nitrate is substantially complete (there is little or no residue when the extract is evaporated). Strontium then is converted to the sulfate, which is ignited and weighed. Quicker but considerably less reliable results can be obtained by using the control methods given for barium.

Several workers [*27–29*] have developed flame photometric methods for strontium. Two milligrams per litre strontium is the lower limit on most of these methods; however, Rains et al [30], using a high-resolution flame spectrophotometer, determined strontium in concentration of 0.1 to 1.0 mg/litre in the presence of several thousand-fold excess of calcium, without prior separation. Strontium and barium have been determined by direct flame photometry by Nakajima [31] and co-workers, in amounts as little as 10 μg.

Both strontium and barium have been determined spectrographically [32]. The range for quantitative determination is from 0.001 to 0.05 percent of the residue remaining after evaporation of the sample. Tungsten was used as the internal standard. Strontium in concentrations of 0.005 to 1.0 mg/litre was determined by Skougstad [33] using a copper-spark spectrographic procedure and an internal standard of lanthanum.

Bicarbonate, Carbonate, Carbon Dioxide

Carbon dioxide dissolves in water in varying amounts depending upon temperature, pressure, and mineral content of the supply. In water, free carbon dioxide increases corrosivity, causing acid attack upon metals with which it comes in contact. In naturally occurring waters, dissolved carbon dioxide is responsible for the dissolution of many minerals picked up by the water in its percolation through the ground. Limestone, for example, is dissolved in this manner, resulting in soluble calcium bicarbonate. Free carbon dioxide present in process waters causes corrosion to the system. In steam condensate, carbon dioxide forms carbonic acid; it is very corrosive and appropriate steps must be taken for its elimination or neutralization.

The total available carbon dioxide content of water is considered to be the sum of that combined as carbonate and bicarbonate, and free carbon dioxide present. These ions exist in equilibrium with each other, their relative concentrations depending upon the pH. Procedures for carbon dioxide determination are given in ASTM Methods D 513. In the most precise method, all the carbon dioxide, whether present originally in combined form as carbonate and bicarbonate, or as free CO_2, is separated from the sample and collected in standard barium hydroxide; the excess of the base is found by titration and calculated to carbon dioxide. In a more routine method, the sample is treated to convert all carbon dioxide to strontium carbonate; the carbonate is then dissolved in hydrochloric acid and the excess is titrated and related to the original carbon dioxide content. Curves are included to enable estimation of the percentage composition of the sample in terms of carbonate, bicarbonate, and free carbon dioxide at all pH levels.

Free carbon dioxide can be estimated very quickly by titrating a sample with standard sodium carbonate or sodium hydroxide until only bicarbonate is present in the solution (phenolphtalein end point); this procedure is much used for carbon dioxide in well waters. Standard sodium hydroxide solution must be used for free CO_2 determinatons on acid waters such as demineralizer cation exchanger effluents; sodium carbonate is not an acceptable titrant in this case. Alkalinity titrations and pH determinations along with the use of nomographs can also be used to determine the concentrations of the various forms of carbon dioxide.

Carbonate and bicarbonate ions are the chief sources of alkalinity in naturally occurring waters, and are important when considering such waters for plant use. Major quantities of soluble calcium and magnesium hardness will be present as the bicarbonates. However, when such supplies are heated sufficiently to drive off part of the combined CO_2, forming carbonates, precipitation of calcium carbonate may occur. The scale-forming characteristics of calcium carbonate may be useful at times. A thin layer laid down inside metallic piping can provide a protective coating, preventing corrosion. In such cases, the control of alkalinity (carbonate, bicarbonate, and carbon dioxide content) is very important.

In boiler water applications, knowledge of the carbonate and bicarbonate content of the water supply is essential for proper treatment. The concentrations of these ions must be accurately controlled and adjusted to obtain optimum removal of hardness in lime or lime-soda ash pretreatment systems. In low-pressure boilers, maintenance of a properly controlled *carbonate reserve* in boiler water is desirable to prevent deposition of calcium sulfate, which forms a very hard scale. Since calcium carbonate is much less soluble than calcium sulfate at boiler water temperatures, the presence of the carbonate ion ensures that residual calcium will be precipitated as the carbonate, rather than sulfate.

In feedwater of higher-pressure boilers, control of the bicarbonate content is essential to minimize breakdown and release of carbon dioxide, which will go off with the steam. Carbon dioxide will dissolve in condensate to form carbonic acid, which is corrosive to steam-condensing equipment and to the condensate return system.

The concentrations of carbonate and bicarbonate alkalinity in water supplies can be calculated, if the total carbon dioxide and pH of the supplies are known. ASTM Methods D 513 include procedures for the determination of total carbon dioxide, and provide graphs and tabular data for estimation of carbonic acid, carbonate, and bicarbonate ions at all pH levels from 2.0 to 13.0.

For control purposes, approximations of reasonable accuracy can be made from alkalinity and pH determinations using data compiled in the form of nomographs [*34*]. These nomograph methods are not applicable when the water supply contains appreciable concentrations of phosphates, silicates, sulfites, and certain kinds of organic matter.

There are additional methods of somewhat restricted accuracy. The titration of samples successively to the phenolphthalein and methyl orange (or other suitable indicator) end points [*4*] can be used to indicate carbonate and bicarbonate concentrations. The interfering ions mentioned in the foregoing also affect this titration method. On boiler waters, color from tannins or lignin derivatives will interfere with detection of the titration end points. A variation of this approach [*35*] in which the sample is titrated between definite pH limits, before and after the carbon dioxide has been boiled off, avoids principal titration errors and eliminates corrections by coupling them with the blank determination.

Another quick method for approximating carbonate in boiler waters depends on the insolubility of barium carbonate and barium phosphate in alkaline solution. An aliquot of the sample is titrated to the phenolphthalein end point, and the titration is then repeated on a second aliquot, to which the difference between the two titrations represents carbonate and phosphate alkalinity and may be calculated to carbonate if the phosphate concentration is known.

Bromide and Iodide

Bromide and iodide seldom are significant in industrial water supplies. Bromides are found primarily in seawater and may also be present in well waters in coastal areas suggesting the intrusion of seawater. Iodide ions are found in almost all waters, but primarily in infinitesimal traces. Aside from considerations of physiological importance, iodide is insignificant in most waters.

Bromides that may be present in freshwater supplies probably are contributed by certain industrial discharges. Bromine also is used as a germicide in the treatment of some metropolitan drinking supplies and in many swimming pools. This is also a source of bromides although the practice is not widespread. Certain connate waters may contain relatively high concentrations of bromide and iodide ions and can be a source of contamination to groundwater supplies.

ASTM Methods D 1246 determine iodide and bromide separately, as well as combined iodide and bromide. In Method A, the catalytic effect of iodide in the reduction of ceric ions with arsenious acid is used to estimate small quantities of iodide. The reaction rate is directly proportional to the iodide concentration, and the ceric ion not reduced is measured indirectly. In another procedure based on reduction of ceric ions [*4*], ferrous ammonium sulfate is added to stop the reaction, the ceric ion remaining oxidizing the ferrous iron to an equivalent amount of ferric iron. The reaction of the ferric ions with thiocyanate ions that are added is the basis of the colorimetric measurement. Time and temperature control are very important.

Method B for bromide, based on the catalytic effect of bromide upon the oxidation of iodide to iodate, is capable of determining 0.01 to 0.1 mg/litre bromide [*36*]. The amount of iodide oxidized in a given period of time is inversely proportional to the amount of bromide present. Optimum conditions for the oxidation are established and limits on potential interferences given. Up to 10 mg/litre iodide causes no significant error.

Bromide in the presence of iodide can be determined colorimetrically using phenol red in the range from 0.1 to 1.0 mg/litre. The bromide is oxidized to bromine, then the bromine reacts with the phenol red to give a blue color. Timing and reagent concentrations are very important; following the recommendations of Goldman and Byles [*37*], results are reported to be good.

In Method C, iodide is determined by oxidizing the iodide to iodate with bromine in a buffered solution. The excess bromine is subsequently reduced by adding sodium formate. Iodine equivalent to the iodate then is liberated from added potassium iodide and titrated. Combined iodide and bromide are measured by oxidizing them to iodate and bromate with hypochlorite, the excess hypochlorite subsequently being reduced by adding sodium formate. Iodine equivalent to the combined iodate and bromate is then liberated from added potassium iodide and titrated. Bromide is calculated from the difference in the two titrations.

There are several variations of the method for determining iodide which involve extraction into various organic solvents and use of alternate oxidation techniques. One method [*38*] capable of detecting 0.1 to 1.0 μg/litre of iodide uses preliminary procedures very similar to those of Method C of D 1246. At the last step, however, phosphoric acid instead of sulfuric acie is used to acidify the sample. Then potassium iodide and starch are added. The iodine-starch complex is purported to be stable in the phosphoric acid medium and the absorbance of the complex is measured spectrophotometrically.

Calcium and Magnesium

Calcium and magnesium are the two major scale-forming contaminants in most raw-water supplies. Practically all boiler water treatment methods have as their major objective the prevention or reduction of calcium and magnesium deposits in the boiler. These two ions from heavy voluminous deposits ranging from hard scales to soft precipitates on heat-transfer surfaces and other internals of the boiler system. Should untreated feedwater be used in a boiler, heat-transfer surfaces soon would become scaled with calcium sulfate (which produces a hard crystalline deposit) and calcium carbonate, which can occur either as a soft deposit or as a hard scale. Calcium carbonate is a major constituent of deposits in preboiler systems. Magnesium salts, such as magnesium silicate and magnesium hydroxide, generally form soft deposits and sludges. These hardness deposits, among others, seriously interfere with heat transfer and reduce efficiency. If such deposits are not prevented or removed at appropriate intervals, tube failures frequently occur.

Since calcium and magnesium react differently to the chemical conditions present in boilers, both should be determined in feedwater analysis, instead of being lumped together as a total hardness determination. Concentrations of calcium and magnesium encountered in industrial waters will vary from several hundred milligrams per litre in raw-water supplies to 1 μg/litre or less in the feedwater for high-pressure boilers.

Incrustation and scale deposits in open cooling systems can form because of the concentration of dissolved solids during evaporative cooling. Calcium carbonate precipitates in the form of scale or sludge when solubility limits are exceeded. In some open recirculating systems, calcium sulfate also may be deposited unless bleedoff is properly adjusted.

Calcium and magnesium ions are important considerations in the dyeing of textiles. They may precipitate certain dyestuffs, producing streaky or spotty dyed goods, or they may act as mordants, causing greater dyestuff absorption and deeper shades.

The standard method for calcium and magnesium determination, ASTM Method D 511, employs conventional gravimetric procedures in which calcium is precipitated as the oxalate and magnesium as the phosphate. Weights of residues from ignition of the precipitates are converted to constituent concentrations.

Time-saving modifications have been used widely for routine testing. For example, the reprecipitation step in each gravimetric procedure may be omitted at a considerable sacrifice in accuracy, perhaps as much as 10 percent of the value found. The precipitated calcium oxalate may be dissolved in sulfuric acid and the resulting oxalic acid titrated with potassium permanganate; the titer is directly related to the calcium content. Finally, titration methods for hardness can be used to determine calcium and magnesium separately in most industrial waters.

Several rapid colorimetric tests exist for the determination of calcium and magnesium. Titan yellow has been used as a reagent for the determination of magnesium, but this colorimetric procedure has been found unsatisfactory by many investigators. A variant called thiazole yellow is reported [*39*] to be a better reagent; it provides a reproducible color that is not affected materially by iron, aluminum, manganese, phosphorus, or calcium. The optimum range is 1 to 6 mg/litre of magnesium, with an accuracy within 5 percent. Magnesium in amounts up to 180 mg/litre has been determined [*40*] spectrophotometrically using *p*-nitrophenyllazo-1-naphthol; this reagent forms a color complex with magnesium having absorption bands at 405 and 580 nm. Other alkaline earths do not interfere, but iron interferes. Xylidyl Blue II has also been investigated [*41*] and proposed as a useful colorimetric reagent for magnesium.

Small amounts of calcium have been determined using glyoxal bis (2-hydroxyanil), which forms a complex with calcium in alkaline solution and is stable in an aqueous alcoholic solution. It has a maximum absorption at 520 nm. Kerr [*42*] investigated optimum conditions, including organic solvents and the effect of foreign ions, and established a method suitable for determining 0 to 4 mg/litre of calcium. Magnesium up to 50 mg/litre does not interfere. If hexanol is used, a quantitative chloroform extraction of the complex, and re-extraction of the calcium back into an acidified aqueous phase, also has been proposed as a preliminary separation [*43*] prior to developing the color. Small amounts of calcium also can be determined [*44*] gravimetrically by precipitating and weighing calcium potassium nickel hexanitrite.

Chloride

Chloride is present (generally as sodium chloride) in practically all waters. Occasionally chloride will be present in combination with magnesium or calcium, although higher concentrations of these salts suggest contamination by seawater, brines, or industrial wastes. The concentration of chloride in natural waters varies from a few milligrams per litre, or less, to several thousand milligrams per litre in some groundwaters. Reasonable amounts of chlorides can be tolerated in many industrial waters and in potable supplies.

Although chloride usually is not the direct cause of corrosion, the chloride ion is small, highly mobile, and will accelerate corrosion reactions in proportion to its concentration, because of its ability to penetrate and increase solution rate of iron, and its contribution to electrolyte content. For this reason, brines can corrode a system at a rapid rate. Chlorides can accelerate stress corrosion of stainless steel alloys, so chloride concentration must be carefully controlled in systems where these metals are used. In low-pressure boilers and cooling waters, chlorides present few problems.

Chloride remains unchanged in process water, and this property makes chloride analysis very useful. Chloride concentrates in boiler waters and evaporative cooling waters in an exact ratio to the amount of evaporation that takes place. Thus, a chloride analysis of makeup water compared with that in the boiler water or cooling water gives a simple procedure for estimating the amount of concentration that is occurring. Comparative chloride analyses in conjunction with nitrate analyses also can be used to indicate contamination of groundwater by sewage wastes.

ASTM Methods D 512 include three high-precision procedures. The first is a mercurometric titration applicable to high-purity industrial water and water relatively free of heavy metal ions. The second is a silver nitrate titration for use with low-purity industrial supplies, process, and waste waters; and the third, a mercuric thiocyanate colorimetric method. In Method A, dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone-bromphenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex. In Method B, the sample is adjusted to pH 8.3 and titrated with silver nitrate in the presence of potassium chromate indicator. The end point is indicated by persistence of the brick-red silver chromate color. In Method C, mercuric thiocyanate reacts with the chloride present, releasing an amount of thiocyanate ion that is equivalent to the chloride. Added ferric iron forms a red color with the thiocyanate ion, which is measured photometrically or by visual comparison.

Method A without sample concentration is for chloride concentrations down to 0.1 mg/litre. Method B is for chloride concentrations above 5 mg/litre in waters where interferences from color or high concentrations of heavy metals are present. Method C can detect 0.02 mg/litre chloride, and primarily is for relatively pure waters where low concentrations of chloride must be accurately known.

Titration methods using a small aliquot are normally employed when the chloride concentration is high. However, concentrations above 1000 mg/litre probably can be determined somewhat more accurately by a more cumbersome gravimetric procedure in which a slight excess of silver nitrate is used to precipitate silver chloride. The precipitate is coagulated by digestion (but not boiling), filtered through a prepared porous crucible, washed free from silver nitrate (hot water), dried at 150°C, and weighed. Strong light will decompose the silver chloride precipitate, causing serious errors.

Chlorine

The determination of chlorine is important because an increasing proportion of industrial water is chlorinated. In addition to use for sterilization of potable water, chlorine treatment is used for control of algae and prevention of bacterial slime growths throughout cooling systems. In cooling towers, continuous contact with free chlorine can cause some deterioration of lumber; in large concentrations, chlorine can accelerate corrosion of metals, especially in the presence of oxygen.

Chlorine in solution exists as *free available chlorine* such as hypochlorite ions (OCl) or hypochlorous acid (HOCl), and as *combined available chloride*, consisting of chlorine combined with ammonia nitrogen or nitrogenous compounds. The sterilizing action of combined chlorine is not as potent as that of free chlorine, but it possesses a longer residual time in water; that is, it is more stable. In a given contact period, about 25 times as much combined chlorine as free chlorine is required to yield the same sterilization effect. Thus, the ammonia content of water is an important consideration in chlorination treatment.

Chlorine residuals may be present in some surface waters where chlorinated industrial and sewage wastes are discharged.

Two methods for chlorine determination are presented in the *Annual Book of ASTM Standards*, Part 31 [*1*]: Methods D 1253; and D 1427. Method D 1253 includes a high-precision and two more routine methods for determining total available chlorine residual. Two of these methods are suitable for differentiating between free and combined residuals. The high-precision method is an amperometric titration with phenylarseneoxide. Routine Method A (which also differentiates between free and combined residuals) is used for rapid control determinations of chlorine residuals up to 10 mg/litre, but is most sensitive below 1 mg/litre. Routine Method B is applicable for chlorine residuals above 1.0 mg/litre, and is particularly useful for measuring high residuals (10 to 300 mg/litre). Both routine methods are colorimetric procedures using orthotolidine to form a yellow color.

The two methods of D 1427 permit determination of chlorine residuals in the presence of most interfering constituents found in industrial waste water. Method A is a starch-iodide titration, and Method B is an amperometric titration. Both cover total chlorine measurement, but only the latter is applicable to determination of free available chlorine.

A rapid method for determining free chlorine residuals above 1.0 mg/litre in cooling waters involves titration of an acidified sample with a standard methyl orange solution. Free chlorine decolorizes the methyl orange until the chlorine residual is exhausted; then the color of the methyl orange persists, indicating the end point. Chromate in low concentrations does not interfere, but at higher levels masks the end point. Xylene cyanole has been used instead of methyl orange, giving a readily discernible green end point in high-chromate waters.

Samples to be analyzed for chlorine should be kept away from direct sunlight prior to analysis. The analysis should be made as soon as possible (not more then 5 min after sampling), because a chlorine residual may decrease with time as a result of any chlorine demand of the sample.

Chromium

Chromium in water is of interest principally in the hexavalent form, in connection with its use as a corrosion inhibitor. It also is a frequent component of industrial wastes, in which it may be present in either the trivalent or hexavalent form, or both. It is of minor importance, however, in water supply for power plants. If introduced as a contaminant into boilers, chromate will be reduced to trivalent chromium and precipitated as chromic hydroxide.

Chromate and dichromate are not found naturally in water, but may be present because of industrial contamination. The presence of chromium compounds in surface water supplies usually indicates discharge of metal plating solutions and similar industrial wastes, or the use of chromate and dichromate-based corrosion inhibitors in cooling water. Obviously, the manner of disposal of blowdown water from cooling towers using chromate inhibitors presents a problem. Discharge of chromates into surface waters should be avoided to prevent potential contamination of irrigation and drinking water supplies, damage to aquatic life and other adverse effects. The U. S. Public Health Service (USPHS) limit for hexavalent chromium in drinking water is 0.05 mg/litre maximum.

Alkaline chromates and dichromates have long been used as corrosion inhibitors in cooling systems. In ferrous metal systems, the chromate or dichromate ion reacts with ferrous ions released at anodic areas, hexavalent chromium being reduced to trivalent chromium and precipitated to form a blocking mixture (thought to be a mixed ferricchromic hydroxide) which seals pores in the iron oxide film and prevents further corrosion. The resulting protective film is tough, adherent, and self-healing, when adequate chromate concentrations are maintained in solution. The maintenance of an adequate chromate concentration to provide substance for the self-healing is essential. Chromate and dichromates are particularly effective as corrosion inhibitors in refrigerator brine systems.

A method for amounts of chromium in excess of 100 mg (in the absence of organic matter) involves oxidation of chromium to the hexavalent form with permanganate or silver nitrate or persulfate, destruction of excess oxidant, and titration with standard ferrous sulfate solution. Excess ferrous sulfate may be used and back-titrated with dichromate, using *o*-phenanthroline, or with permanganate.

Graham proposed a method which depends on the reaction of hexavalent chromium with diphenylcarbazide in acid solution to produce a reddish-violet color. The optimum range is up to 5 mg/litre and the accuracy is about 4 percent. Phosphoric acid has been shown to mask iron, the most important interfering element [*46*]. A similar method has been proposed for the determination of chromium in samples of polluted water, industrial wastes, or sewage [*4*]. Organic material is decomposed by fuming with strong acids, and other interfering metals are extracted. Chromium is oxidized to the hexavalent state with permanganate, the excess permanganate destroyed with sodium azide, and the color developed with diphenyl-carbazide. See ASTM Methods D 1687 for similar procedures using either permanganate or hypobromite for oxidation. Goodman [*47*] simplified the diphenylcarbazide color development by preparing the reagents as a single mixture of dry powders rather than separate solutions.

Carmoazine reagent [(2-sulfo-1-napthylazo)-1-naphthal-4-sulfonic acid] can be used to determine chromium [*48*] both visually and photometrically in the microgram-per-litre range. According to the author, no other ions interfere. Polyanskii [*49*] used 1-naphthylamine to determine chromium. The sensitivity of this method was increased by extracting the colored complex with isoamyl alcohol. The sensitivity was 0.1 mg/litre.

Copper

Copper is rarely found in natural waters and, when it exists, is usually derived from industrial wastes. Copper sulfate and stabilized copper compounds now are being used extensively in the treatment of reservoir water to control the growth of algae and diatoms, providing another source of copper in various waters.

Knowing the copper content of industrial waters is important mainly because of corrosion and deposition processes in which it is a factor. Copper can be deposited in metallic form in pipes and boiler tubes, presumably with the dissolution of an equivalent amount of iron. So far, the role of copper in boiler corrosion has not been satisfactorily explained; however, copper deposits in boilers as a spongy mass or is laid down in sheets. Corrosion in the preboiler system usually is the source of such copper. Some authors believe copper is not the primary cause of corrosion in boilers, but accelerates corrosion once it has started. Very small amounts of copper will also attack aluminum, particularly in hard water.

Analysis for copper content of water also can be used to monitor corrosion of copper, brass, and other copper alloy fittings and tubes. Concentrations of ammonia above 10 mg/litre in water along with dissolved oxygen can result in fairly significant copper dissolution. Carbon dioxide and sodium bicarbonate also can cause corrosion of copper and copper alloys.

Several colorimetric agents for use in determining copper are in existence. Sodium diethyldithiocarbamate, which produces a yellow color with copper, lacks sensitivity and selectivity. Extraction of the colored product with a suitable organic solvent increases the sensitivity and simplifies the removal of interferences. Ammonium thioglycolate added during extraction will help interferences from iron, nickel, manganese, and chromium. Ethylenediaminetetraacetic acid (EDTA) can be used to eliminate interference from zinc and lead. The method can be used in the range from 0.1 to 1 mg/litre. If interfering substances are not present in troublesome concentrations, determination can be made directly on the sample.

The procedure using (2-hydroxyethyl) dithiocarbamate (cuprethol) is superior to that utilizing sodium diethyldithiocarbamate; routine Method C of ASTM Methods D 1688 employs this reagent for the determination of copper in relatively unpolluted waters. No extraction step is involved.

Precision Methods A and B of D 1688 use neocuproine to develop a color with copper, as a basis for its determination. The copper is reduced to cuprous, and the color complex then extracted with chloroform. Table 5 compares the three methods presented and indicates their applicability.

A procedure using bathocuproine offers promise of being an improved method for copper [*4*], and is recommended for unknown and polluted waters because of its relative freedom from interferences.

A very selective and sensitive reagent, nickel diethyl dithiophosphate, has been used [*50*] for the determination of copper. To determine copper in water, 1 to 2 litres of sample is acidified and then extracted three times with small portions of 0.005 *M* nickel diethyl dithiophosphate and carbon tetrachloride. Copper in the amount of 0.01 mg was determined at a dilution of 1 to 10^9. This procedure for trace amounts of copper was modified by Nemodruk and Stasynchenko [*51*] to be faster, simpler, and more accurate.

Oxalyldihydrazide has been used [*52*] to determine from 0.02 to 1 mg of copper per millilitre of seawater without using an extraction. To 10 ml of sample was added 2 ml of saturated oxalyldihydrazide, 10 ml of ammoniacal 5 percent ammonium chloride, and 10 ml of 40 percent aqueous acetaldehyde. A 1-h waiting period was required for complete color development. At

TABLE 5—*Copper analysis methods.*

Method D 1688	Precision Method A (Neocuproine)	Precision Method B (Neocuproine)	Routine Method C (Cuprethol)
Basis of measurement	colorimetric	colorimetric	colorimetric
Range	0.05 mg/litre Cu or over	0.002 to 0.100 mg/litre Cu	0.05 mg/litre Cu or over
Application	all types of industrial water and industrial waste waters containing 0.05 mg/litre Cu or more	industrial waters such as steam condensates and deionized water	industrial waters relatively unpolluted. Does not involve organic extraction; therefore more rapid than Method A
Summary of method	the copper is reduced with hydroxylamine hydrochloride and the pH adjusted to 4.0 to 6.0. The cuprous reacted with neocuproine and the yellow color extracted with chloroform is read or compared	same as Method A except choice is given between chloroform and isoamyl alcohol as the organic solvent used for extraction	cupric ions form a yellow-colored chelate with cuprethol [bis-(2-hydroxyethyl) dithiocarbamate]. The colored compound formed at a pH between 5 and 6 is read or compared
Interferences	none from the ions commonly found in industrial water or industrial waste water. Interfering ions are removed	none of the ions commonly found in low-solids industrial water	excessive concentration of interfering ions will rarely be encountered in unpolluted water. If Bi, Co, Hg^{+2}, Ni, CN, and sulfide ions present, use Method A
Instrumentation or special equipment	Nessler tubes, filter photometer, or spectrophotometer (capable of reading at 457 nm)	Nessler tubes, filter photometer, or spectrophotometer (capable of reading 454 to 457 nm)	Nessler tube, filter photometer, or spectrophotometer (capable of reading at 435 nm)

low concentrations of foreign metals, only chromium interfered. Zinc dibenzyldithiocarbamate [*53*] has been used for the determination of copper in potable water. A single extraction of an acidified sample is made with a chloroform solution of zinc dibenzyldithiocarbamate and can be applied to colored or turbid waters. Other materials likely to be present do not interfere, and the method is suitable for routine use. Copper in the amount of 0.02 mg/litre can be detected.

Low concentrations of copper are determined also by the potassium ferrocyanide method [*54*]. Copper in a sample from which lead has been removed as lead sulfate is first concentrated by precipitation as copper sulfide. Any iron present is removed after the precipitate has been converted to nitrate, and potassium ferrocyanide is added to develop the reddish color, which is then compared with standards.

The dithizone method proposed for copper (also used for zinc and other metals) depends upon formation of stable, colored metal dithizonates from extraction of aqueous solutions with dithizone in carbon tetrachloride or chloroform. By adjustment of pH, use of complexing agents, and other techniques, separation of metal dithizonates is made. This method is time-consuming and it is less accurate than the cuprethol or cuproine methods.

A direct Zincon method, described later under *Zinc*, also has been adapted for determination of copper.

An electrolytic method for copper also has been used. It involves deposition of copper metal on a platinum cathode and subsequent weighing of the electrode. This method is an excellent one for waters of high copper content, such as plating wastes. ASTM Method E 53 [*55*] can be used for the electrolytic determination after first concentrating the sample.

Cyanide

Cyanide does not occur naturally in water, but is the result of contamination. Waste waters from certain chemical processes and metal plating industries are the chief source of the contaminant in surface waters. Residues for insecticides and rodenticides can also be a source.

The chief reason for concern with cyanide in water is its highly toxic character. In low concentrations it can kill marine life and useful bacteria, thus upsetting the natural purification abilities of streams and promoting buildup of other organic pollutants. Cyanide also may be detrimental to sewage treatment processes.

The major problem in analyzing for cyanide is the removal of interfering substances. ASTM Methods D 2036 include procedures for removing interferences and making the determination. Methods for removal of sulfides, fatty acids, and oxidizing agents are outlined, followed by distillation procedures for removing most other interferences. After interferences are removed, cyanide is determined either by a modified Liebig titration method using *p*-dimethylaminobenzalrhodanine internal indicator, or by a colorimetric method using pyridine-pyrazolone if the concentration is below

1 mg/litre. Provisions also are made for determining the concentration of cyanide that is amenable to chlorination treatment.

Fluoride

Fluoride is present in almost all natural water supplies. The fluoride content varies considerably with the source, and with the extent of contamination by waste discharges. Flourine has little significance in industrial waters, but in drinking water in amounts of 1 to 1.5 mg/litre it is an effective preventive of dental caries, if ingested during the period of permanent tooth development. Above this amount, fluorine may cause mottling of teeth. For potable water supplies, fluoride in excess of 1.0 to 1.5 mg/litre should be removed by appropriate treatment processes.

Fluoride occasionally is used in cooling water treatment to prevent precipitation of aluminum ions. In this application it functions by forming a soluble complex, and can be considered a deposit inhibitor or antifoulant. Fluoride also will precipitate in the presence of higher concentrations of calcium and magnesium. In waters containing fair amounts of the fluoride ion, the fluoride content will be significantly reduced during lime-soda softening.

ASTM Methods D 1179 provide two procedures for the determination of fluoride. Precision Method A [*56*] based upon the bleaching effect of the fluoride ion on zirconium-organic complexones uses SPADNS reagent (sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate). This method tolerates many interferences and determines fluoride in the range from 0.00 to 1.40 mg/litre. No waiting period is involved for color fading; the reaction is immediate, color is stable and follows Beer's law in the concentration range mentioned. The high-precision method provides for the elimination of interferences by incorporating a distillation procedure, and should be the method of choice on unknown waters.

If interferences are known to be absent, or present in sufficiently low concentrations, the distillation may be omitted, and routine Method B used.

Method B depends upon the bleaching effect of the fluoride ion on zirconium alizarin color.

A direct photometric method [*57*] using the wine-red cerium (III)-alizarin complexone to produce a blue color with fluoride also can tolerate relatively high amounts of interferences.

Hydrogen

Hydrogen occurs in the atmosphere in very minute quantities but is found free in nature in significant amounts in the gases of volcanoes and fumeroles. It has also been found occluded in rocks such as granite and has been reported to be sometimes present in natural gas. Hydrogen dissolved in natural waters is practically nonexistent and in the past was not regarded as an important constituent of industrial water. It has now been recognized that the rate of corrosion reactions in expensive boiler systems can be followed by comparing hydrogen concentrations in the water and vapor in various parts of the system. The hydrogen produced is a by-product of the dissolution of iron in water (corrosion reactions). The methods used for measurements of hydrogen depend on elaborate instrumentation [*58, 59*], since the concentration sought is of the order of micrograms per litre.

ASTM Methods D 1588 present two methods. The method of highest precision is based on the separation of hydrogen and measurement of its thermal conductivity compared with the thermal conductivity of air under the same conditions. Zero to 40 μg/litre can be determined with an accuracy of ±5 percent. The alternative method is a volumetric determination where the dissolved gases are removed from the water sample by boiling and collected. The gases are then analyzed in an Orsat-type apparatus. Both methods are intended for analysis of steam condensates but may be extended to waters of similar character.

Analysis for dissolved hydrogen has become of interest in the nuclear power field due to the use of hydrogen as a suppressor of water dissociation in the primary systems of pressurized water nuclear power plants. The concentrations of interest are much higher than in the case of boiler systems, up to 25 mg/litre and higher. A method often used employs a gas transfer apparatus for volumetric determination of the total dissolved gas evolved from a water sample under vacuum. A Blacet-Leighton apparatus is used to determine the proportion of hydrogen in a sample of the gas by measuring the reduction in gas sample volume after removing the hydrogen by exposure to heated copper oxide.

Iron

The presence of iron in water is objectionable because it contributes to problems of taste, discoloration, turbidity, and deposits. For many uses, such as high-pressure boiler feedwater, process waters for fabric dyeing and paper making, photographic film manufacture, icemaking, and food processing, the water must be almost entirely free from iron.

The occurrence of iron in water varies widely depending on source of the supply. The iron content of some deep wells and industrially contaminated streams can be very high, while other sources may be iron-free. Iron, if present (uncomplexed) in natural waters, normally is found in the form of ferrous salts; however, upon contact with air it is readily oxidized to ferric salts, which precipitate to give characteristic rust-colored deposits. Ferric iron in many instances will remain in suspension in water, because of occasional difficulty in coagulating ferric hydroxide. It can be removed by energetic flocculation followed by filtration.

Corrosion is the chief source of the iron in boiler water. The iron often creates serious problems in high-pressure steam-generating systems. Corrosion of metals in boiler and preboiler systems releases iron in ionic form, and iron oxides which circulate with the water and may not be removed by blowdown. Such oxides form adherent coatings and can lead to tube failures by overheating, caustic gouging, and hydrogen damage. On surfaces of high heat transfer, ferric iron complexes with sodium silicate, if present, to form a very hard, strongly adherent deposit called acmite.

Cooling waters containing suspended or dissolved iron also can develop serious fouling problems due to deposition of iron oxide or reaction products of iron with treatment constituents such as chromate and phosphate. Dissolved or suspended ferric and ferrous iron also can foul ion exchange resins used for water softening.

The analysis of iron in water usually is done spectrophotometrically or colorimetrically, although a few titrimetric procedures exist for milligrams-per-litre concentrations. ASTM Methods D 1068 are based upon the intensity of an orange-red color produced by the reaction of ferrous iron with orthophenanthroline or bathophenanthroline. Method A uses orthophenathroline, and is designed for iron concentrations in excess of 0.05 mg/litre. It also is capable of distinguishing the distribution of iron between the ferrous and ferric states. The proportion of soluble and suspended iron can be obtained by difference from determinations made on filtered and unfiltered samples. Method B uses the more sensitive color reagent bathophenanthroline, and is capable of detecting less than 1 μg/litre of iron. It is particularly applicable to high-purity water and steam condensates. Table 6 indicates areas of applicability of the three iron methods.

Good results also have been obtained with a 2-2′ bipyridine [*60*], 2,2′,2″ tripyridine, and with thioglycollic acid (mercaptoacetic acid) [*61*]. The principle of the bipyridine method is the formation of a pink complex with ferrous iron at a pH of 3 to 4. Tripyridine develops a reddish purple color with iron over a wide pH range. The use of this reagent along with ethylenediamine to complex heavy metals is the basis for a standard method [*4*]. The reaction between thioglycollic acid and iron gives a relatively stable, reddish purple color. A thiocyanate [*62*] method also has been used.

Comparative results on samples of low iron concentration using bathophenanthroline, orthophenanthroline, bipyridine, and thiocyanate methods have been reported [*63*], and Herre [*64*] made a detailed comparison of thioglycollic acid, potassium thiocyanate, sulfosalicylic acid, ferron, and *o*-phenanthroline. The bathophenanthroline method has been modified to eliminate the extraction step, the lower limit being 5 μg/litre iron [*65*]. Ethyl alcohol is added to effect the solution of the iron-bathophenanthroline complex in water. Grat-Cabanca [*66*] has studied interferences in the bipyridine method with particular attention given to cobalt, nickel, and manganese. He found that no interference from these ions resulted if the ratio of the interfering ion to the iron concentration did not exceed 15, 22, or 80, respectively.

Several colorimetric agents exist for iron and a number of new reagents

TABLE 6—*Iron determinations.*

Method D 1068	Precision Method A	Precision Method B
Basis of measurement	colorimetric, *o*-phenanthroline	colorimetric, bathophenanthroline
Range	concentrations of iron above 0.05 mg/litre in industrial water and industrial waste water	low concentrations of iron (200 μg/litre and under) in industrial water
Application	Industrial water and industrial waste water. For dissolved and total iron	industrial water with low iron concentrations. Total iron
Summary of method	the ferrous iron, solubilized with acid, forms an orange-red complex with 1,10-phenathroline. The intensity of the color produced is proportioned to the amount of ferrous iron in the water. Ferric iron is converted to ferrous with hydroxylamine hydrochloride for total and dissolved iron	for total iron the iron is reduced with hydroxylamine hydrochloride and reacted with bathophenanthroline to form a red ferrous complex. The complex is extracted with *n*-hexyl or isoamyl alcohol and color intensity measured
Interferences	interference if Cu, Co, Cr, Zn are ten times Fe concentration; Ni when in excess of 2 mg/litre; Bi, Ag, and CN− must be absent; methods given for removal of interferences	if the pH is between 3.3 and 3.7, a 1-mg/litre concentration of the following ions does not interfere: Cu, Mn, Al, Zn, Mg, Na, SiO_2, NO_3^-, $PO_4^{\equiv}$
Instrumentation or special equipment	Nessler tubes, filter photometer, or spectrophotometer capable of reading at 510 nm	Nessler tubes, filter photometer (green filter), or spectrophotometer capable of reading at 533 nm

have been proposed. Several of these may be applied to specific problems, but many have serious interferences.

In collecting iron samples, if the concentration of iron is less than 0.1 mg/litre, it is necessary that the sample be collected under acid to assure full recovery of iron. It is often convenient to run both iron and copper on the acidified sample.

Load

Lead is practically nonexistent in natural waters; in cases where lead is present, it is directly due to corrosion reactions or waste contamination. Mine waters and wastes from metal plating industries are the most common sources of contamination in raw-water supplies. Most instances of lead being present in water may be traced to contact with lead piping or lead-bearing jointing compounds used with threaded piping. The character of the water determines its plumbo-solvency. Naturally occurring waters that are highly acid or contain large amounts of carbon dioxide and are low in calcium and magnesium bicarbonates are apt to dissolve significant amounts of lead. Organic content in acidic waters also increases the plumbosolvency.

The lead content is primarily of interest in potable water supplies because it has a cumulative poisoning effect in the human body. For industrial uses, lead is not usually a significant problem.

Lead, especially in small amounts found in waters is usually determined with dithizone [*67*]. The lead dithizonate precipitate is soluble in chloroform or carbon tetrachloride and imparts a red color to the solution. A method using a preliminary dithizone extraction and reextraction into an acidified aqueous phase [*4*] isolates the lead for subsequent determination. Only bismuth, thallium, and stannous tin interfere, and a procedure is proposed for the elimination of bismuth and tin interference [*4*]. The method determines from 0.01 to 0.05 mg of lead.

Before the introduction of dithizone, small amounts of lead were determined by comparing colloidal precipitates of lead sulfide with standards similarly prepared. Electrolytic methods for small amounts of lead have also been used, but they do not compare favorably with dithizone.

Polarigraphic methods for low concentrations of lead have been developed. Ullman [*68*] and co-workers devised a procedure using a quiet mercury pool cathode cell to determine down to 0.01 mg/litre lead in waste waters. The method is also capable of determining like concentrations of cadmium, copper, nickel, and zinc on the same sample.

Manganese

Manganese occurs in soil and rocks as manganese dioxide and can be dissolved in natural waters by the action of bacteria under anaerobic conditions [*69*]. The presence of complexing agents such as carbon dioxide, tannins, and lignins accelerate the rate of manganese concentration. This dissolved manganese is readily oxidized to manganese dioxide by air, and is objectionable because of the formation of a brown manganese dioxide precipitate. If process water is not treated for removal of manganese, this precipitation can take place in the system, giving rise to staining and other objectionable characteristics, much the same as those of iron. The function of manganese in boiler waters has not been thoroughly investigated, but it may be anticipated to accelerate corrosive tendencies which may be present. In cooling systems, manganese has been shown to cause corrosion reactions in copper alloy tubing.

ASTM Method D 858 uses persulfate to oxidize manganese ions to permanganate; the purple color produced is the basis for determining the concentration. The method is capable of determining both soluble and insoluble manganese. Provisions are made for elimination of interferences from organic matter and halogens. The method also includes corrective procedures to compensate for other color-producing ions. Similar methods exist using perioxidate as the oxidizing agent.

A method [*70*] for manganese using tetrabase (4-4′-tetramethyldiaminotriphenylmethane) can be useful. While not as accurate, and subject to more interferences than the persulfate method, it has the advantage of greatly increased sensitivity.

Formaldoxime has been used to produce a reddish-brown color with manganese in alkaline media, and is the basis for colorimetric methods [*71*]. Interference by iron and copper is eliminated by complexing with cyanide in the presence of tartrate, and by removing the excess cyanide with zinc. Zinc and many other metals do not interfere.

Nickel

Nickel is very seldom found in natural waters, but has become significant in industrial supply or process waters because of the increasing use of stainless steels and other nickel-containing alloys in water systems. Aside from the presence of nickel as an indicator of corrosion-erosion of such alloys, this determination is of importance in water chemistry for high-pressure boilers. Nickel behaves much like copper in this environment and may be precipitated as the oxide or as metallic nickel. Its possible role in corrosion of other metals has not yet been elucidated.

In ASTM Methods D 1886 nickel is determined with both sodium diethyldithiocarbamate and dimethylglyoxime. Method A, using sodium diethyldithiocarbamate, is subject to more interferences than Method B, using dimethylglyoxime, but is more sensitive, being able to detect 0.001 mg/litre. The nickel diethyldithiocarbamate is extracted with carbon tetrachloride in the presence of citrate, as in the copper salt. A correction for copper is made by reading the absorbance of the sample at two wavelengths, one the maximum for nickel and the other the maximum for copper.

Method B depends on the formation of a wine-red complex of nickel with ammoniacal dimethylglyoxime. While not as sensitive as Method A, it has the advantage of fewer interferences and is a more rapid method, being able to determine from 0.01 to 5.0 mg/litre nickel.

Heptoxime [*4*] has been used as a colorimetric reagent in determining nickel. For use of this reagent, iron and copper are first removed by precipitating with cupferron and extracting with chloroform. The nickel is then separated from other interferences by extracting the nickel heptoxime with chloroform. After separation, the nickel is re-extracted into the aqueous phase with hydrochloric acid, where the color is developed with heptoxime. Nickel in the range of 0.05 to 0.25 mg is determined.

A derivative of heptoxime, 4-isopropyl 1,2-cyclohexanedionedioxime, has been reported [*72*] as the most sensitive of the dioxime-type reagents for the spectrophotometric determination of nickel. The use of this reagent was further improved by extraction of the nickel salt into xylene [*73*] so that sensitivities of 0.005 mg/litre nickel could be obtained. Ratios of iron, cobalt, and copper to nickel of 20, 2, and 8, respectively, can be tolerated.

Nitrate

Nitrate in low concentrations occurs in most natural waters and ranges in concentration generally from 0 to 70 mg/litre, the extremes being rare. It is mostly derived from nitrogenous organic matter of animal origin; decay of vegetable matter in soil yields very little nitrate. For this reason, significant concentrations of nitrate in water may be indicative of water sources polluted at some earlier time with sewage or animal wastes. The strata through which the water percolates can also be a source of significant amounts of nitrate. Nitrate in water generally is of serious concern only where the supply is used for potable purposes. Nitrate in concentrations above 20 mg/litre has been reported as the cause of methemoglobinemia in infants, a disease characterized by blood changes and cyanosis, in which the hemoglobin apparently becomes incapable of transporting oxygen.

Nitrates find applicability in water treatment in corrosion-inhibitor compounds for cooling systems; in low-pressure boilers, nitrate alone or in conjunction with certain organic compounds gives effective control of intergranular corrosion (embrittlement) of boiler metal.

ASTM Method D 992 is a rapid, simple, and precise colorimetric procedure. A yellow color is developed in the sample by the reaction of nitrate ion with concentrated sulfuric acid and a chloroform solution of brucine alkaloid. An accuracy of 0.5 mg/litre is obtainable in the 0 to 50-mg/litre range.

One method [*74*] purported to be very reliable is based on the formation of 4-nitroso-2,6-xylenol by reacting the nitrate in the sample with 2,6-xylenol in a highly acidic medium, in the presence of ammonium chloride. The concentration of the 4-nitroso-2,6-xylenol which is directly related to the nitrate content is determined by reading the optical density at 304 nm. Provisions are made for removal of interference from nitrate and ferrous ions; several other ions investigated do not interfere. The method determines 0 to 50 mg/litre of nitrate-N with a sensitivity of 0.13 mg/litre.

Another method [*75*] that is simple and rapid is based upon the ultraviolet absorbance of nitrate. The sample is filtered and acidified, and then read at 220 nm and 275 nm. Nitrate absorbs at 220 nm but not at 275; absorbance at 275 nm is traceable to organic interference and is used to calculate the appropriate correction. Nitrite, chromate, and detergents interfere; corrections for these can be applied, but they make the test more time-consuming and less accurate.

Much-used colorimetric procedures based on the yellow color developed in reacting phenoldisulfonic acid with nitrate ions have been found by some investigators to be less reliable than the brucine alkaloid method, although much work has been done to improve this method. Besides being subject to interference from chloride, it has been shown [*76*] to give low results in the presence of ammonium ions. The sample can be treated to eliminate these interferences, but special precautions must be taken to avoid loss of nitrate. If both chloride and ammonium interferences are present, further sample treatment complications arise. In addition, this approach is not satisfactory for samples containing organic matter.

Nitrite

Nitrite in natural water is generally regarded as evidence of sewage pollution. Its presence indicates that nitrogeneous organic matter from sewage or animal wastes is undergoing active oxidation or nitrification and that the process is not complete. The occurrence of nitrite is also possible if nitrate-containing water supplies come in contact with certain reducing materials.

Nitrites are occasionally used for corrosion control in closed cooling systems. Discharge of nitrite-treated cooling water into surface supplies may create pollution problems, or be mistakenly interpreted as indicative of sewage dischargers. When sampling waters for nitrite analysis, the bottle should be sterile, and the determination should be made as soon as possible after collection of the sample.

The ASTM Test for Nitrite Ion in Undustrial Water (D 1254) provides two procedures for determining nitrite ion. The most accurate method is colorimetric and is based upon the diazotization of sulfanilic acid by the nitrite ion, followed by coupling with alpha-naphthylamine. The reaction takes place at a pH of 2.0 to 2.5 to produce a reddish purple color which can be measured photometrically at 520 nm or by visual comparison. Its application is to samples that contain less than 0.5 mg/litre nitrite and are not highly polluted. This range can be extended by dilution. A thorough discussion of interferences is also included.

The alternative method is a titrimetric procedure for samples with a nitrite content of 30 to 100 mg/litre. It is primarily applicable to systems having a high nitrite content, particularly those where nitrite is added as a corrosion inhibitor. The method is based on the reduction of permanganate by nitrite ions. A known volume of acidified standard permanganate solution is reacted with the sample, the excess permanganate reacted with a known excess of standard sodium oxalate, and the excess oxalate back-titrated with standard permanganate. Reducing agents obviously interfere. Other diazotization-coupling procedures have used sulfanilamide and *N*-(1-naphthyl) ethylenediamine hydrochloride [*77*] and sulfanilic acid and *N*-(1-naphthyl) ethylenediamine hydrochloride [*78*].

Another procedure [*79*] which determined nitrite plus total nitrate and nitrite is very similar to the brucine alkaloid test for nitrate. It was found that at sulfuric acid concentration below 25 percent, only nitrite reacted with the brucine alkaloid to give the yellow color. Thus, a method was devised based on the brucine color development in approximately 17 percent sulfuric acid followed by further development in 50 percent acid, which gave nitrite values directly and nitrate by difference. The method is fast and convenient, giving results in the range from 0 to 1 mg/litre nitrogen with 2 percent accuracy.

Nitrogen

Dissolved nitrogen is not ordinarily of interest in industrial water. In pressurized water nuclear power reactors, the concentration of dissolved nitrogen in the primary water is sometimes important because of the possibility of radiation-induced reactions of nitrogen with dissolved oxygen to produce nitric acid, or with dissolved hydrogen to produce ammonia. These reactions can produce wide variations in the pH of the primary water. Nitrogen has been determined with the gas transfer and Blacet-Leighton apparatus. Dissolved oxygen and hydrogen are removed from the total gas, and the remainder reported as inert gas, most of which is nitrogen.

Oxygen

Oxygen is dissolved in varying amounts in most waters. It is essential to the life of fish and other aquatic organisms. In pure water at room temperature, oxygen dissolves to concentration levels of approximately 8.5 mg/litre. The solubility decreases as the dissolved solids and temperature increase, but increases with increasing pressure. In industrial waters, dissolved oxygen is primarily of interest because of its relation to corrosion reactions. Minute amounts of oxygen in boiler water and feedwater can cause severe corrosion. Experience has shown that the dissolved oxygen content should be below 0.03 mg/litre, and preferably below 0.005 mg/litre in feedwater for high-pressure boilers.

In other waters, dissolved oxygen may not be the direct cause of corrosion, but it will greatly enhance other corrosive tendencies. An example is the corrosion of copper and copper alloys by ammonia. The corrosivity of carbon dioxide is also greatly enhanced by the presence of oxygen.

The methods in ASTM D 888 are applicable to industrial waters and have a wide range of usefulness. The basic approach common to precision Methods B and C, and to routine Methods D and E, all depends on the quantitative oxidation of manganous hydroxide by dissolved oxygen and the subsequent quantitative release of iodine by the reaction of the resulting manganic compound with potassium iodide. Special sampling equipment is required and the foregoing reactions are carried out before the sample is exposed to the air.

The differences in the four methods—B, C, D, and E—relate to the manner in which the resultant iodine is titrated. A potentiometric titration with dilute sodium thiosulfate is the most sensitive and accurate. The less-precise methods use starch to detect the end point, and different concentrations of sodium thiosulfate for different concentration ranges of dissolved oxygen.

Some colorimetric procedures have also been devised for determining dissolved oxygen. Among these are precision Method A of ASTM D 888, which requires only one reagent, an indigocarmine dye [*80, 81*], and is used to determine dissolved oxygen at from 0 to 50 μg/litre. Another [*82*] uses leuco methylene blue, which is oxidized by the dissolved oxygen to methylene blue. Concentrations down to 2 μg/litre can be detected.

Four methods for determining dissolved oxygen in industrial waste water are incorporated in ASTM D 1589 and are designed to cope with various types of interferences. Included are the Alsterberg (azide), Rideal-Stewart (permanganate), the Pomeroy-Kirschman-Alsterberg modification, and a polarographic method. ASTM Methods D 1589 discuss the appropriate application of each approach.

Instrumental methods for continuous monitoring and recording of dissolved oxygen are available. The required equipment is relatively expensive, but can be justified where the need for continuous measurement is great and where qualified personnel are available for maintenance of the equipment.

Phosphate

Phosphate occurs in certain rocks and sands, municipal sewage, animal manure, and in soil, and consequently may be expected in water. Aside from naturally occurring phosphates, additional phosphates eventually are added to water supplies through agricultural runoff, and the widespread use of phosphate-built detergents. In groundwaters, phosphate is found in minute quantities, the amount dependent upon the original pollution of the water and strata through which it has percolated. This suggests the utility of phosphates as additives to underground waters, to conveniently trace their flow.

Phosphates and polyphosphates are used extensively in the treatment of boiler water. Metaphosphates are used as stabilizer additives in water supply systems, and also as corrosion inhibitors and scale preventives in once-through and recirculating cooling systems. A film of iron metaphosphate is deposited on the metal surfaces of dynamic systems, inhibiting corrosion. In cooling systems, reversion of metaphosphates and polyphosphates to orthophosphate often occurs rapidly, for several reasons. This leads to precipitation of calcium phosphate, and the formation of fouling deposits.

The phosphate ion is important in treatment of feedwaters and boiler waters. Phosphates are used almost universally as scale preventing chemicals in boilers operating above 2758 kPa (400 psi). Phosphate is preferable to soda ash in this pressure range because it is stable, while the carbonate partly decomposes to produce hydrate alkalinity and releases additional carbon dioxide into the steam. Calcium hardness entering a phosphate-treated boiler is precipitated as an alkaline calcium phosphate (hydroxyapatite) when proper hydrate alkalinity is maintained. Incoming mangesium hardness precipitates as magnesium hydroxide. Both these precipitates are soft, only slightly adherent sludges when compared with other forms of precipitation. Even in boilers where the incoming calcium and magnesium from feedwater are practically zero, phosphate excess often is maintained in the boiler water as a guard against unexpected contamination, or hardness pickup from condenser tube leakage.

Phosphates usually are injected directly into boiler drums. If phosphate treatment must be added to the feedwater ahead of the boiler, metaphosphate usually is selected, and feed methods carefully controlled to prevent hydrolysis of polyphosphate to the ortho form in the preboiler system. At the lower temperatures encountered in feedlines and economizers, and in the absence of optimum alkalinity conditions, calcium phosphate can form as an adherent scale, instead of the soft sludge developed in the boiler at the much higher temperatures.

It can be seen that, depending upon the application, analysis of orthophosphate and determination of the ratio of orthophosphate to meta- or polyphosphate are of considerable importance. ASTM Methods D 515 provide four approaches to the determination of phosphate. The application and suitability of the various methods are indicated in Table 7. Only Routine Method B for phosphate does not provide for determining phosphorus present in the more complex phosphate species such as tripolyphosphate, metaphosphates, and pyrophosphate. When it is essential that all of the phosphorus be determined, conversion of the complex phosphates to orthophosphate is made by boiling an acidified sample as described in Precision Method A and in Routine Methods A and C. A more rapid procedure for converting polyphosphates [*83*] has been reported and adopted in Routine Method A. The difference between the orthophosphate concentration before and after such conversion is a measure of polyphosphate phosphorus.

TABLE 7—*Phosphate methods.*

ASTM Method D 515	Gravimetric Method	Routine Method A	Routine Method B	Routine Method C
Basis of measurement	gravimetric	volumetric	colorimetric	colorimetric
Test for	total $PO_4^{\equiv}$	ortho- and total $PO_4^{\equiv}$	ortho-$PO_4^{\equiv}$	ortho- and total $PO_4^{\equiv}$
Range	10 mg or more of $PO_4^{\equiv}$	0.1 mg/litre or more of $PO_4^{\equiv}$	2 to 25 mg/litre	0.1 to 1.5 mg/litre (can be extended)
Precision	3 percent for 10 mg; 1 percent for 50 mg	Approximately 2 percent	2 percent difference between duplicate determinations	varies with quantity determined. Generally good
Application	all industrial water	all industrial water	boiler water and boiler feedwater; suitable for routine analysis	relatively uncontaminated waters
Interferences	phosphite: converts to $PO_4^{\equiv}$; As and V: precipitate with $PO_4^{\equiv}$; must be removed HCl, H_2SO_4, HF, and NH_4^+ salts thereof: retard precipitation of ammonium phosphomolybdate	same as gravimetric method	strong color; High concentration of ferric iron	above 0.5 mg/litre iron, 25 mg/litre SiO_2, 1000 mg/-litre Cl^- oxidizing agents bleach blue color
Summary of method	successive separations of *o*-phosphate are made by precipitating as ammonium phosphomolybdate and then as magnesium ammonium phosphate; ignited and weighed as magnesium pyrophosphate	*o*-phosphate reacts with ammonium molybdate in acid medium to form a molybdophosphate, which is reduced to molybdenum blue complex with amino-naphthol-sulfonic acid. Color intensity is proportional to phosphate concentration. Bismuth salt added to sulfuric acid reagent intensifies blue color fourfold	measurement of the yellow color of phospho-vanado-molybdic acid which is developed in the sample	*o*-phosphate is reacted with ammonium molybdate to form phosphomolybdate, which in turn is reduced with $SnCl_2$ solution to molybdenum blue
Instrumentation	analytical balance	none	spectrophotometer or filter photometer for range 400 to 420 nm	visual color comparison; spectrophotometer or filter photometer at 650 nm

Frequently it is desirable to estimate the concentration of a particular species. Tripolyphosphate and pyrophosphoric acid may be determined by a combined titration and gravimetric determination of pyrophosphate. Ortho- and metaphosphates do not interfere with this method. Both Bell [*84*] and Jones [*85*] have reported methods for determination of metaphosphates in the presence of the other phosphate species.

Silica

Silica concentration can be a very important consideration in some industrial installations such as steam generation and cooling-water systems. The silica is brought into these systems in the makeup (raw or partially treated) water, or by airborne dusts. Natural (raw) waters may contain more than 100 mg/litre of silica in solution. The silica and other materials in the makeup water will concentrate in the boiler or cooling water system due to evaporation, and form deposits when solubility limits are exceeded. It is therefore important to determine that the silica concentration in the boiler or cooling water increases in proportion to the concentrations of other constituents present in the makeup water. If the silica in the boiler or cooling water is less than expected, the formation of siliceous deposits in the system may be indicated.

Silica is of special importance in steam generation, because under certain conditions it can form troublesome scales of silica and complex silicates in the boiler, or siliceous deposits in turbines. Because of the very low heat-transfer characteristics of these materials, extremely thin layers can cause metal overheating, corrosion, and failure of boiler tubes, as well as reduced heat transfer. The silica in high-pressure boilers can be carried over with the steam. As the boiler pressure increases above 2758 kPa (400 psi), the tendency for silica to be selectively carried into the steam increases; with constant pH and boiler pressures, carry-over is proportional to the amount of silica in the boiler water. As pressure rises, the ratio of silica in steam to silica in boiler water increases rapidly. This silica deposits hard, glassy scales on turbine blades, resulting in pluggage of small passages and imbalance of the rotor. Investigations have shown that the key to minimizing silica scales is to keep the silica in the boiler water at a sufficiently low level to maintain silica in the steam at not more than 0.02 mg/litre [*86*].

Silica can also cause formation of deposits in cooling-water systems, but here it usually is considered of minor importance unless the concentration is beyond the solubility limit (usually 150 mg/litre or higher), or if the magnesium content and pH value are high.

In other industrial applications, silica may be added as part of the treatment program (example: corrosion control in potable water distribution systems). Silica analysis is frequently used to maintain proper treatment levels in systems of this type.

Procedures for the determination of silica are included in ASTM Methods

D 859. Table 8 gives a summary of the important aspects of the methods, and will aid in the selection of the proper procedure applicable to specific problems.

Colorimetric Method B of Method D 859 has been suggested for the determination of silica in high-pressure boilers, where silica, even in very low concentrations, is of high importance. Special precautions [*87*] must be taken during sampling to avoid loss of silica to the sampling equipment. In sampling steam, errors are said to result if the pressure of the steam is reduced ahead of the condenser.

Sulfides

Sulfide is present in water generally as the result of industrial waste contamination or decomposition of sulfate by anaerobic bacterial action. Sulfide can be very damaging to equipment and industrial processes. In relatively high concentrations, it will attack normally resistant alloys such as stainless steel and brass and cause rapid deterioration. Sulfide can be substantially removed by acidification followed by aeration. Complete removal can be accomplished by subsequent chlorination.

Hydrogen sulfide is a toxic gas with a characteristic offensive odor and taste, and is fairly soluble in water. In water it reacts as an acid and can be actively corrosive. Under certain conditions in the presence of oxygen, it may even be oxidized to sulfuric acid. In addition, hydrogen sulfide reduces and precipitates constituents of many cooling-water treatment chemicals, causing unwanted deposits. Because of these objectionable characteristics, it is desirable to remove it from process and potable waters.

Hydrogen sulfide is found occasionally in surface waters, resulting from miscellaneous pollution or anaerobic decomposition of organic compounds. It occurs most commonly in well waters located near "sour gas" oil fields, or as a result of anaerobic bacterial reducing action on inorganic sulfur compounds such as sulfate. It may also be produced in soils by bacterial action, and is a consideration in the corrosion of buried metal piping. Hydrogen sulfide may be produced in sodium sulfite-treated boiler waters with operating temperatures of 274°C (525°F) and above. On high-temperature surfaces (superheaters, etc.), the sulfite breaks down to sodium sulfide and sodium tetrathionate. The sodium sulfide is then hydrolyzed to hydrogen sulfide and passes into the steam, where it is very corrosive.

Quantitatively, and semiquantitatively, odors indicating hydrogen sulfide in water can be confirmed with lead acetate paper, which is quickly darkened by exposure to the vapor from a slightly acidified sample. In ASTM Method D 1255, hydrogen sulfide is determined as part of the total and dissolved sulfides, and the concentration can be calculated from the concentration of dissolved sulfides and the pH of the sample.

It is best to analyze sulfide-containing samples immediately. When this is not possible, the sulfide content should be fixed by adding a suitable

TABLE 8—*Silica methods.*

ASTM Designation D 859	Precision Method A	Precision Method B	Routine Method C	Routine Method D
Test for	total silica (colloidal and crystalloidal). When used with Method B, C, or D, colloidal silica can be determined by difference.	crystalloidal silica	crystalloidal silica	crystalloidal silica
Range	as low as 1 mg/litre	below 1000 μg/litre	below 10 mg/litre	below 10 mg/litre
Precision	0.4 mg/litre	1.3 μg/litre + 3 percent of concentration determined	0.1 mg/litre	0.1 mg/litre
Type of water	raw water, cooling water, boiler water, waste water	steam condensate, ion exchange bed, nuclear reactor	raw water, cooling water, boiler water, waste water	raw water, cooling water, boiler water, waste water
Interference	no interference	no interfering material present	turbidity, color (tannin, Cu+ ion), chromate ion interferences	same as C, except tannin does not interfere
Applicable to	need for total silica content	system containing very low silica	rapid control analysis where no color is present due to tannins or other organics.	rapid control analysis where color is present due to tannins
Instrumentation	none	spectrophotometer 815 nm or filter photometer 640–700 nm or 815 nm	same as B or use matched Nessler tubes or Duboseq-type color comparator	same as C
Theory	silicon compounds dissolved or suspended in water are concentrated and precipitated as partially dehydrated silica by evaporation with either perchloric or hydrochloric acid, followed by HF treatment	reactions of soluble silica with molybdate ion, blue color developed with 1-amino-2-naphthol-4-sulfonic acid. The color is read photometrically and compared with standards	(*a*) utilizes yellow silicomolybdate color complex for comparison or (*b*) alternative, to increase sensitivity and eliminate color interference, 1-amino-2-naphthol-sulfonic acid is added providing blue color for comparison measurements	in the presence of a reducing agent such as sodium sulfite, soluble silica reacts with molybdate ion to form a blue complex. The color is read photometrically and compared with standards

quantity of zinc acetate or cadmium chloride solution to precipitate zinc or cadmium sulfide.

Frequently, because of the presence of sewage or interfering components, hydrogen sulfide is separated by evolution in a stream of inert gas and collected in a zinc acetate or cadmium chloride solution before making a determination. Tests have shown that the segregation of hydrogen sulfide by inert gas transfer is not quantitative and that the error is large when the concentration is low.

ASTM Method D 1255 determines total and dissolved sulfides. This is a colorimetric procedure based on the fact that *p*-aminodimethylaniline, ferric chloride, and the sulfide ion react in acid solution to produce methylene blue. The concentration range of the method is 0.1 to 20 mg/litre of sulfide, and the accuracy is ±0.1 mg/litre for clear, colorless solutions and ±15 percent for colored and turbid solutions.

Widely used titrimetric procedures for sulfide depend upon the reducing action of sulfide on a standard iodine solution in an acidified medium. The excess iodine is back-titrated with standard sodium thiosulfate, using starch as an internal indicator. Other reducing agents interfere.

An amperometric back-titration has been suggested by Goldman [*88*] and is an adaption of the phenylarsenoxide titration for chlorine (see ASTM Methods D 1253 for chlorine). Two 10-ml aliquots of standard iodine solution are added and titrated successively with 0.00564 *N* phenylarsenoxide solution on the same sample at a pH of 4. The difference between the two titrant volumes is equivalent to the sulfide present. From 0 to 0.2 mg/litre sulfide may be determined in this manner. It is stated that the range can be extended by adjusting sample volumes and reagent concentrations, and that color and turbidity should cause no interference.

Sulfate

Sulfate ions are relatively abundant in natural waters, especially in hard waters. In industrial waters, sulfate is of interest mainly where evaporative processes introduce potential scaling problems and where control of total dissolved solids is a major consideration. Sulfate often is a constituent of boiler deposits and heat exchanger scales, softening and other treatment procedures being required for deposit control. The determination of sulfate for regulation of allowable concentrations in boiler water and in cooling towers (where sulfates often are increased by addition of sulfuric acid for alkalinity reduction and pH control) can be useful. The determination of sulfate is also useful in the estimation of total dissolved solids.

Sulfate concentration in potable water supplies also deserves consideration. High amounts of sulfate impart a faintly bitter taste to the water, and cause laxative effects, especially on children. While the human body usually can adjust to relatively high sulfate waters, certain environmental conditions may indicate their use to be inadvisable.

ASTM Methods D 516 provide three tests for determining the sulfate concentration of water samples. These methods and their applicability to various types of water are listed in Table 9.

There are several other titrimetric procedures for determining sulfate. In the benzidine procedure, an addition product of benzidine and sulfate is precipitated from an acidified solution, washed, redissolved in hot water, and titrated with standard sodium hydroxide. This method, while not highly accurate, is especially useful for determining sulfate in the presence of relatively high amounts of sulfite. In another procedure [*89,90*], the sulfate is precipitated with barium chloride, filtered, and the barium sulfate redissolved in a known volume of 0.05 *M* EDTA. The EDTA is then back-titrated with standard barium chloride solution using a suitable metal phthalein as indicator. Several other variations of this approach exist.

Sulfite

The occurrence of sulfite salts in natural waters is rare, because sulfite is so readily oxidized by air. Because of this ease of oxidation, sulfite finds widespread application as an oxygen scavenger in boiler waters to prevent corrosion. At high temperature and boiler pressure, sulfite can break down to yield sulfur dioxide, and, in the presence of alkali, hydrogen sulfide to the steam. In such instances, the sulfite concentration must be carefully controlled. It is desirable to limit the use of sulfite to as low a concentration as practicable for complete oxygen removal, including necessary residuals.

Sulfur dioxide is formed when sulfur-containing compounds are burned or when certain metallic sulfides are strongly heated in air. It occurs naturally in the gases emanating from volcanoes and fumaroles and is present in the air surrounding manufacturing areas or cities, because of the combustion of fuels and other sulfur-containing materials. It is readily soluble in water, where it becomes sulfurous acid or salts thereof, and has been found in hail, snow, and especially frost in the neighborhood of cities and towns. Sulfurous acid has also been found in numerous mineral waters and in springs near active volcanoes. In other naturally occurring waters, both dissolved sulfur dioxide and sulfite, because they are readily oxidized by the oxygen in the air, are unlikely to occur except in very special cases.

Sulfur dioxide has many uses in manufacturing, but in water and waste treatment its use is confined mostly to dechlorination procedures and to chromate-reduction waste treatment applications. In dechlorination, sulfur dioxide reacts with chlorine to form sulfuric acid and hydrochloric acid, both of which are neutralized by the natural alkalinity of the water being treated.

Total sulfur dioxide in water includes free sulfur dioxide, bisulfite, and sulfite ions. Like carbon dioxide, the relative concentrations of the three ionic species depend upon the pH of the solution. The determination of sulfur dioxide usually is based upon its reducing properties in solution, the same approach used for determining sulfite ions.

TABLE 9—*Sulfate.*

ASTM Method D 516	Precision Method	Routine Method A	Routine Method B
Basis of measurement	gravimetric	turbidimetric	volumetric
Range	20 to 100 mg/litre $SO_4^=$ (can be extended)	10 to 100 mg/litre $SO_4^=$	5 to 1000 mg/litre $SO_4^=$
Precision	1 percent of amount present	as good as 5 percent or 2 mg/litre, which ever is greater. Depends on interferences and skill of analyst.	single operator—0.5 mg/litre
Application	all types of industrial water and industrial waste water	rapid routine testing of industrial waters	rapid determination of $SO_4^=$ over wide range in industrial water for routine or control tests
Summary of method	sulfate ion is precipitated and weighed as barium sulfate after removal of silica and other insoluble matter.	sulfate ion is precipitated as barium sulfate and a suspension made Glycerin and sodium chloride are added to stabilize suspension and minimize interferences	sulfate ion is titrated in alcoholic solution with standard barium chloride using thorin as the indicator. End point change: yellow to pink, relatively sharp
Interferences	$\left.\begin{matrix} SO_3^= \\ S^= \end{matrix}\right\}$ may oxidize and precipitate $SO_4^=$	insoluble material—must be removed dark color water quality affects suspension of barium sulfate	cations: removed by ion exchange above 2 mg/litre F^- 50 mg/litre NO_3^- $\left.\begin{matrix} \text{2 mg/litre } PO_4^= \\ SO_3^=, CrO_4^=, S^= \end{matrix}\right\}$ can be eliminated 1000 mg/litre Cl at low $SO_4^=$ concentration
Instrumentation or special equipment	analytical balance	photometer suitable for measuring between 350 and 425 nm cell path of 40 nm	microburet ion exchange column magnetic stirrer helpful

ASTM Methods D 1339 list three volumetric methods for the determination of sulfite in industrial waters. Two precision methods, A and B, fix the sulfite in the sample by adding hydrochloric acid, potassium iodide, and potassium iodate before it is exposed to the air. The iodine chloride formed reacts with the sulfite present, and the excess is then back-titrated with sodium thiosulfate.

Method A uses a special sampling apparatus to exclude air and allow addition of the fixing reagents before the sample is exposed to the air. After fixing, the sample is drained into a beaker and titrated using an electrometric dead-stop apparatus. The technique allows determination of 0.0 to 6.0 mg/litre sulfite as Na_2SO_3.

Method B is a simplification of Method A. The sample is collected in a manner to exclude air, fixed immediately upon opening, and titrated to a starch indicator end point. It is designed for 6 mg/litre Na_2SO_3 and up.

Routine Method C is a direct titration of the sample with potassium periodate after addition of hydrochloric acid and potassium iodide. It is designed for control tests where good precision is not required and where the sulfite concentration exceeds 3 mg/litre.

Sodium and Potassium

Sodium and potassium are found in practically all waters. The ubiquitous sodium is of importance when salinity or total dissolved solids are a consideration in the use of the water. Sodium also is important in boiler waters, where it constitutes a large portion of the cations present. At one time, there was a trend toward the use of potassium salts for hideout control in boiler water treatment, but this trend has slackened and potassium now is of lesser importance. Sodium concentrations in boilers are easily removed by blowdown, and sodium salt deposition rarely is encountered, except in areas of water starvation or under hideout conditions.

The analysis for sodium sometimes can be used as an indication of the purity of water; for example, in steam condensates, the sodium concentration can be used to indicate water carry-over from boiler system into the steam. In demineralizer effluents, sodium determinations will indicate the completeness of cation exchange.

Sodium and potassium can be determined gravimetrically or by a flame photometer. The flame photometer (ASTM Methods D 1428) provides by far the simplest and most rapid method for potassium and sodium in low concentrations. Method A, using either direct-measuring or internal-standard flame photometers, is especially recommended for concentrations of sodium and potassium between 1 and 100 mg/litre. Method B covers the range from 0 to 1 mg/litre, using the direct-intensity method with either type of instrument, and is applicable to high-purity waters. Special precautions are required to avoid exposing the instrument to dust, drafts, and unclean air when working in these low concentrations. Method C is designed for analysis of deposits and is satisfactory for sodium contents of 0.1 percent or more.

Glass electrodes sensitive to sodium ions have been used to determine sodium concentrations electrometrically, with direct-reading instruments. The sodium electrode also is sensitive to potassium and hydrogen, but much less so, and their effect can be minimized. Bower [*91*] used such an electrode to determine sodium in irrigation waters. The effect of hydrogen ions was eliminated by buffering, and that of potassium ions by precipitating with tetraphenylborate. Very good agreements with flame photometer determinations were found.

Zinc

Zinc is found in small quantities in most industrial waters, resulting from corrosion of galvanized iron and brass in condensing, cooling, and distributing systems. A determination for zinc may be made as an indication of deterioration of particular equipment, for identification of the source of this constituent in water-formed deposits, to determine the concentration of zinc in systems using zinc salts as corrosion inhibitors, or to determine zinc as a pollutant in waste water.

The nephelometric procedure [*92*], in which interfering substances are removed by hydrogen sulfide and turbidity is then developed with ferrocyanide, has been used successfully. The most suitable range for direct comparison with standards is 1 to 10 mg/litre. Since the zinc content is concentrated during the procedure, the lower limit in the original sample is about 0.05 mg/litre and the optimum comparison level about 0.2 mg/litre.

A turbidimetric method using sodium diethyldithiocarbamate also has been reported. [*93, 94*].

Zinc may be determined with dithizone (diphenylthiocarbazone). The reaction product is red when extracted into carbon tetrachloride, and this is used to measure the zinc content photometrically. There are several procedures that use various complexing agents to eliminate interferences. Among these, bis (2-hydroxyethyl) dithiocarbamate is purported [*95*] to be the best. Zinc in the amount of 0.01 mg/litre can be determined.

A direct method using zincon to develop a blue color with zinc, in which heavy metals including the zinc are complexed with cyanide, has been reported [*96*]. The zinc is released selectively with chloral hydrate and reacts directly with the zincon reagent. This procedure is the basis for ASTM Methods D 1691.

Methods of Reporting Results

The reporting of results is an important part of every analysis. Just as poor sampling can render an analysis valueless, poor reporting can hamper interpretation. Refer to ASTM Method for Reporting Results of Analysis of

Water (D 596) and ASTM Method for Reporting Results of Examination and Analysis of Water-Formed Deposits (D 933). Results should be reported in a form that is amenable to comparison, and explanatory references may be necessary to ensure completeness or to detail the meaning of the data. For example, odor thresholds should be accompanied by a record of the temperature of analysis. If an analysis for organic extractables is run, it is necessary to report the solvent used, such as *hexane-extractables* or *chloroform-extractables*. Similarly, when analyzing for phosphate, it is possible to determine total phosphate, orthophosphate, and polyphosphate. When reporting, it is necessary to indicate the results properly. Any departures in analytical procedure that were necessitated must be recorded and reported. If some constituents were not measured directly, this should be noted; for example, *dissolved solids* (*by difference*).

ASTM Method D 596 presents recommendations as to the nature, extent, and form in which results of analysis should be presented (see Methods D 1192, D 860, D 3370, D 1066, and D 887). It can serve as a guide to accurate reporting. It also contains a table of conversion factors for converting milligrams per litre to equivalents per million and vice versa.

Analytical results must be reported in a manner that will not imply a fictitious significance. If numerical values are improperly reported, they may lead to serious misinterpretation. The reported value should contain but one digital value that is not absolutely precise. This digit is the last one to the right. A weight of 4.7165 g implies a precise measurement accurate to ±0.000*n*, whereas 4.7 g would be the reported value for weighing the same object on a single-beam balance accurate to ±0.*n* g. The value *n* is used to designate the least significant figure. The plus-or-minus sign describes a variance inherent in the measuring process. The usual way of describing this variability is by the root-mean-square of the variance, known as the standard deviation.

In making calculations, the result will not have significance greater than the least significant value used in the computation. For example, 6.250 times 1.1 equals 6.8750, but must be rounded to 6.9. The method of rounding dictates that, if values of 5 or greater are dropped, the preceding digit is raised by one. Values of 4 or less are dropped without any change in the preceding digit; for example, 1.008 times 4.3 equals 4.3344, which is rounded to 4.3 in practical application.

Zeros are never added to values to the right of the decimal point if the precision is not warranted. A temptation often exists to balance the columns of numbers in tabulating results. For example, assume a water analysis:

pH	6.83
Aluminum as Al, mg/litre	0.25
Nitrate as NO_3, mg/litre	6.5

These values tell the reader something about the methods that were used. The pH reading of 6.83 indicates the use of a precise potentiometric technique. A less precise instrument would give a result reported as 6.8, while a color comparison procedure would probably be estimated as 7. The accuracy of the aluminum and nitrate methods is 0.01 to 0.5, respectively. Adding a zero to 6.5 to show 6.50 would be improper.

Methods of Checking Analysis

Before any analysis is finally reported, it should be thoroughly checked for possible errors. In general, errors inherent to the analytical procedure are avoided by running replicate samples. However, other errors can occur which will not be obvious. For example, mislabeling, recording erroneous aliquots, getting the sample sequence out of order, errors in taking or recording instrument readings, or misreading calibration curves are all mistakes which have plagued analysis occasionally. Procedures for discovering such errors are essential.

As mentioned earlier in this chapter, an important part of every analysis is a description of the physical appearance of the sample. Even though this description must be brief and limited in information, it can be used as the first check on the analysis. There must be a correlation between appearance and the reported results. For example, if 15 mg/litre iron is found, the physical description generally should indicate presence of a precipitate or magnetic particles. If neither is present, and the pH is not acidic, an error is indicated. The intensity of yellow color of a chromate-treated cooling water can serve as a check on the chromate analysis. If a sample is reported to have significant amounts of oil present, the description should have noted an oily film, cloudy appearance, or a large amount of suspended solids. Other correlations will become obvious to the analyst upon consideration.

When a complete water analysis has been run, an anion-cation check should be made. Proper balance can be checked by totaling separately the determined concentrations in equivalents per million of all anions and cations. Deviation from a balance indicates an error (see ASTM Method D 596).

When it is not practicable to determine all cations (for example, during field investigations), it is possible to determine remaining cations *by difference*, using readily obtained total anions (expressed in equivalents per million) as the basis. Total calcium and magnesium (expressed in epm) subtracted from total anions (in epm) will closely approximate sodium and potassium concentration (also in epm) in the sample. As an alternative, missing cations can be computed, using hypothetical combinations of determined anions and cations, and compared with total dissolved solids as determined by conductimetric or gravimetric procedures. With this method, calcium (in epm) is combined with epm of anions in the sample, in the order: carbonate (or bicarbonate), sulfate, chloride, and nitrate, until all calcium has been combined. Then magnesium (in epm) is combined with equivalent quantities of remaining anions, in the same order. Any remaining uncombined anions (alkalinity, sulfate, chloride, or nitrate) after all calcium and magnesium have been combined may be assumed to exist as sodium or potassium salts. When *equivalents* of the hypothetical combinations are converted to milligrams per litre, the total of all salts so computed should agree closely enough with determined total dissolved solids to provide a reasonable check for errors.

The relationship between the various constituents can also serve as a check. For example, carbonate could not be present in a sample with pH at 4.0 (acid to methyl orange indicator).

Special attention should be given to samples that represent an entire system such as a boiler system or a cooling system. For example, if samples of cooling water makeup and circulating water from an evaporative cooling tower are received, there should be a logical relationship between the two. The cooling water should be a concentrated solution of the makeup. If the tower water has been treated with sulfuric acid to reduce alkalinity and prevent $CaCO_3$ deposition, the hardness and sulfate concentrations in the circulating water should increase by an appropriate concentration factor. The calcium concentration may vary slightly with alkalinity changes, but the magnesium does not; thus, magnesium hardness can be used to calculate the concentration factor. The chloride content should be similarly concentrated. By using these concentration factors, a check can be made on the amount of sulfuric acid used to reduce the alkalinity to the observed value, and therefore the observed sulfate content. Serious deviation of determined results from these computed cross-checks indicates possible error in analysis or variation in system control. When checking any series, similar procedures can be used. Look for constituents in one sample that should appear all through the series. Also, concentration or dilution factors should appear in certain other samples. Cross-checking can reveal inconsistencies and possible errors which otherwise might not be apparent.

Previous analyses on samples that are run periodically serve as an excellent check on current results. Large deviations or sudden changes may indicate a system upset, but also could be the result of analytical error. Such unexpected results should be checked carefully before reporting.

As one can see, each sample has its own unique origin and set of physical characteristics. The history and observed properties can assist the analyst in selecting the proper laboratory procedures for analysis. Once the analysis is complete, a review of the origin of the sample and its physical appearance along with cross-checking of the reported results, both within the analysis and through any series, provides a final check for detection of possible errors.

pH

The pH of water is a measure of its hydrogen ion activity. It is used to indicate the acidity or basicity of aqueous solutions, which includes natural waters, and is the result of the dissociation properties of the solutes. Both important and useful, pH measurements have widespread application. These measurements are used in many programs for effective water treatment, purification, and corrosion control.

ASTM Method D 1293 covers the determination of pH in industrial waters and industrial waste waters; it is an electrometric procedure using a glass electrode. The method, along with its Appendix, gives a comprehensive discussion of the apparatus used, electrode treatment, preparation and use of reference buffer solutions, standardization, and procedures for pH determination of batch samples and flowing samples using flow cells.

Electrometric methods of measuring pH are by far the most accurate, but other methods for approximating pH can be used where precise control is not necessary. In the routine procedures for acidity and alkalinity in Method D 1067, indicator dyes are used to show the end points of the titrations to reference pH levels. The indicators are useful because they change color in various ranges of hydrogen ion concentrations. There is a large number of weakly acidic (or basic) organic dyestuffs that undergo such color changes. The most suitable and accurate indicators are those which change color relatively sharply within a narrow range of pH. Such dyes make possible relatively rapid and inexpensive methods for estimating pH. The prepared sample is read by matching colors with a graduated set of permanent standards mounted in a slide or roulette wheel, or prepared in the form of ampoules. Standards are prepared from buffer solutions, or they may be colored glass or solutions.

Errors in this approach arise from personal differences in color perception, temperature variations, differences in total salts concentration, chlorine, and specific indicator properties (buffer effect of the indicator).

Dye-impregnated papers also exist for approximating pH levels.

Interpretation of Analytical Results

Any collection of analytical data is meaningless unless an informed and logical interpretation can be made. Interpretation in many cases is both the beginning and the end of an analysis. In setting up an analytical program, the interpretations to be made will influence the choice of determinations. For example, to determine whether a water treatment program is functioning effectively, not only must the results of the analysis be interpreted in terms of the system, but also the constituents to be analyzed and the tests to be run must be chosen with the nature of the interpretation required in mind.

Several factors will influence the interpretation. The type of water and the system, the number and location of sampling points, the frequency of sampling and testing, and the sensitivity of the methods employed are important considerations. A single sample of river water could hardly be used to interpret the nature of the river as a supply source. No information would be obtained as to variations at different depths, variations with respect to location or seasonal changes, or occurrence of periodic contamination. On the other hand, such an analysis might help determine what type of analysis is needed, and what sample treatment or precautions are necessary for future analyses. In the first case, an interpretation that is too extensive may lead to an erroneous picture and future trouble. As noted, proper interpretation of a single sample can serve as a useful, although limited, tool in guiding future work.

The amount of time elapsed between sample collection and the actual analysis is another important factor to consider when interpreting data. Chemical and physical changes can take place after a sample is drawn, and such possibilities must be considered.

Choosing significant data is an important part of interpreting results. In a well-planned program of analysis, only the significant constituents will be analyzed. Therefore, in interpreting the results, only the significance of the concentrations reported and their interrelation remain to be translated into meaning. Past analysis also will have an influence on interpreting a current analysis.

An example will help illustrate the interpretation of significant data. Suppose heat exchangers in an evaporative, open recirculating cooling system are to be protected from corrosion by controlled deposition of a thin, impervious layer of calcium carbonate. If the water supply is amenable to this approach, such deposition can function as an inexpensive but effective corrosion control procedure. However, close regulation of certain important constituents must be maintained. If the circulating water is too acidic (relatively speaking; not necessarily in the free-acid range), corrosive conditions will prevail and the protective scale will be removed, or its formation prevented. On the other hand, conditions too favorable for scaling will permit excessive buildup of calcium carbonate deposition. An equilibrium condition is the desired state. To maintain this equilibrium (in actual practice, very slightly scaling) several factors must be known and regulated. These are the calcium concentration, the methyl-orange alkalinity, total dissolved solids, temperature, and pH. By utilizing Langelier Saturation Index data (available in the form of nomographs, charts, and tables), appropriate calculations can be made to determine the scaling or corrosive nature of the cooling water. Adjustments in scaling or corrosive tendencies can then be made by altering the alkalinity and pH of the circulating water. Similar analyses and interpretations must be made on the makeup water added to the cooling system. In maintaining such a corrosion control system, frequent interpretations must be made about the significance of changes in concentration of the various constituents. Each change in concentration must be considered in relationship to the other constituents. An increase of 20 mg/litre in calcium content of makeup water may or may not signal the need for control adjustment. If the alkalinity or total dissolved solids also change appropriately, no adjustment in chemical feed may be necessary. The importance of proper interpretation, which in this example involves a special calculation, is apparent. The various constituents are interdependent, and corrosion control can be maintained successfully only after due consideration of all the influencing factors.

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Chapter 12—Sensory Examination of Water

It is paradoxical that complaints about water quality are usually based on subjective properties, that is, odor, taste and appearance, but analytical emphasis is usually chemical, physical, or biological. The reason for this anomaly is that the latter properties are more readily standardized, and values may be reported within relatively narrow numerical limits. Subjective properties must be measured by persons. Since people vary in sensory acuity, it is much more difficult to establish either intensity or characterization values for subjective properties. Although one often sees threshold odor or taste data presented in absolute values, there should be cognizance of the implied uncertainty of such values. Individuals vary in sensory ability from day to day or within a day. Groups of individuals show even greater tendency to vary. Consequently, subjective data are best described in a statistical or probability manner. An average or median value plus the range or associated confidence limits tell much about the distribution of a sensory property.

Sensory testing of water is generally restricted to taste and odor, color and appearance. Taste and odor are usually combined as a single term in water technology, probably because consumer complaints on these properties are often difficult to separate. Most recent published information actually concerns odor and says very little about taste. Much more needs to be learned about both properties. Color may be rated against fixed standards, but often color or appearance judgments are recorded as part of the analytical summary of water quality. In the following section, various aspects of sensory testing will be examined.

Panelists

Any sensory testing program is doomed to failure if the persons involved lack interest or are not properly trained. Greater flexibility exists for selecting panel members in research than in field operations. Research panelists may be screened for their sensitivity to taste and odor stimuli, and the panel may be tailored to specific needs. This is not the case in water and waste treatment plants or field survey crews. Field personnel are selected for abilities other than their sensory response. Often, very few persons, or perhaps only one, are available for these measurements. In such circumstances, they must be trained to best utilize their sensory skills. Complex interactions of mixed stimuli and person-chemical interactions well be operating. It is necessary to get relative response data to specific standard stimuli from personnel concerned with sensory measurement.

Individuals without prior sensory panel testing experience are sometimes preferred in research. They do not have prejudices about methods or responses. All persons require adequate training. Persons vary considerably in the time required for training before their responses to reference substances become stabilized. Some persons report reproducible, uniform threshold values almost immediately. Others gradually improve their sensitivity over a period of training. A confidential record summarizing such personal facts as age, physiocardiac and allergy history, smoking habits, and calibration test results has been found to be helpful in long-range studies. Individual results or comparative performance data among panelists should not be discussed; comparison tends to discourage less-sensitive persons, instills a false competitive undertone to panel testing, and may bias subjective testing results.

Good morale and motivation must be maintained. One method which has been successful is an informal newsletter. Newsletters summarize the objectives and overall results and describe how the results fit into the scheme of water quality control. This has been very effective. Panelists have volunteered comments and useful suggestions, and there has been no difficulty in keeping them interested. Temporary physical discomfort caused by allergies, colds, etc., will affect sensory response. Panelists should be excused during these periods. A change in personal habits may permanently affect sensory acuity. Persons who stop smoking have been found to have increased odor sensitivity to reference materials. This is quite obvious if calibration records are maintained, but it is otherwise difficult to discern.

Persons show marked differences in response to various tastes and odors. These differences cannot be reconciled or estimated by a single reference or substance. Only long-term experience with several references will permit reasonable evaluation of individual acuity. The differences between individuals must also be considered. The ultimate purpose of the sensory tests will determine the panel make up. If only persons with average sensory responses are used, the results will not be representative of the general population and may be misleading in water quality control. Persons representing an extreme of the general population are the ones who most often register complaints. It may be necessary to use supersensitive persons if quality control limits are sought. If a general response range is sought, then a broader-response panel must be used. Obviously, the larger the panel, the more it is likely to represent the general population.

In some cases, sensory studies are begun with a large number of panelists and these are gradually reduced in number without any significant loss in discriminating power. In extensive tests [*1*],[1] eight persons excellently represented a group of approximately 50 for olfactory response. The number of panelists will be determined by balancing cost and time against the precision desired. Panels of 15 to 30 persons are routinely used in food and beverage product development or water research. In water quality control, only a few are needed because concern is usually with threshold or absence of taste and odor rather than suprathreshold conditions or sensory quality profiles.

Two kinds of fatigue may be involved in sensory testing. Physical fatigue is caused by overextending the sensory systems by too many tests and is easily avoided by properly designed experiments. It is a good practice to run only a few tests at one session for each individual. These sessions should be randomized during the day. There is both a day-to-day and time-of-day variability in sensory response. In some cases this may be unimportant, but it exists and should be recognized. A second form of fatigue is physiological. Certain chemical substances such as mercaptans paralyze the olfactory senses. After such substances are inhaled, subsequent olfactory response is partially or completely deadened.

Panelists should be cautioned that eating highly flavored foods or excessive smoking prior to sensory testing may influence results. A good practice is to ask panelists to refrain from smoking or eating for at least 30 min prior to the tests. Excess use of cosmetics will also affect results. It is important to have panelists wash their hands in odor-free soap prior to handling the glassware used in the tests. This prevents interference by materials carried on the hands.

Testing Laboratory

Measurement of taste and odor should be made in a controlled environment. Very few laboratories have such facilities, but they are necessary if reproducible, meaningful results are to be obtained. Background odors interfere with the ability to distinguish the intensity and character of sensory response. Excessive heat, humidity, or distracting activity also influence responses. These extraneous conditions explain the discrepancy of taste and odor results reported by various laboratories.

An odor-testing laboratory used in research on taste and odor in water will be described as an example of the considerations involved. The laboratory is divided into two areas devoted, respectively, to sample preparation and sensory testing. The areas are separated to prevent bias in the panelists' judgment which might arise from their observing sample dilutions being prepared. Guessing tendency is reduced. Samples are passed between the analysts and the panelists via sheetmetal pass throughs (Fig. 1). The panel area has separate automatically controlled humidity temperature

[1] The italic numbers in brackets refer to the list of references appended to this chapter

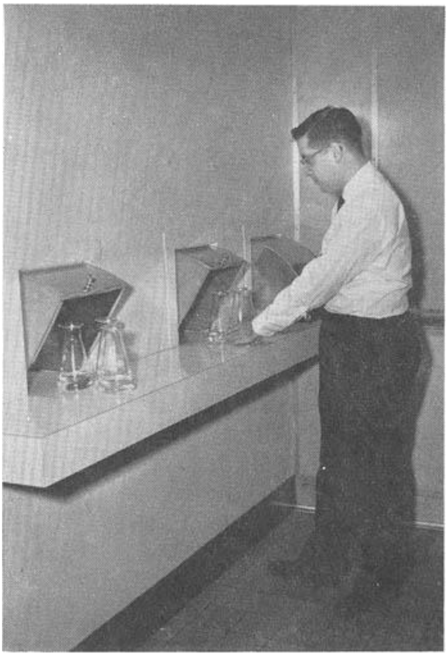

FIG. 1—*Tester passing samples to panelist—Mellon Institute.*

units. Safelights which may be fitted with various monochromatic filters are provided over each booth (Fig. 2). This is important if the samples being tested are colored. Color bias is eliminated by selecting a filter that will mask the color. This prevents the panelists from estimating the sample concentration or differentiating the sample from odor-free blanks by color intensity. The atmosphere is kept odor-free by activated-carbon filters on the exit ducts of the dehumidifier and air conditioner and a separate wall-hung carbon filter. Normally ambient conditons are 21°C (70° ± 2°F) and 40 to 45 percent relative humidity. Panelists making odor measurements in the laboratory are shown in Fig. 3.

The sample preparation area contains a water bath for sample temperature adjustment. The bath, controlled at 40° ± 1°C, is kept in a hood to minimize odor or water volatility in the working area. Great care is taken to see that these areas are kept clean and odor-free. All primary dilutions of odorants are made in another laboratory. No odorous materials are stored, and both smoking and eating are prohibited in this area. Glassware for the sensory tests is not used for any other purpose. It is thoroughly cleaned in chromic acid and detergent with numerous tap and odor-free reagent water rinses after each use. Reagent or dilution water is prepared by first distilling tap water, then passing the distillate through fresh columns of activated carbon. The carbon is changes regularly, and reagent water is always freshly prepared prior to use. Odor tests are made with 500-ml wide-mouth

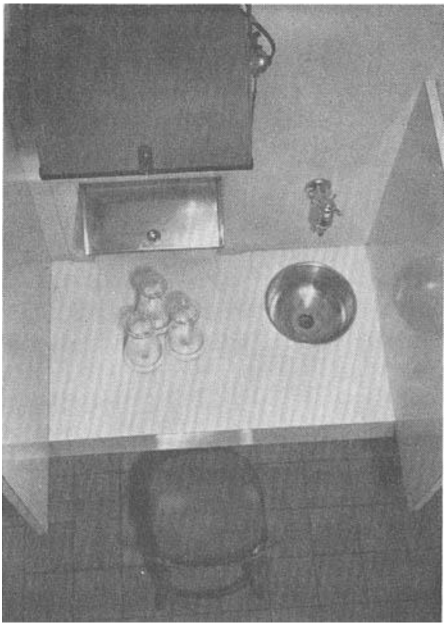

FIG. 2—*Taste and odor panel testing booth—Mellon Institute.*

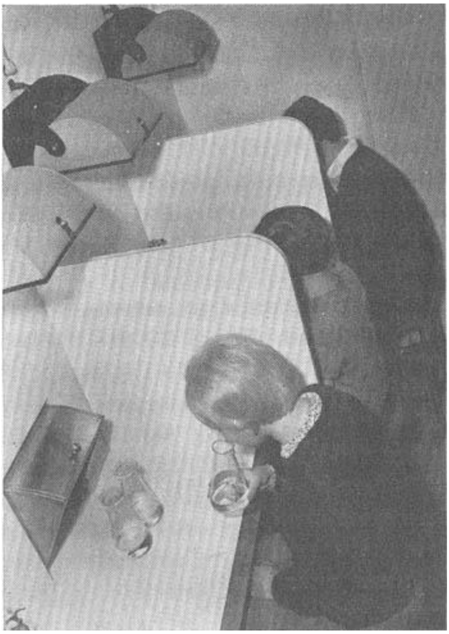

FIG. 3—*Panelists making odor measurements—Mellon Institute.*

Erlenmeyer flasks covered with watch glasses. These flasks were chosen rather than the often-used, ground-glass-stoppered flasks because the latter are difficult to free from trace odors and they do not provide as large an opening for the nose during odor testing. Details of construction and operating practices and precautions are given in the original reference [*2*].

Mathematical Evaluation

Statistical methods of testing are important in evaluating sensory testing information. They provide a basis for experimental design and facilitate interpretation of findings.

Analysis-of-variance procedures are generally used to test for the significant elements contributing to experimental results. This technique is excellent if the basis and limitations are recognized. It assumes that the variate (results) is normally (Gaussian) and continuously distributed. In odor testing, the results are based on stepwise dilutions in discrete intervals, hence the continuity assumption is not strictly valid. But if the dilution intervals are not greater than that corresponding to the accuracy of the tests plus the variations in personal response, this deviation is not too important. There are other important assumptions in analysis-of-variance tests. Whether these assumptions preclude valid use of the technique for data interpretation depends on the intent. If the interest is only in evaluation of data on hand, these assumptions are of no concern. But if statistical inferences are to be drawn from the data and the findings are to be extended to other applications, the limiting assumptions apply.

Certain limitations in subjective testing might occur in the scoring systems, the time of judging, the analytical systems, etc. These invalidate conventional analysis of variance. The limitations dictate the use of larger samples and nonparametric techniques for evaluation of the results. The results of organoleptic testing may be classified in two forms, (1) quantal responses and (2) scalar responses, which represent continuous distributions. Quantal responses are those in which the criterion is acceptability and the answer is yes or no. There is no intermediate value or extension. Quality characteristic ratings, on the other hand, can often be described by continuous scales in which intermediate values are possible. Quantal or preference ratings are used to select materials or characteristics that deviate slightly from small sample lots. A good example would be the tests for odor preference of several substances by the use of the method of ranked pairs. Each substance is given a preference rating against every other substance. The ratings are ranked and the ranks analyzed by a procedure based upon maximum-likelihood statistics.

Many subjective qualities are measured by a system of ranking. Thus an array of samples is arranged by the tester in ascending (or descending) order for such things as intensity of taste or odor. Scoring is a similar procedure except that samples are assigned some value from a prearranged scale. These scoring methods depend upon familiarity of the testers with the samples. The smaller the differences between samples, the greater the panelists' training must be to denote these differences and the greater the chance of low precision. Ranking methods are fast and allow many samples to be tested in a reasonable time.

The number of steps or grades in the scoring scale to be used must be developed from experience and the precision of the test. Five- to ten-point scales are usually used in sensory testing although fewer and more steps have been used. The common 0 to 5 scale denotes "no odor" to "intense or objectionable odor" for the respective extremes. At times, several qualities may be rated and multiple scoring systems may be assigned. The food industry uses such systems routinely. It is necessary that those conducting the test indoctrinate the testers thoroughly, select a useful scale, make trial runs, and refrain from implying a degree of accuracy or acceptability not inherent in the system.

Rating scale results are incorporated in standard experimental, statistical designs. The number of tests is determined by the number of samples, panel size, and consideration of the type of error (I or II). Type I error rejects the null hypothesis when it is true. Type II error accepts the null hypothesis when in fact it is false. The null hypothesis is the basis of the test. Detailed mathematical explanations are available [*3*]. Commonly, scoring scales are prepared in which the panelists rate the acceptability on some prescribed scale such as 1 for extremely poor to 9 for excellent.

Odor references may be rated by various scales. Sometimes, quality characteristics are described as acrid, sour, sweet, etc., and in other cases these are translated into a numerical or weighted value. It has been recognized that the odor type is important in considering both odor classification and odor threshold. Condequently, the "hedonic index" has been recommended for mitigating the differences between these two systems. Briefly, the geometric value of odor threshold is assigned to one scale and a numerical value of the quality (characterization) to another scale. The product of these has been suggested as an index (hedonic) for rating odor in water. Although this is a gross simplification, it denotes the nature of the problem and an attempt to facilitate communication between investigators in the water field. An acceptable system would allow everyone to evaluate odor values with the same degree of objectiveness.

The hedonic index [*4*] operates on the assumption of a continuum of physiological preference and a superimposed scale of successive categories of response (like and dislike). In characterization testing, it is desired to record the "first impression," not a reasoned, intellectual rating. The hedonic scale is a simple system which testers readily understand, but it is liable to bias and suffers from any limitations of the test subjects and limited test conditions. It is necessary that the proper statistical design and method of evaluation be employed. Limitations are caused by interactions such as those between persons and odor types. Another objection is the fact that strong odor types often predominate over weak odor types.

If subjective test values are to be useful, they must account for possible fractionation. In water work, it could mean that a given sample location, say on a stream, could yield odor values which are not representative of any other locations, even those nearby, because the odor components weather or decompose. The hedonic index will require modification, or some new scale will have to be developed to meet the needs of water investigators. Complex odors are best studied by profile methods. It has been noted that, as a complex odor sample is diluted with reagent water, different odors are detected than the one associated with the original sample. Instrumental methods supporting the odor test are the best means of studying the nature of the components of the odor mixture.

Odor-profile evaluation promises to be an acceptable means of evaluating odor changes along a waterstream containing multiple municipal and industrial effluents.

A number of methods for conducting and evaluating subjective testing have been developed. The proper choice depends on the complexity of the tests, the discriminatory power desired, and economics. It should be emphasized that the proper statistical design of experiments must be made before tests are begun. It is usually too late to rectify a poorly planned experiment after the data are obtained. There is an ever present need to balance practical or applied efficiency against statistical efficiency. Little purpose is served if complex statistical forms are used when the problem does not merit such sophistication.

Probably two testing procedures are best known and most used: the *triangular* and the *paired comparison* tests. The *triangular* test is made by presenting three coded samples to the tester. One differs from the other two and the tester must distinguish the different flask. The testing procedure is one of the best available if subtle differences exist between samples. Such differences are involved at threshold dilutions of odorous waters. The ranking tests described elsewhere are preferred when large differences exist. In *paired testing*, the unknown sample is presented to the tester who matches the unknown with one of a series of randomized dulutions of a known substance or mixture. An estimation of the unknown is derived from the over-all results.

Other techniques are available for specific purposes. These include paired comparisons and duo-trio methods. The duo-trio is a paired test with the standard also presented to the tester but in a manner differing from the triangle test. First a paired sample is identified and given to the tester and later two unknowns in random order. The tester must pick the different sample. Although the samples are tested against the standard, the probability is 0.5 rather than 0.33 as in the triangle test.

Series tests are often used in water treating plants. A series of dilutions is prepared and testers select one or more odorous samples from the array. If odor thresholds are to be measured, care must be exercised to avoid having panelists first exposed to suprathreshold concentrations.

In its simplest form, the Weber-Fichner law defining response to sensory stimulation states that the sensation produced is approximately proportional to the logarithm of the concentration. This fundamental rule provides a guide to all sensory responses.

Organic Chemicals

Organic substances are the chief source of taste and odor. They are contributed to waters by industrial and municipal wastes, agricultural activities, decay of vegetation, algae-actinomycete reproduction, and other natural man-made processes. Floods loosen decaying vegetation and cause sudden increases in lignin and tannin concentrations. These substances impart color; a few operators have been able to correlate color and quality. The organic materials rarely occur as single components. Usually a number are present simultaneously and their combined sensory effect may be quite unlike that of any of the original materials. Research has generated many synthetic organic chemicals that are not readily biodegradable. If these persistent or refractory substances also cause taste and odor, then special treatment procedures are dictated. Often the sensory effect attributed to specific organics is caused by other substances.

There have been many reports of the sensory effect of common detergents. Investigation showed no sensory effect at levels of detergent considerably greater than those found in most waters (maximum 10 mg/litre). Taste thresholds of 50 mg/litre were found, but even higher levels were necessary for detection of odor. Usually perfumes in packaged detergent products are detected rather than the detergent itself. The presence of detergent, especially in potable supplies from wells, is considered an indicator of pollution. Often it is detected through foaming before infiltration of other products is noted. Hard detergents are essentially not biodegradable, and activated carbon treatment for sensory quality control is not usually effective except at very high carbon dosages. Adsorption on carbon is enhanced below pH 9. Chlorination may lead to odorous chloroproducts. Introduction of soft or biodegradable detergents has decreased the possibility of long-term persistance of these substances. However, their presence is usually the first indicator of contamination.

Regardless of the source of organic material, water treatment personnel should monitor its presence on a regular basis. Analyses made during taste and odor problems are not too informative unless a base line has been established during trouble-free periods.

Organic chemicals can cause a bad taste in fish and other aquatic foods. The chemicals become concentrated in the flesh.

Although there have been many attempts to correlate taste and odor with specific chemical properties, no completely successful scheme has been developed. As new analytical devices of greater sensitivity are evolved, each in turn has hopefully been assigned to correlation of sensory properties with chemical structure. Claims for instrumental-sensory correlation have never been universal and are usually restricted to a minor group of substances.

Some of these correlations may be valid, but their weakness lies in dependence on limited physical or chemical property evaluation. The devices identify a single chemical or chemical fragment (radical or ion). The human nose measures a number of properties simultaneously, integrates them, and produces a composite sensory effect. Consequently, the nose far surpasses the most complex instrumentation for taste and odor monitoring.

The effect of phenol on taste and odor in water has been a controversial subject for many years. In water technology, "phenol" is a term used to describe a variety of hydroxy derivatives of benzene or its condensed nuclei. The substances constituting phenols are actually defined by the analytical test used. Consequently, varying concentrations of phenol may be reported on the same sample depending on the method of test or the modification of a given method. The chemicals reported as phenols exhibit individual taste and odor effects if tested separately. A wide range of threshold values will result.

The present U. S. Public Health Service recommended limit for phenol is 0.001 mg/litre in drinking water. This limit is based on taste and odor rather than toxicological considerations [*5*]. Since phenols are found in many industrial waste waters, there had been a long history of attempts to demonstrate a correlation between phenol content and the taste and odor of water. Because of the limitations just noted and the presence of other substances in water that modify the effect of phenols, it is not surprising that controversy has existed. Phenols are not only found in industrial and municipal waste waters but are also produced by decomposition of vegetation. These naturally occurring phenols are periodically flushed out by rainfall and cause typical taste and odor problems. Extensive studies [*6*] have examined the relationship between phenols in industrial waste waters and sensory quality. The results were very complex. No useful correlation was found between phenol level and odor following incremental chlorination. Although phenolic compounds are often a factor in sensory quality, it is misleading to base taste and odor control solely on phenol content.

Inorganic Chemicals

Inorganic chemicals are less often associated with taste and odor in water than are organic substances. They impart tastes rather than odors. Sulfides are one of the most troublesome inorganic chemicals. The major water supply in Florida, the Ocala limestone formation, contains concentrations of 1.0 to 4.0 mg/litre of dissolved sulfides (measured as hydrogen sulfide). The odor persists because the water pH ranges from 7.2 to 7.8. Adjustment of pH to 9.0 or higher removes odor and improves taste. The hydrogen sulfide remains in the water as long as dissolved sulfides are present. Aeration, chlorination, and ion exchange are all used in treating these waters.

Inorganic chemicals play an indirect role in biologically produced taste and odors in water. Nitrogen and phosphorus compounds from agricultural runoff and packaged detergents, for example, provide important biological nutrients. These stimulate algal and biological growth and may not only make water unpalatable but limit its use in domestic and industrial operations.

Dissolved salts are a factor in water quality. The saline water desalting research program is the major hope for many nations without suitable water supplies. Inland chloride problems may be caused by discharge of industrial wastes or deep-well brines. These obvious pollutants are usually controlled before they reach taste threshold concentrations. Fluorides in the concentration used in water treatment are not usually considered a factor in sensory quality.

Biological

Microscopic flora and fauna flourish or perish as a function of their aqueous environment. Environmental factors include temperature, pH, chemical composition, sunlight incidence, and dissolved oxygen level, among others. Food and elemental nutrient requirements depend on the specific organism. These microorganisms frequently consume complex organic matter and produce intermediate substances as a consequence of their metabolic processes. The metabolic intermediates and final products may cause taste and odor problems. Algae, actinomycetes, protozoa, rotifers, copepods, sulfur and iron bacteria, and crustacea are among the most important microorganisms. Biological action, both anaerobic and aerobic, destroys or modifies odorous compounds. But odorous by-products may form from materials that have little or no odor and these can modify the character and intensity of specific odorants.

Biological self-purification of streams is an important factor in neutralizing man-made wastes. This self-purification capacity is an economically significant phenomenon. It should not be exceeded, however, and it should be equitably apportioned among municipalities and industry.

Taste and odor components of biological origin are very likely to appear with seasonal frequency. Flushouts after low-flow periods of high biological activity are a common difficulty. Where rivers freeze, anaerobic bottom deposits are swept downstream during spring thaws. Thermal shocks that destroy the natural stream biota can also induce tastes and odors. Decay of vegetation is the leading cause of taste and odor in Western and Southwestern states where high solar intensity acts upon shallow supplies. As carbonaceous matter is metabolized, the concentration of by-product carbon dioxide is increased; this in turn stimulates biological growth.

Algae are the most troublesome microorganisms, as far as tastes and odors are concerned. If they do not cause the problem directly, they provide food for other organisms which produce odorous metabolic products. Decomposing algae release nonvolatile essential oils that are taste and odor factors [*7, 8*]. Organic sulfur compounds have been identified as products of bacterial decomposition of algae. Water use contributes fertilizing materials for these organisms. Phosphate particularly promotes proliferation of algae.

Frequently, taste and odor problems occur long after algae blooms have passed their peak; actinomycetes feeding on the algae are reported to be the cause. This is confirmed by the observation that various waters containing unlike algae populations will have similar odors after a period of heavy growth. Pure algae cultures have been developed which yield earthy, grassy, and fruity odors [*9-11*].

To minimize algae- and protozoa-created taste and odors, new reservoirs should have the topsoil stripped and surrounding vegetation cut back. Furthermore, domestic and industrial wastes which contribute nutrients should be kept out of reservoirs. Since algae blooms occur at predictable intervals, preventive measures are possible, for example, by treating incipient blooms with an algicide.

Actinomycetes are organisms closely related to both bacteria and fungi. They are colonial in behavior and are usually associated with soils, although an aquatic group is a significant source of taste and odor in water. They impart an earthy, musty, or woody odor to water and to fish flesh. An earthy-smelling compound, geosmin [*12-14*], and related chemical compounds have been isolated from actinomycetes. Mucidone, a chemically different compound that produces a musty odor, has been isolated from natural waters [*15*].

Quite often, tastes and odors have been attributed to algae when the real cause was actinomycetes [*16*]. These organisms grow in mud or silt, especially if organic matter and nutrients are plentiful. They are quite temperature-sensitive; 15°C represents a minimum for spore germination and vegetative growth. Rising temperature increases growth, with no apparent inhibition up to 38°C. They will grow in the dark in the laboratory, but shallow waters up to depths of 28 cm (11 in.) enhance growth. Deep bodies of water tend to discourage growth. Complex organic substances (such as proteins) in water provide nutrients. Shallow-water reservoirs with luxurious growths of grasses and rushes will harbor high concentrations of actinomycetes in warm weather. Algae (planktonic and attached) serve the same nutrient purpose. The degree of alkalinity affects growth; the greater the alkalinity, the more favorable the environment. Growth is poor under acidic conditions.

The metabolic by-products of actinomycetes, such as aromatic amines, ketones, aldehydes, saturated fatty acids, and unsaturated aromatics have been found to cause taste and odor in water. Minimum concentration in raw water appears to be about 0.2 mg/litre actinomycetes. Isoamyl and isobutyl amines, fatty acids, and unsaturated aromatics have been identified as significant odorous metabolic by-products.

Streptomyces spores are very small and pass through common bacterial filters. Sand filters in water-treating plants are therefore not effective in removing them. Spores passing the filters can become attached to mineral deposits in water distribution mains. There they can grow and impart taste and odor not found in the water leaving the treatment plant.

Time or duration of odor production depends on temperature and source of nutrition. The first odor is usually fishy and runs two to ten days. The next phase depends on the nutrient supply. If the primary stages of the actinomycete growth have exhausted the nutrient, small sex cells are formed as a zygote or seed. This ends the odor conditions. When sufficient nutrient remains, the primary stage forms a motile zygote which develops into a large secondary filament. These rapidly growing secondary filaments contribute a grassy taste and odor to raw water which lasts two to ten days and then changes to a pungent marshy odor. This odor may also last two to ten days, and, if enough nutrient is available, will alter to a potato-bin or slightly musty odor. If the nutrient is exhausted at any time, the odors soon cease. This sequential development provides a clue to the occurence of recognizable types of odor. It should serve as a guide to the waterworks operator to assure action in the early stages of actinomycete activity.

Copper sulfate treatment of water for algae control is a preventive measure widely used. Use of copper sulfate or copper citrate and other chemicals for weed or algae control may upset the natural biological balance. Cumulative build up of these compounds in fish caught for human consumption poses questions about toxicological or palatability factors. If copper sulfate levels are high, fish are eventually killed, thus creating further biological imbalance which may result in increased growth and incidence of algae.

Control of actinomycetes in reservoirs has not been successful. Various chemicals have been tried with incomplete control and unfavorable economics. It remains necessary to treat actinomycetes at the water plant, because inflow of sewage and vegetal matter induces prolific growth in reservoirs. The resulting odors have been a major problem in certain areas, such as the Southwestern part of the United States, during the period April to November, when temperature and light are conducive to actinomycete propagation.

The taste and odor remaining in water is a function of the treatment employed. Where actinomycetes are present, addition of as much as 10 mg/litre of chlorine may be necessary to reach the breakpoint. Threshold odors rise with additions of chlorine until a free available chlorine residual is present. The chloro-derivatives are especially odorous and not amenable to complete oxidation even when a residual chlorine content is present. Large additions of activated carbon will minimize odor but may not remove all of it. The point of addition of the activated carbon is important. If chlorine or chlorine dioxide are used, they will be preferentially absorbed by the activated carbon. The carbon should therefore be added after these agents have had enough time to become effective.

Taste

"Taste and odor" are used jointly in the vernacular of water technology. Most of the reported studies concerning the taste and odor problem actually emphasize or deal exclusively with odor. This arises from the inability to separate the two sensations because taste is usually masked by olfactory sensations. In some cases, taste tests are more sensitive than odor tests, but very little has been published on taste alone. Four basic tastes are recognized: *salty*, *sweet*, *sour*, and *bitter*. Variations of these are caused by olfactory influences. Taste results from the presence of a substance in an aqueous layer on the tongue, causing excitation of the receptor cells. As in olfaction, different cells respond to different basic tastes. Taste is an overall summation of these individual responses. Adaptation to taste, as in the case of odor, occurs because the frequency of nerve impulses decreases under the action of a steady stimulus. Taste sensitivity changes with age, as does the spatial arrangement of the taste buds.

The same basic testing considerations important in odor testing apply to taste testing. Background odors, temperature, and humidity should be regulated; color bias should be recognized and controlled if necessary; and the equipment used in the test should be free of foreign tastes. The taste test is made by having the panelist(s) rinse the mouth with taste- and odor-free water, expectorate the rinse, and repeat the procedure with the substance being tested. The rinse water should not only be free of background taste but be at sample temperature. Sample sizes should be reasonable, neither too large nor too small. The sample size is controlled in some degree by the basic taste. Sweet tastes usually require somewhat larger samples than bitter tastes, because the latter cause sensation somewhat more rapidly. Usually, taste testers make several tests per session without loss of precision, although this has to be established in each situation. Threshold measurements are based on the premise that concentrations in excess of these values are unacceptable. This is true for odor but does not apply to mineral-induced taste. Consumers prefer slightly mineralized water to distilled water. Consequently, psychological scaling methods have been suggested as alternatives to taste threshold measurements for establishing limiting standards for mineralization.

An important consideration in taste testing is the possible hazard from toxic substances. These may be the sensory factors in the water or the reagents used in preparing the sample. Samples of water having residual chlorine require dechlorination if the presence of organic tastes is to be discerned. The dechlorination reagent of choice is sodium thiosulfate. Sodium arsenite is often used in odor testing but should not be used in taste testing because of the toxicological hazard.

Odor Terminology

The two most common descriptions of an odor are its *intensity* and its *characterization*. Intensity is a measure of relative strength. Characterization is the description of how it smells. For example, sweet and pungent are two common characteristics. The *threshold odor* is the concentration of an odor which is just barely detectable to the individual. *Suprathreshold odor* concentrations are those exceeding the threshold concentration. Since people differ, often considerably, in their sensitivity to a given odor, the actual threshold odor value for a given sample will vary. In fact, it is more precise to report a range of threshold odor values together with the number of observations rather than an average, because an average is usually based on too few determinations to have application to the population as a whole.

Odor changes are not usually tolerated by the water consumer. It should be noted that the preceding statement did not say "the absence of odor." Odor analyses are concerned with threshold or near-threshold odor numbers or odor intensity index values. These are related terms. The threshold odor number, *TON*, is the number of times a sample must be diluted for the odor to be just detectable. For example, if 25 ml of sample in a standard 200-ml testing volume is just detectable, the dilution factor or *TON* is 8. Such numerical values are easily comprehended for samples of low-odor intensity, such as potable or drinking waters. But some natural waters and some industrial waste waters have intense odors. The threshold odor number system gives extremely large numerical values for such waters. To avoid the difficulty of interpreting results the odor intensity index, *OII*, system is used. The *OII* is the number of times a sample must be diluted in half with odor-free water to reach threshold odor concentration. In the example given in the foregoing, the *OII* would be 2^3 or 8 by this system. *TON* and *OII* values are therefore related as follows:

$$TON = 2^{OII}$$

There is another significance to the *OII* values. It has been shown [*1*] that one *OII* value represents the order of reproducibility of the threshold odor determination.

Odor Parameters

Any study of odor in water requires a reproducible method of test. Extensive research [*1*] led to the development of a standard procedure, ASTM Test for Odor in Industrial Water and Industrial Waste Water (D 1292) [*17*]. This procedure uses a three-flask array in panel testing. Two flasks contain odor-free blanks and the third may be either a sample dilution or a third blank. The test samples are prepared so that concentrations are gradually increased from subthreshold level. Exposure to suprathreshold concentrations usually interferes with subsequent threshold odor measurement.

Reproducibility with several odorants has been found to be of the order of approximately one-fold dilution or one *OII* unit. This means that dividing a given odor sample in half by odor-free water in each step of the dilution sequence is approximately equal to the accuracy of the panelists. Dilutions of less than 50 percent are often used, but this is unjustified. The natural variability for any person from day to day or even within a day may well exceed this implied accuracy even under ideal environmental conditions.

Very important effects for person-chemical interaction have been demonstrated. In other words, the kind of odorant and the choice of panelist are highly interdependent with regard to the threshold odor result. This should not be surprising. People vary in their ability to detect a given odor and they also vary in their relative sensitivity to various odors. This contributes to the range of personal preferences for many products from perfume to water. In these studies, a variety of odor testing procedures was evaluated. It was found that the environmental conditions were more important than the test method if similar precautions were used.

The literature contains references to threshold odor tests made at a variety of temperatures. Many plants use 60°C because this corresponds to hot-water service in domestic applications. Others use lower temperatures, particularly 40°C, which approximates body temperature. Statistical evaluation of odor tests at 21°C, 40°C, and 60°C showed that (1) odor response varied by 4 *OII* values (16-fold change of concentration) between the least and most sensitive person, and (2) between 21° and 60°C there was an increase in overall sensitivity by the panel, corresponding to a decrease in odorant concentration equivalent to 1.4 *OII* units. Although higher temperatures do improve odorant volatility, there are other considerations. Panelists preferred 40°C. They complained of losing initial odor sensations on second inhalation and of steaming at 60°C. At 21°C, room temperature, they regarded the odor sensation as being dead. The 40°C temperature has been incorporated as a standard condition by ASTM. These tests also demonstrated that person-chemical interaction and the overall variability of the test procedure were approximately one *OII* value.

Background odor may interfere with olfactory response. There has been little published evidence to support this somewhat obvious generalization. Food and beverage laboratories recognize this fact and do provide odor-free atmospheres in their sensory testing laboratories. Few water laboratories have such facilities. As part of the foregoing investigation, the background odor effect was established for the standard odorants *n*-butanol and *m*-cresol. Measurement of the threshold odor of each was made with the same odor and with the differing odor in the atmosphere. The results showed that there is a marked effect. The olfactory system is confused. If *m*-cresol was the background odor, then detection of *n*-butanol in the threshold test was enhanced but detection of *m*-cresol was hindered. Similarly, a background of *n*-butanol suppressed detection of *n*-butanol and enhanced detection of *m*-cresol in the threshold test. The only possible recommendation is that background odor must be eliminated during odor testing.

Odor Mixtures

Reports describing odors in water are often conflicting. This may be because the complex effects of mixtures of odors are not usually recognized in the water pollution field. Rarely are odors in natural or industrial waste water the result of only one substance; more often they are a composite of a number of odorants. When individual odorants mix, the result may be one of additivity, synergism, or antagonism. If the substances combine to give an odor intensity equivalent to the contribution of the individual odors, this is additivity. For example, a mixture of one part A and one part B of equal odor intensity combine to produce an intensity equal to either 2A or 2B. Synergism takes place when the combined odor intensity of the mixture is greater than would be expected by simple addition of these separate intensities. This occurs if A plus B produce an odor greater than 2A or 2B. Similarly, antagonism is the suppression of combined odor effects so that A plus B produces less odor than simple addition.

As if the odor mixture effect were not complicated enough, it is necessary to consider that measurement involves persons of varying olfactory ability. The previously cited examination of procedures and environmental factors showed that there are significant person-to-person differences and person-to-chemical interactions. The interaction refers to the varying sensitivity of a given person to different kinds of odors. The effect of mixtures of odorants in aqueous solution was studied. To do this, statistically-designed experiments were devised so that the effects of person-to-person differences and of person-to-chemical interactions could be isolated from the effect of odor mixtures. Theoretical models were developed which were based on the concepts of additivity, synergism, and antagonism [*18*]. These mathematical models were developed for binary and for complex higher-ordered mixtures. Several methods of data analysis were employed to eliminate any bias possible from the choice of experimental procedure. Eight odorants of differing sensory, physical, and chemical properties were selected: *m*-cresol (phenolic); *n*-butyl mercaptan (sulfide); pyridine (amine); acrylonitrile (unsatrated); *n*-amyl acetate (ester); *n*-butanol (alcohol); 2–4 dichlorophenol (chlorinated phenol); and acetophenone (ketone). These were studied as binary mixtures and as a blend of all eight. For the binary mixture study, solutions were prepared of two components where one was 0, 25, 50, 75, or 100 percent of the total. Threshold odor measurements were made by panelists using the ASTM Method D 1292 at 40°C. Synergism or antagonism of olfaction was the rule rather than the exception. It was also an excellent demonstration of the importance of precise dilution preparation in sensory testing. Often, very minor changes in relative concentration of one component may change the resulting sensory response greatly.

An olfactory test of a complex mixture of eight odorants showed that most of the 14 panelists either detected odor in the basic mix (containing ⅛ threshold concentration of each of the eight odorants) or required further dilution to get to threshold concentration. Only a few required higher concentrations than the basic mix.

Recent studies by others have also shown these complex odor effects. These laboratory and field investigations [*19,20*] were approached in an entirely different manner but reached the same conclusions. Some of the same chemical odorants were used, thus facilitating comparison.

There is important practical meaning in these results for persons concerned with water pollution control. Conceivably, several waste-water streams, each with no perceptible odor, may mix in the receiving water body to produce unacceptable tastes and odors. It is obvious that use of single-odor threshold values as criteria for acceptable water quality is inadequate. The combined effect of all contributors must be considered if meaningful and realistic data are to be obtained.

Threshold Odors

It is very difficult to find information on the threshold odor concentration of chemicals in aqueous solution. Available data are questionable because of the lack of environmental and procedural control. A summary of threshold odor values obtained by ASTM Method D 1292 at 40°C for various chemicals is given in Table 1.

The wide range of odor threshold concentrations has practical significance. This range, particularly at the lower end, is of more importance than the average value. This is the segment of population most apt to recognize impaired water quality and register complaints. For example, the average phenol threshold is at 6 mg/litre, but the most sensitive testers could distinguish 17 μg/litre. The lease sensitive testers required 17 mg/litre, a thousand-fold difference! These are interesting values because the U. S. Public Health Service Drinking Water Standards [*5*] specify a limit of 1 μg/litre phenol. This limit, which is below the 17 μg/litre lower limit found in these tests, is based on taste and odor induced by chlorination. Chlorination of phenolics may greatly alter and intensify the odor of the parent substance.

Chlorination

Chlorination destroys bacteria and organisms such as algae, and directly or indirectly destroys tastes and odors. There are situations, however, when chloro derivatives are more obnoxious as taste compounds than the original chemical. Chloro derivatives are handled by a variety of methods. For example, addition of ammonia prior to chlorination often prevents formation of chlorine-reaction products. Ammonia-chlorine treatment prevents creation of odors by chlorination but in itself does not remove odors.

The chlorine requirement of waters varies as a function of the complexity

TABLE 1—*Odor threshold concentrations for various chemicals*[a].

Chemical	Number of Panelists	Number of Observations	Threshold Odor Level,[b] mg/litre	
			Average	Range
Acetic acid	9	9	24.3	5.07 to 81.2
Acetone	12	17	40.9	1.29 to 330
Acetophenone	17	154	0.17	0.0039 to 2.02
Acrylonitrile	16	104	18.6	0.0031 to 50.4
Allyl chloride[c]	10	10	14 700	3 660 to 29 300
n-Amyl acetate	18	139	0.08	0.0017 to 0.86
Aniline	8	8	70.1	2.0 to 128
Benzene[d]	13	18	31.3	0.84 to 53.6
n-Butanol	32	167	2.5	0.012 to 25.3
p-Chlorophenol	16	24	1.24	0.02 to 20.4
o-Cresol	13	21	0.65	0.016 to 4.1
m-Cresol	29	147	0.68	0.016 to 4.0
Dichloroisopropylether	8	8	0.32	0.017 to 1.1
2–4 Dichlorophenol	10	94	0.21	0.02 to 1.35
Dimethylamine	12	29	23.2	0.01 to 42.5
Ethylacrylate	9	9	0.0067	0.0018 to 0.0141
Formaldehyde	10	11	49.9	0.8 to 102
2-Mercaptoethanol	9	9	0.64	0.07 to 1.1
Mesitylene[d]	13	19	0.027	0.00024 to 0.062
Methylamine	10	10	3.33	0.65 to 5.23
Methyl ethyl pyridine	16	20	0.05	0.0017 to 0.225
Methyl vinyl pyridine	8	8	0.04	0.015 to 0.12
β-Naphthol[d]	14	20	1.29	0.01 to 11.4
Octyl alcohol[d]	10	10	0.13	0.0087 to 0.56
Phenol	12	20	5.9	0.016 to 16.7
Pyridine	13	130	0.82	0.007 to 7.7
Quinoline	11	17	0.71	0.016 to 4.3
Styrene[d]	16	23	0.73	0.02 to 2.6
Thiophenol[c]	10	10	13.5	2.05 to 32.8
Trimethylamine	10	10	1.7	0.04 to 5.17
Xylene[d]	16	21	2.21	0.26 to 4.13
n-Butyl mercaptan	8	94	0.006	0.001 to 0.06

[a] *Journal*, American Water Works Association, Vol. 55, 1963, p. 913.

[b] Threshold values based upon pure substances.

[c] Threshold of a saturated aqueous solution. Solubility data not available.

[d] Dilutions started with saturated aqueous solution at room temperature; solubility data obtained from literature for correction back to pure substances.

of their components. It may change suddenly. For example, during thermal overturns of reservoirs, raw-water characteristics are subject to sudden modification. It is important to note that although there may be a relationship between organic content of water (as measured by chlorine demand) and taste and odor in some cases, this is not a dependable correlation. Many organic compounds do not exert a chlorine demand and, conversely, chlorine demand is not indicative of absolute organic concentration. Chlorine reactions are dependent upon the concentration of reactants, reaction time, pH, temperature, and chemical, physical, and biological factors. Low chlorine-demand waters are usually acceptable over a longer period of time after treatment because chlorine levels have been adequate to maintain residual chlorine and not just initiate chemical reactions.

Chlorine dioxide has been used to treat phenolic contamination but it is not applicable to all situations. It is useful, however, where sewage, algae, and certain industrial wastes affect taste and odor quality. European plants often use ozone for odor control, but economic considerations preclude its use in the United States. Reservoirs tend to stratify and anaerobic zones are created. The decomposition of organic matter in this zone leads to increased taste and odor problems and an associated increase in chlorine demand. Often, other problems occur simultaneously, such as requirement for manganese removal. Oxidation, flocculation, pH adjustment, and chlorination must then be used for treatment of the water.

Chlorine reactions with phenolic compounds have been the basis of numerous studies. The various chloro-phenolics differ considerably in taste and odor potential, and in the treatment required. Most important is the fact that a phenolic concentration far lower than its threshold level may produce decided medicinal odors after chlorination.

Not all organic matter is destroyed in plant chlorination processes. Some organic material becomes associated with colloidal particles of high electrophoretic charge which frequently escape coagulation and settling steps. These materials are considered a principal source of post-treatment tastes and odors.

A survey of water-treating plants showed that taste and odor problems associated with dechlorination of samples originally containing a chlorine residual were not uncommon. Before taste or odor tests can be made on such waters, they must be dechlorinated. Unfortunately, the commonly used dechlorination reagents, sodium thiosulfate and sodium arsenite, frequently induce sensory effects. Dechlorination with thiosulfate often releases a sulfurous odor. This is most noticeable when the water is near the threshold odor level and no dilution with odor-free water is needed. Sodium arsenite is less apt to produce odor, but it is not used in many laboratories because of its acute toxicity. Although a variety of reagents has been tested for dechlorination, none have been found to be better than sodium arsenite. There is need to study this problem.

It was found that the ammonia nitrogen in most waters, less than 0.5 mg/litre, does not generally produce sufficient chloramine to modify threshold odor measurement significantly. If proteins and other nitrogen-containing substances are present, this simple criterion based on ammonia nitrogen may not apply.

Odor profile analyses from the raw-water source through the steps in water treating plants have been found to be a very valuable aid in adjusting treatment dosages and maintaining finished water quality.

Activated Carbon

The use of activated carbon for adsorption of taste and odors from organic chemical contaminants is common. The dosage required is not predictable from simple measurement of odor intensity or characterization of the raw water. It is a function of the physical-chemical properties of the entire water-impurity system. Some organic chemicals are preferentially adsorbed. In the absence of adequate adsorption capacity for all the organic materials present in water, equilibrium conditions are created, controlled by varying relative adsorption of individual components. Desorption of previously adsorbed materials may take place [*21*]. Adsorption in the presence of suitable capacity follows the universally accepted Fruendlich adsorption isotherms.

Although carbon is an efficient adsorbant for organic chemicals, it is rarely used by itself. Economic considerations prompt its use in conjunction with other treatment processes. The combined treatment is dictated by maximizing efficiency at lowest cost. Carbon is most frequently added in granular form as a slurry, with the point of application governed by the raw-water quality. In some cases it has been added to raw water prior to chlorination to minimize particularly obnoxious chloro-organic formation. In other cases it has been added after the coagulation process to remove residual taste and odor components. One practice which merits critical review is that of adding activated carbon in the flash mixers preceding coagulation. The coagulant forms a matrix around the carbon, preventing effective use of its adsorption capacity. Addition of the carbon in large basins requires multipoint application, usually through distribution nozzles at the basin surface. The carbon then settles through the water, which is traveling in a horizontal direction. Another form of carbon treatment used in some areas is the fixed activated-carbon tower, down which the water is allowed to percolate.

Instrumental-Sensory Correlation

Recent developments in analytical instrumentation have expanded the potential for instrumental-sensory correlation. Despite these advances, the human nose is still a more sensitive detector of many organic materials than the best man-made detectors. Particularly promising are the ionization detectors used with gas-liquid chromatography. The flame-ionization and electron-capture detectors have been used to detect nanogram and picogram concentrations of organic elements of complex tastes and odors. The chromatographic and various infrared and other spectrograph techniques may provide a key to greater understanding of sensory properties. Of immediate practical use is the possibility of monitoring selected waste waters or raw waters for specific organics known to be associated with taste and odor in water problems. The early-warning feature of such a monitoring program would be helpful to many industrial waste water and domestic water treatment plant operators.

Correlations of instrumental and sensory responses have been made, but the results are meager [*22*]. Typical are the characterizations of specific gas-liquid chromatographic peaks separated from actinomycete cultures as woody, musty, or earthy odors [*23*]. The changes in gas-liquid chromatographic profiles of natural waters are being studied to provide an indication of potential taste and odor problems and to indicate those organic contaminants meriting further characterization by spectrographic procedures [*24*].

References

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Chapter 13—Sampling and Identification of Deposits in Steam and Water Systems

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Pure water in an uncorrodible vessel would never leave a deposit. Although this ideal case has been very nearly reached in some instances, deposits are still found in most water or steam systems. The examination and analysis of these deposits provide the person responsible for water treatment with information about phenomena in the water system, and will frequently indicate to him the means for correcting the condition that caused the deposit.

This chapter covers the nature of deposits in steam and water systems, the sampling of deposits for analysis, and methods for identification of the constituents of the deposits. Quantitative chemical analysis is dealt with in Chapter 14. Some of the instrumental methods discussed in this chapter are not at present widely used in the examination of deposits, but brief descriptions are included because there are instances where they can be used to advantage. Deposits may be divided into three general classes: inorganic, organic, and biological.

As shown in Fig. 1, inorganic deposits result from corrosion of containing surfaces; from precipitation by chemical reaction between two or more constituents of the water; or precipitation from physical causes, such as change in solubility with pressure or temperature, by evaporation to dryness, or by relief of supersaturation. Closely akin to these, but still somewhat distinct, is the sedimentation of suspended matter.

Organic deposits generally result from precipitation of organic materials naturally present in the water supply, contamination of condensate returns by process materials, or precipitation of certain organic treatment chemicals.

Biological deposits may occur as a result of precipitation, due to changing conditions, of biological matter present in the raw-water supply, or they may be formed where they are found because of utilization of nutrients in the water and a favorable environment for biological growth.

The number of possible techniques available to the modern analyst is so large that only a bare outline can be given in this chapter. References in the chapter will suggest where more detailed information can be found.

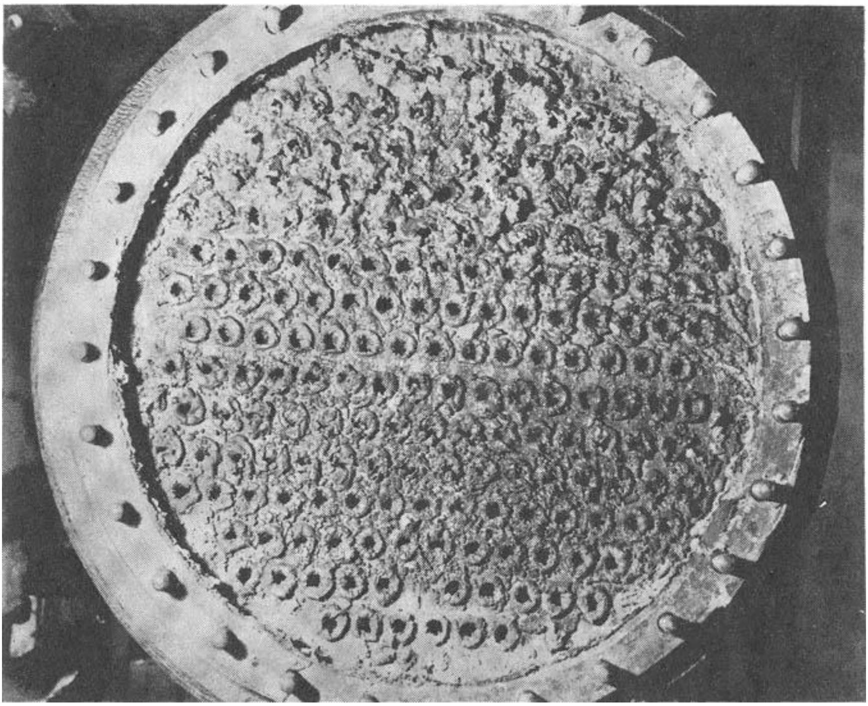

FIG. 1—*Deposits on the waterside of a heat exchanger.*

Classification of Deposits

Since most of the crystalline water-formed deposits have the same composition and structure as hydrothermal minerals, it is both helpful and logical to use the mineral scheme for classification. For diagnostic purposes, one of the most important types of information is the identification of the compounds in a deposit according to the mineral species present.

Basic Compounds

Some relatively soluble metallic salts form, with the hydroxide of that metal, very insoluble basic double salts. These are most often found on metallic surfaces as corrosion products where water carries a considerable amount of oxygen. An alkaline condition is not required and the compounds may be formed at pH values below 7.0. Copper can form basic carbonates, chlorides, and sulfates. Atacamite ($\alpha CuCl_2 \cdot 3Cu(OH)_2$) is frequently found as a hard, very adherent corrosion deposit in condenser tubes. Zinc forms a basic carbonate, as $2ZnCO_3$; $3Zn(OH)_2$ and a basic magnesium chloride, $MgCl_2 \cdot 5Mg(OH)_2 \cdot 8H_2O$, may be formed in seawater.

Carbonates

Carbonates of most of the alkaline earth and heavy metal elements are insoluble. The respective bicarbonates are much more soluble. However, heat and an increase of pH value shift the bicarbonate to the normal carbonate form to produce the respective insoluble compounds. Aragonite ($\gamma CaCO_3$) and calcite ($\beta CaCO_3$) are found in heat exchangers and softener and boiler sludges. Of the two, calcite is the more stable and is the high-temperature form. Dolomite ($CaCO_3 . MgCO_3$) may also be found where the calcium-magnesium ratio is favorable to its formation. Occasionally, modified forms of calcium carbonate such as ankerite ($CaCO_3 . (Fe, Mg, Mn) CO_3$) and gaylussite ($CaCO_3 . Na_2CO_3 . 5H_2O$) precipitate in low-pressure boilers.

Siderite ($FeCO_3$) may precipitate from waters containing ferrous bicarbonate or may form as a corrosion product in condensate containing carbon dioxide. Normal carbonates of other heavy metals are rarely formed in industrial water.

Hydrated Oxides

The class of hydrated oxides contains principally the trivalent corrosion and precipitation products of iron and aluminum. The term "hydrated oxide" is more one of custom than exactitude. The formula $M_2O_3 . H_2O$ is correct for composition, but $MO(OH)$ is more correct for structure.

The "hydrated oxides" of iron and aluminum are interrelated in that temperature and time cause the more highly hydrated forms to lose water and undergo alterations of crystal structure. This relationship is shown in the following diagram:

$$\begin{tikzcd}
\begin{array}{c}\gamma Fe_2O_3\\ \text{(maghemite)}\end{array} \arrow[r, "\text{heat}"] & \begin{array}{c}\alpha Fe_2O_3\\ \text{(hematite)}\end{array} \\
\begin{array}{c}\gamma FeO(OH)\\ (\gamma Fe_2O_3 \cdot H_2O)\\ \text{(lepidocrocite)}\end{array} \arrow[u, "\text{heat}"'] & \begin{array}{c}\alpha FeO(OH)\\ (\alpha Fe_2O_3 \cdot H_2O)\\ \text{(goethite)}\end{array} \arrow[u, "\text{heat}"'] \\
\begin{array}{c}\gamma Al_2O_3\\ (\gamma\ \text{alumina})\end{array} \arrow[r, "\text{heat}"] & \begin{array}{c}\alpha Al_2O_3\\ \text{(corundum)}\end{array} \\
\begin{array}{c}\gamma AlO(OH)\\ (\gamma Al_2O_3 \cdot H_2O)\\ \text{(boehmite)}\end{array} \arrow[u, "\text{heat}"'] & \begin{array}{c}\alpha AlO(OH)\\ (\alpha Al_2O_3 \cdot H_2O)\\ \text{(diaspore)}\end{array} \arrow[u, "\text{heat}"'] \\
\begin{array}{c}\gamma Al(OH)_3\\ (\gamma Al_2O_3 \cdot 3H_2O)\\ \text{(gibbsite)}\end{array} \arrow[u, "\text{heat}"'] &
\end{tikzcd}$$

It is believed that the γ monohydrates (lepidocrocite and boehmite) in industrial deposits are more likely formed by recrystallization from rapidly precipitated amorphous gels. The α monohydrates (goethite and diaspore) are more likely to have formed without the gel precursor. The γ forms are usually formed at lower temperatures than the α forms.

There is also a series of hydrated oxides of zinc, but the composition of this series is indefinite. X-ray patterns show differences but are designated only as ZnA, ZnB, and ZnE. The principal mode of formation is by the corrosion of metallic zinc in hot water. ZnE is the common species.

Hydroxides

Simple hydroxides precipitate from solutions of high pH values, or under special conditions hydrolyze in corrosion reactions. Brucite ($Mg(OH)_2$) is found in boiler and softener sludges but it can also form in environments of relatively low pH values such as those found in lower stages of seawater evaporators. Calcium hydroxide ($Ca(OH)_2$) may scale out in lines carrying lime slurries or in superheaters and steam lines by thermal hydrolysis of a previously deposited calcium carbonate.

Ferrous hydroxide ($Fe(OH)_2$) has been identified in corrosion pits, and nickel hydroxide ($Ni(OH)_2$) in exfoliated flakes from cupro-nickel stage heaters.

Metals

Free metals in a deposit are usually the end product of a reducing condition acting on a solution or an oxide of the metal. Dendritic copper is present in many high-pressure boiler sludges and sedimentary deposits. Copper lends weight to the mass of sludges, and part of its undesirability is caused by the settling tendency it provides in areas of low water velocity.

Metallic iron may be found in some corrosion products either as an inversion product of ferrous oxide at high temperatures or as a result of isolation by the corrosion of surrounding grains. In the former case, Fe_3O_4 is also formed as follows:

$$4FeO \rightarrow Fe + Fe_3O_4$$

Metal Oxides

Metal oxides are invariably the products of corrosion reactions, the dehydration of hydrated oxides, or the decomposition of carbonates. The oxides may be loose and porous or compact and adherent according to conditions of formation. Oxygen for the formation of the oxide can be provided by dissolved oxygen in the water or by bound oxygen from molecular H_2O. In the latter instance, hydrogen is produced.

Magnetite (Fe_3O_4) is formed under the greatest variety of conditions. FeO, Fe_3O_4, and Fe_3O_3 can all be found in aqueous corrosion products of iron according to the amount of oxygen present. Fe_3O_4 and occasionally FeO are the products in steam.

The two copper oxides, cuprite (Cu_2O) and tenorite (CuO), may both be components of boiler sludge or corrosion films on copper, brass, or bronze. High oxygen concentration and high pH values are favorable conditions for the formation of tenorite, whereas cuprite is more likely the solid phase of a lower pH and lower dissolved oxygen concentrations.

Corundum (αAl_2O_3) has been found in high-pressure boilers and turbines as an alteration of precipitated alumina. Zincite (ZnO) is a hot-water corrosion product on metallic zinc.

Organic Salts

The mono- and di-hydrates of calcium oxalate ($CaC_2O_4 \cdot H_2O$ and $CaC_2O_4 \cdot 2H_2O$) are practically the only organic salts of sufficient insolubility to be found in industrial deposits. Certain food liquors containing oxalic acid and calcium cause severe oxalate scaling in evaporators.

Phosphates

The insoluble phosphates in industrial waters are formed by the reaction of soluble calcium, magnesium, or iron with a soluble phosphate added as a form of treatment. Most boilers today are treated to precipitate the calcium purposely as hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$) sludge. Although it is usually fluid and soft, it can form a compact scale. It may also undergo an alteration in areas of high heat-exchange rates and highly concentrated boiler water to form a hard scale, wilkeite ($Ca_{10}O[(Si, P, S)O_4]_6$). Sodium calcium phosphate ($NaCaPO_4$) forms under similar conditions.

Other calcium phosphates, whitlockite ($\beta Ca_3P_2O_8$) and dicalcium phosphate ($CaHPO_4$), have crystallized out in chemical lines feeding boiler drums.

Magnesium hydroxyphosphate ($Mg_3PO_4 \cdot Mg(OH)_2$) is a sludge component of boiler water having a high phosphate and a low silica concentration.

A low-temperature ferric phosphate, vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$, is occasionally found in cooling systems. It frequently is mixed with iron oxides in deposits having a glassy appearance.

Silica

Uncombined silica as quartz or cristobalite forms by the hydrothermal alteration of solid silicates or by direct crystallization from dissolved silica. Quartz (SiO_2) is one of the hardest of the minerals, but crystal size is small in water-formed deposits so that the extreme hardness of the natural mineral is not imparted to the deposit. A unique property of solubility in high-temperature steam provides a mechanism for its crystallization as a solid when the steam temperature is reduced. Quartz formation in steam turbines is caused by volatile transport of silica from the boiler water. Cristobalite is another form of crystalline silica in steam turbine deposits. Uncombined silica may also be a component of siliceous boiler scales.

Free silica in heat exchanger deposits results from the deposition of sand or dirt suspended in the cooling water. The principal property of such deposits depends upon the substance forming the matrix of the individual grains of silica.

Simple Silicates

The silicates of single cationic elements are classified as simple silicates. The calcium and magnesium silicates have incongruent solubilities and contain water of hydration when formed hydrothermally. The composition of the solids is dependent upon temperature and pressure as well as on the relative concentrations of the dissolved reacting ions.

The hydrous magnesium silicates, serpentine ($3MgO \cdot 2SiO_2 \cdot 2H_2O$), talc ($3MgO \cdot 4SiO_2 \cdot H_2O$), and sepiolite ($2MgO \cdot 3SiO_2 \cdot 2H_2O$), are soft, rather poorly crystallized compounds. Detection by instrumental means is not always successful. They are more frequently components of soft sludges rather than hard scales. The formation results from the alteration and crystallization of an absorption complex of dissolved silica on magnesium hydroxide. Serpentine forms under the most varied conditions and for this reason is the most common of the three forms.

The hydrous calcium silicates, gyrolite ($2CaO \cdot 3SiO_2 \cdot H_2O$), xonotlite ($5CaO \cdot 5SiO_2 \cdot H_2O$), and foshagite ($5CaO \cdot 3SiO_2 \cdot 3H_2O$), like the hydrous magnesium silicates, crystallize poorly but unlike them may be hard, tough, and highly insulating. The common form is xonotlite, with gyrolite and foshagite being somewhat rare.

The anhydrous simple silicates, fayalite ($2FeO \cdot SiO_2$), mullite ($3Al_2O_3 \cdot 2SiO_2$), olivine ($2(Mg, Fe)O \cdot SiO_2$), and forsterite ($2MgO \cdot SiO_2$), are commonly high-temperature dehydration products of related hydrous forms. Willemite ($2ZnO \cdot SiO_2$) is one of the few anhydrous simple silicates formed hydrothermally.

The sodium silicates, Na_2SiO_3 and $\beta Na_2Si_2O_5$, are somewhat soluble in high-temperature steam and therefore are components of turbine blade deposits. Their water solubility is appreciable, so that they may be removed by washing the turbine internally with wet steam.

Complex Silicates

Silicate compounds of more than one cationic element are classified as complex silicates. These hydrothermally formed compounds are often crystallized from environments of very high heat input and are usually hydrous. Regions of high heat input become highly concentrated in boiler water salts that contain sodium silicate. Conditions favorable to reactions with oxides of aluminum, iron, and calcium to form the respective sodium silicate complexes exist in these regions. The sodium silicate complexes are not easily corrected by treatment of the water, since they may form in water with no hardness present.

All are very hard and adherent and resist dissolution by ordinary acid cleaning procedures. They may form in place on the steam-generating surface or by reaction with sodium silicate and accumulated iron oxides as in the case with acmite ($Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$). Analcite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) is the commonest aluminum analog and may be present is sludge form as well as scale. Natrolite ($Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$) and noselite ($5Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2SO_3$) occur much less frequently than analcite. Acmite has also been found in turbine blade deposits, suggesting that the components of the reaction may be steam soluble.

Cancrinite ($4Na_2O \cdot CaO \cdot 4Al_2O_3 \cdot 2CO_2 \cdot 9SiO_2 \cdot 3H_2O$) forms when calcium sludge is contained in the concentrated sodium silicate and sodium aluminate reaction liquid. Pectolite ($Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$) is a boiler scale under aluminum-free conditions.

Sulfates

Of all the scale formers, calcium sulfate is most readily recognizable because of the large crystals which are formed. Anhydrite ($CaSO_4$) crystallizes on heat-exchange surfaces in the form of large needle-like crystals which grow perpendicular to the heat-exchange surface. The individual crystals can be seen by the naked eye. Hemi-hydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) are lower-temperature forms of calcium sulfate, the former more likely to be found on steam generating surfaces and the latter in nonsteaming exchangers.

Celestite ($SrSO_4$) and barite ($BaSO_4$) are highly insoluble but rather rare because of the infrequency of strontium and barium in industrial water.

All sulfate scales are difficult to remove as they do not respond to acid cleaning.

Sodium sulfate occurs in superheater and turbine blade deposits as thenardite (Na_2SO_4-V), metathenardite (Na_2SO_4-I), Na_2SO_4-III, and burkeite ($2Na_2SO_4 \cdot Na_2CO_3$).

Sulfides

Sulfides of metals are quite insoluble but generally do not protect metals on which they are formed. Sulfides are usually associated with corrosion in the presence of hydrogen sulfide or with a reducing reaction on a sulfate. Cuprous heat-exchanger tubing may contain chalcocite (Cu_2S) or covellite (CuS).

Boiler and superheater tubes have contained ferrous sulfides (FeS) pyrrhotite and troilite, probably as high-temperature reduction products from sulfur originally as sulfate or sulfite.

A list of water-formed compounds is contained in Table 1 of Chapter 14.

Sampling of Deposits

Deposits are sampled at least twice before being submitted to chemical or physical tests. The field man first collects the gross sample from its point of formation, and the technician then prepares this sample for final examination. Deposits are not homogeneous but may differ in composition from one part of a system to another. It is therefore important that the field samples be taken from the point of occurrence without physical or chemical alteration.

Sampling Adherent Deposits

The removal of a sample that adheres closely to the surface upon which it has been deposited is often extremely difficult. This is true of many deposits in boiler tubes, pipelines, and condensers. It is sometimes possible to remove a short section of a pipe or condenser tube, and then to dislodge the deposit by mechanical or thermal shock.

In most instances, a portion of the deposit must be removed without damage to the surface to which it adheres. Removal of a hard adherent deposit, such as analcite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$), anhydrite ($CaSO_4$), gehlenite ($3CaO \cdot Al_2O_3 \cdot 2SiO_2$), serpentine ($3MgO \cdot 2SiO_2 \cdot 2H_2O$), magnetite ($Fe_3O_4$), quartz ($SiO_2$), or magnesium hydroxide ($Mg(OH)_2$), will require the use of a chisel, a hammer, or an excellent steel scraper. The use of such tools to remove an extremely adherent deposit requires care. A representative sample should be obtained, but damage to the equipment must be avoided. It is often impossible to remove those samples of a deposit that would be most desirable for solving the problem of deposition. Any sample, in such cases, is better than none, even though it may not be the most desirable one.

Hard, adherent deposits are sometimes encountered on the buckets, nozzles, and diaphragms of steam turbines. A closely adherent deposit can be removed from the buckets of a steam turbine by peeling or scraping downward over the surface of the bucket with a sharp penknife, the cutting edge of the knife being used with the point down. A small envelope, with the sealing flap open and extending upward, is a very good receiving receptacle. Squeezing the edges of the envelope will make the sealing flap concave. By holding the top edge below the point of the knife in peeling, the loosened deposit drops conveniently into the open envelope. Similar deposits often found in heat exchangers or evaporators can be removed for sampling by cracking.

Loosely Adherent Deposits

Deposits that adhere loosely to the surface upon which they have formed are readily removed. Many types of scrapers can be used: knife, spatula, spoon, a thin piece of wood, sheet metal, or even cardboard. Deposits of this kind are sludge in steam generators (boilers), cooling towers, cooling systems, air-conditioning systems, feedwater heaters, water softeners, condensers, and heat exchangers, and also biological deposits in various water systems.

Thin Films

Some deposits, particularly on rough or irregular surfaces, may be so thin that scraping does not remove much of the material. If the deposit is not too hard, a stiff bristle brush may be much more effective than scraping. If the deposit is tightly adherent, and the surface is smooth, thermal or mechanical shock will sometimes loosen it. Thermal shock may produce some alteration or decomposition of the deposit; note should be made in the information accompanying the sample when this method has been used.

Biological Slimes

It is frequently impossible to identify a biological slime definitely if it is allowed to become dry before examination. If at all possible, therefore, the deposit should be kept in its environmental water. In some cases, where gas formation is active, as with sulfate-reducing bacteria, it may be necessary to refrigerate the sample during shipment, or to add a bactericide. The latter procedure of course kills the bacteria; it would make preparation of cultures impossible. The discretion of the sampler must be relied upon in such instances.

Selection of Samples

The selection of a sample or samples is usually somewhat limited, but there are instances where a wide choice is possible. In cases where it is possible to select the samples of a deposit, such selection is best guided by a thorough consideration of the problem involved. Very often, the removal of a number of samples will result in more informative analytical data than would be obtained from one composite representing the entire mass of deposit. A typical example is the sampling of deposits from a steam turbine. Samples from each stage are more desirable than a composite sample from all stages. Conversely, in the case of a tube failure in a steam generator, if inspection shows other sections of the boiler to be in satisfactory condition, a single sample from the affected area should suffice.

Deposits sometimes are encountered in layers. Usually it is possible in such cases to select several samples so that the individual layers may be examined in the laboratory, if desired.

Sample Quantity

The most desirable amount of deposit to be submitted as a sample is not specific. The quantity of deposit that can be removed is often limited. In such instances it is better to submit a single mixed sample of half a gram or less than to collect no sample.

A deposit of 5 g is desirable for an extensive X-ray diffraction study, although informative data may be obtained with as little as 0.1 g. A routine chemical analysis usually is possible with a sample of 10 g, but an elaborate laboratory investigation might require as much as 100 g.

Although there is a difference of opinion about the desired amount of deposit to be submitted as a sample, it is definitely best to provide considerably more sample than laboratory examination might require.

Labeling and Shipment of Samples

After collection in the field, the sample must be properly protected to prevent change or contamination during shipment. A glass or plastic container is adequate for samples of deposit only, and a clean wooden box sealed against atmospheric moisture is suitable for samples that include the underlying surface. Biological deposits must be collected and kept in contact with the mother liquor, and be shipped in refrigerated containers.

The gross sample should always be accompanied by a detailed history. This includes the name and description of the equipment from which the sample was removed, the precise location, the appearance and extent of the deposit prior to removal, the exact method used in removing the sample, the temperature and pressure of the liquid or vapor phase from which the deposit was formed, the chemical analysis of the water, and an account of any abnormal or unusual conditions existing during formation of the deposit. Further details are given in ASTM Field Sampling of Water-Formed Deposits (D 887) [*1*].[1]

Laboratory Sampling

The final sampling is made by selecting a small representative portion from the gross sample for examination by special instruments. If the sample is received in contact with its original confining surface, the same precautions must be taken as described earlier in removing it from that surface. If it is possible to make a separation of heterogeneous layers, it may be advisable to do so, and to make separate examinations of these smaller select

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

portions. The composition next to the confining surface may be different from that which was in contact with the water. Separation of these two different surfaces should be made to ascertain this possibility. After the final separations have been made, the handling of the sample for each type of instrument becomes part of a specialized technique for that particular instrument. For example, portions on which index of refraction is required should be *crushed* to final size, whereas the portions should be *ground* for X-ray and spectrographic examination. Various other physical and chemical treatments may be given to portions of the sample undergoing identification.

Methods of Identification

The examination of any deposit begins with visual observation and the recording of the description in terms of size, shape, contour, color, odor, hardness, and magnetism. The choice of subsequent methods for identification is frequently suggested by the visual appearance. In the case of inorganic deposits, the proper step, after visual examination, is to study them under magnification. This often reveals characteristics not visible to the unaided eye. The texture of various layers is more pronounced, and recognition of individual crystals may be possible.

After crushing or grinding, but before other tests are run, it is desirable to heat a small amount of the sample gently in a crucible and to note its behavior. A pronounced darkening of the sample is frequently indicative of organic matter. The odor as the sample is heated can be used to identify many types of organic material, such as carbohydrate, protein, amines, oil, coal, sulfur compounds other than sulfate, and a number of others. The suspicion of a given type of organic compound from the odor on heating may be verified by extracting the sample with a suitable solvent, and using the microscope, X-ray diffraction, or absorption spectroscopy to help confirm the initial suspicion. Table 1 indicates the various techniques applicable to the detection and identification of the types of material listed, and is intended as a reference to the instrumental descriptions that follow.

The identification of water-formed deposits is not a matter of using the proper single method, but of coordinating a number of methods to make each supplement the others [*2,3*]. No single method tells all there is to be known about a sample. Each has a special field of application with its inherent advantages and disadvantages. The applications and limitations of commonly used methods of identification are discussed in the following so that the proper instrument or combination of instruments may be applied to the investigation of these deposits.

Biological Microscope

The term "biological microscope" does not refer to a particular type of microscope but rather to the use to which the microscope is put, namely the

TABLE 1—*Comparison of principal fields of application and limitations of the methods used for identification.*

Instrument	Principal Application	Limitations
Biological microscope	identification of microorganisms in industrial water samples. Recognition of inorganic suspensions and differentiation from organic matter.	number of organisms must be sufficiently great to be observable in the microscopic field.
Chemical (petrographic) microscope	identification of individual crystals and amorphous clumps. Examination of microstructural details. Qualitative microchemical analysis.	particle size must be not less than 10 μm. Crystals must be non-opaque. Sample must be insoluble in immersion medium.
X-ray diffraction	identification of crystalline compounds.	compounds must not be amorphous but particle size may be less than 0.01 μm.
Spectroscope	qualitative detection of cationic constituents.	sample must be low in volatile constituents.
Spectrograph	quantitative estimation of minor cationic constituents.	same as for spectroscope.

examination of biological matter. The essential requirement is to magnify the objects under observation so their distinctive form and features become readily recognizable. The biological microscope operates functionally as illustrated in Fig. 2. Light from a source such as a lamp is reflected in a mirror

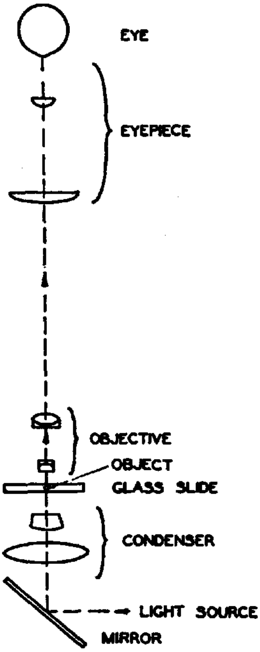


FIG. 2—*Functional diagram of biological microscope.*

located at the base of the instrument. The reflected beam is directed upward through a condenser and through the sample, which has been mounted on a glass slide and covered with a thin cover glass. The image of the microorganisms is magnified as the light continues upward through the lenses of the objective and the eyepiece. The magnified image is either observed directly at the eyepiece or photographed with a camera.

The living matter in biological deposits may consist of either single cell or multicell species performing the functions of growth, reproduction, and metabolism. Wide variations exist, however, in the conditions under which these functions are performed. Indeed the environmental conditions are often quite limited in this respect for any one kind of organism. For maintenance of life some organisms require iron, some sulfur, some carbon, all with or without oxygen, and they may be deprived of these essentials by changes in industrial operations. Thus, in addition to the living organisms, the sample may contain metabolic by-products and skeletons of dead organisms.

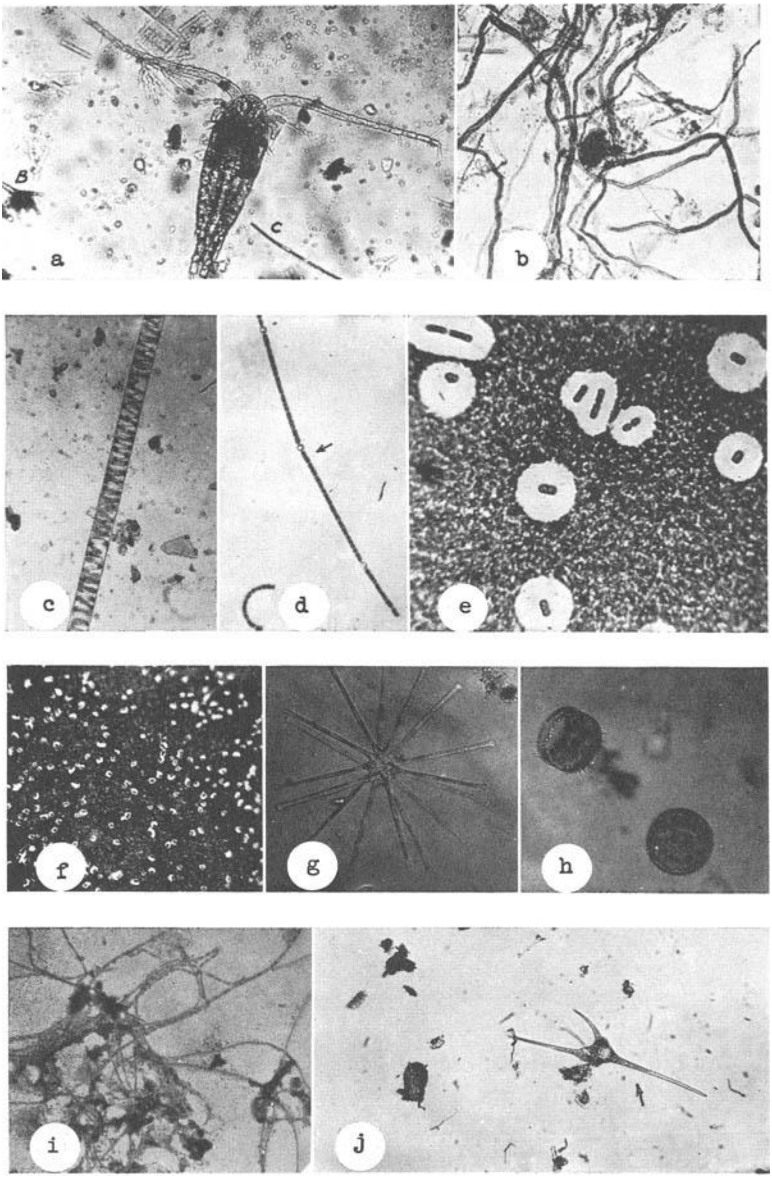
Observations of the material are made by enclosing a small drop of the sample-bearing liquid between a glass slide and a cover glass. The outlines of the objects under examination are observed under transmitted light. The various shapes may be described as similar to rods, filaments, chains, stalks, and capsules. Figure 3 shows some typical examples of magnified biological material.

Identification of the specific species is made by recognition of characteristic shapes and colors or by characteristic reaction to reagents. Some organisms will adsorb specific dyes and be recognizable by this property. Inorganic oxide sheaths may be dissolved from an organism by acids, thereby exposing features not recognizable with the sheath in place. If the sheath is iron oxide, the dissolved iron will color the liquid between the cover glass and the slide, suggesting an iron bacterium.

Recognition by shape is sometimes difficult and, for confirmatory information, the organisms may be inoculated into a culture medium. After a suitable incubation period the medium is tested for specific metabolic by-products of the organism. For example, the formation of hydrogen sulfide in a sulfate culture medium is confirmatory evidence of the presence of sulfate-reducing bacteria.

Not all samples as received in the laboratory are suitable for biological examination. When the number of organisms is so small that a single drop of liquid might not contain any observable individuals of a suspected species, the sample may be centrifuged to concentrate the organisms and the observation made on the concentrate. On the other hand, samples may contain so much clay or other suspended matter as to greatly interfere with the examination. Such samples may be diluted to reduce the concentration of impurities, or separation of biological from inorganic material must be made before mounting the sample under the microscope.

The report of a microscopic examination usually indicates only those recognized microorganisms for which definite proof of presence was estab-



(*a*) (*No. 10*) *Cyclops large organism. Also shows* (*A*) *Synedra,* (*B*) *Ceratium, and* (*C*) *Nastoe.*

(*b*) *Crenothrix with ferric oxide sheath in place.*

(*c*) *Spirogyra.*

(*d*) *Anabena.*

(*e*) *Gram positive bacillus.*

(*f*) *Gram positive cocci.*

(*g*) *Asterionella.*

(*h*) *Stephanodiscus.*

(*i*) *Crenothrix with iron removed and stained with methylene blue.*

(*j*) *Ceratium.*

FIG. 3—*Typical biological shapes.*

lished. Quantitative values are assigned only when specific cultures can be made.

A microscope with three objectives (×10, ×43, and oil-immersion ×97), two eyepieces (×5 and ×10), and an Abbé condenser can be purchased for about $400. A more adequate assembly, including an illuminator and a mechanical stage, can be bought for about $700.

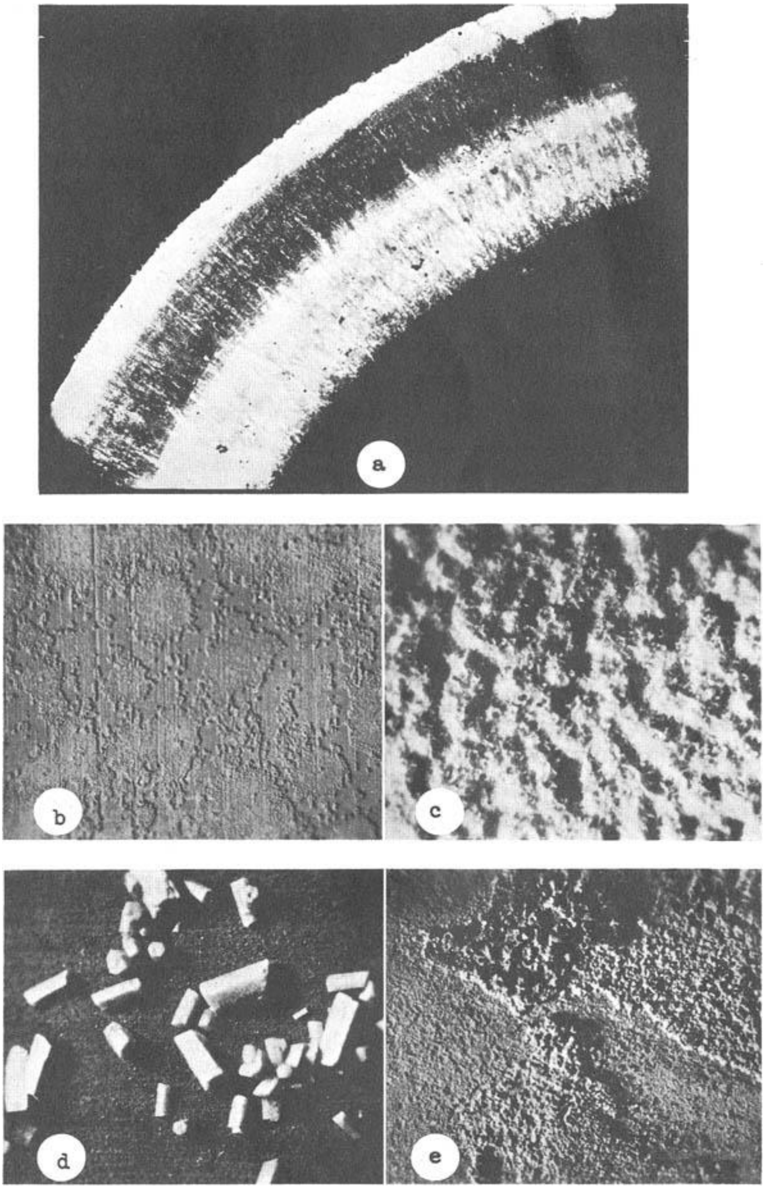
The ASTM Test for Iron Bacteria in Industrial Water and Water-Formed Deposits (Method D 932) [*1*]; ASTM Tests for Sulfate-Reducing Bacteria in Industrial Water and Water-Formed Deposits (Method D 993) [*1*]; and ASTM Identification of Types of Microorganisms and Microscopic Matter in Industrial Water and Industrial Waste Water (Method D 1128) [*1*] provide for identification of some bacteria and other microorganisms of industrial importance. There are other sources [*4–6*] of detailed information on the use of the biological microscope.

The Chemical Microscope

The chemical (or petrographic) microscope is so named because of the accessories and design which make it particularly suitable for the study of both optical properties and microchemical reactions. Rocklike deposits lend themselves most readily to direct examination by this microscope. Figure 4 illustrates the magnified structures of some typical water-formed deposits.

The functional operation illustrated by Fig. 5 is similar to that of the biological microscope with the addition of a polarizer and analyzer. Light from a source such as a lamp is reflected by the mirror and passes through the polarizer and condenser. The polarized light passes through the sample, which is supported by a glass slide mounted on a mechanical, graduated stage. The image of the object is magnified as the light passes upward through the objective, the analyzer, and the cross-hair eyepiece.

When ions in a solution react to form solid particles, the particles usually consist of repeating geometrical arrangements of the atoms in a three-dimensional network. This network of atoms or ions is called a crystal. If conditions were such that only one solid phase could precipitate from a solution, and the conditions of precipitation remained constant, the resulting solid product would consist of one or more cyrstals of the same substance. Ordinarily, however, it is possible for more than one substance to precipitate from a water at the same time, and the conditions of precipitation are seldom constant, so that we rarely have a single homogeneous deposit containing only one crystal phase. Also, variations in the composition of the water and changing conditions may give rise to a deposit consisting of layers of material of varying composition. Berry, Allen, and Snow [*7*] of the U. S. Steel Corp. have described a technique for examination of polished sections by reflected light, using a metallurgical microscope. While their studies were applied to refractories, the techniques are equally applicable to detailed study of the layering in a coherent scale of sufficient thickness. The edge of a deposit is ground approximately flat on a medium-grit polishing paper, after



(*a*) *Striated calcium sulfate scale.*
(*b*) *Ferric oxide scale.*
(*c*) *Magnesium phosphate scale.*
(*d*) *Calcium sulfate lienic hydrate deposits.*
(*e*) *Magnetite scale.*

FIG. 4—*Typical water-formed deposits.*

which the piece is impregnated by immersion in a molten resin, such as glycol phthalate. The piece is removed while still hot, and allowed to cool in air. This resin is fairly hard at room temperature, and allows wet polishing of the surface of the scale without extensive tearing out of individual grains.

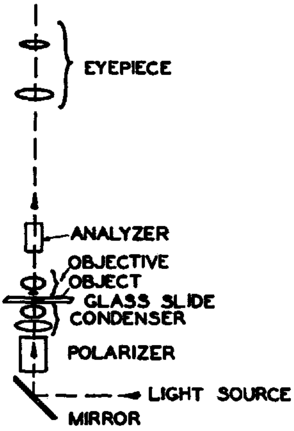


FIG. 5—*Functional diagram of chemical microscope.*

Many of the epoxy resins, especially those of low viscosity, are also excellent impregnating materials. Many crystal phases can be recognized by their shape and brightness under reflected light, even though direct observation of optical properties cannot be made.

In some cases, it is possible to make thin sections of a scale, so that the structure may be examined by transmitted light under the microscope. Observation of birefringence and crystal orientation may suggest the compounds present in such a scale. Most boiler scales and sludges are not sufficiently coherent, however, nor do they consist of sufficiently large crystals for such techniques to be fruitful.

A crushed sample, preferably 100-mesh or finer, is suitable for two types of microscopic examination. Many crystals and compounds in deposits from water can be identified and their amounts estimated by examination of the powder under a chemical microscope equipped with polarized light, or with a petrographic microscope. Identification is accomplished by immersion of the powder in oils of various refractive indexes; determination of the indexes of the crystalline compounds is made by observing their relief against the oil of known refractive index.

Refractive indexes are determined by crushing the sample to a size which will free from the agglomerate as many single crystals as possible without at the same time producing particles too small for clear resolution under the microscope. Sludge particles are often too small to provide optical data. Large-size particles are no deterrent because these can be crushed to sufficiently small size for measurements.

Amorphous material and glasses, as well as crystallized compounds, have optical characteristics that can be measured and may form a basis for identification. For examination of this type of material, optical microscopy is superior to X-ray diffraction.

Chemical microscopy is simply the technique of performing normal qualitative chemical tests on a microscope slide. The advantage of the microscope for this purpose is twofold. In the first place, observation of the crystals formed by these qualitative tests may permit distinction between several ions, all of which form precipitates with a given reagent. The second advantage is that the tests are quite rapid, and may be carried out with a very small volume of solution. This is of utmost importance where the size of the sample is limited. Chamot and Mason's *Handbook of Chemical Microscopy* [*8*] gives details for carrying out most of the common microchemical tests, and also gives illustrations of many of the crystals formed by these reactions. Tests for phosphate, ferrous and ferric iron, copper, zinc, nickel, calcium, magnesium, manganese, sodium, sulfate, chloride, and a number of others can be readily made by this method.

The results from observations with the chemical microscope include a description of the appearance of the magnified gross structure, and a report of the presence of specific compounds and elements as determined from their refractive indices and reactions with spot-test reagents. The chemical microscope is a standard instrument and differs from the biological microscope in that it is equipped with a graduated rotating stage and polarizing prisms. Normal cost is between $650 and $1400. Detailed procedures for petrographic examination and tables of optical data are available in standard texts [*9–12*].

X-Ray Diffraction

X-ray diffraction produces a pattern of lines on photographic film or peaks on a recorder chart. The position of the lines on the film or the peaks on the chart for any given type of X-radiation is determined by the distances between layers of atoms in the crystalline components of the sample. These interatomic distances can be calculated from the measured positions of the lines or peaks, and used to identify the crystalline compounds of a sample.

The essential functioning of the X-ray diffraction unit is illustrated in Fig. 6. X-rays pass through a collimator tube which restricts the beam to a very

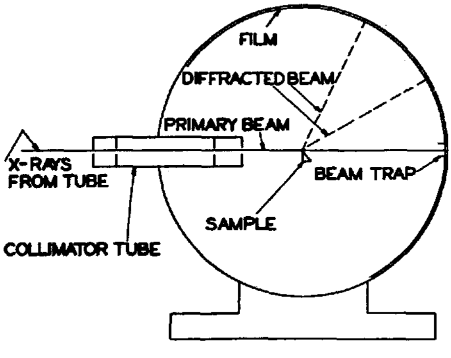


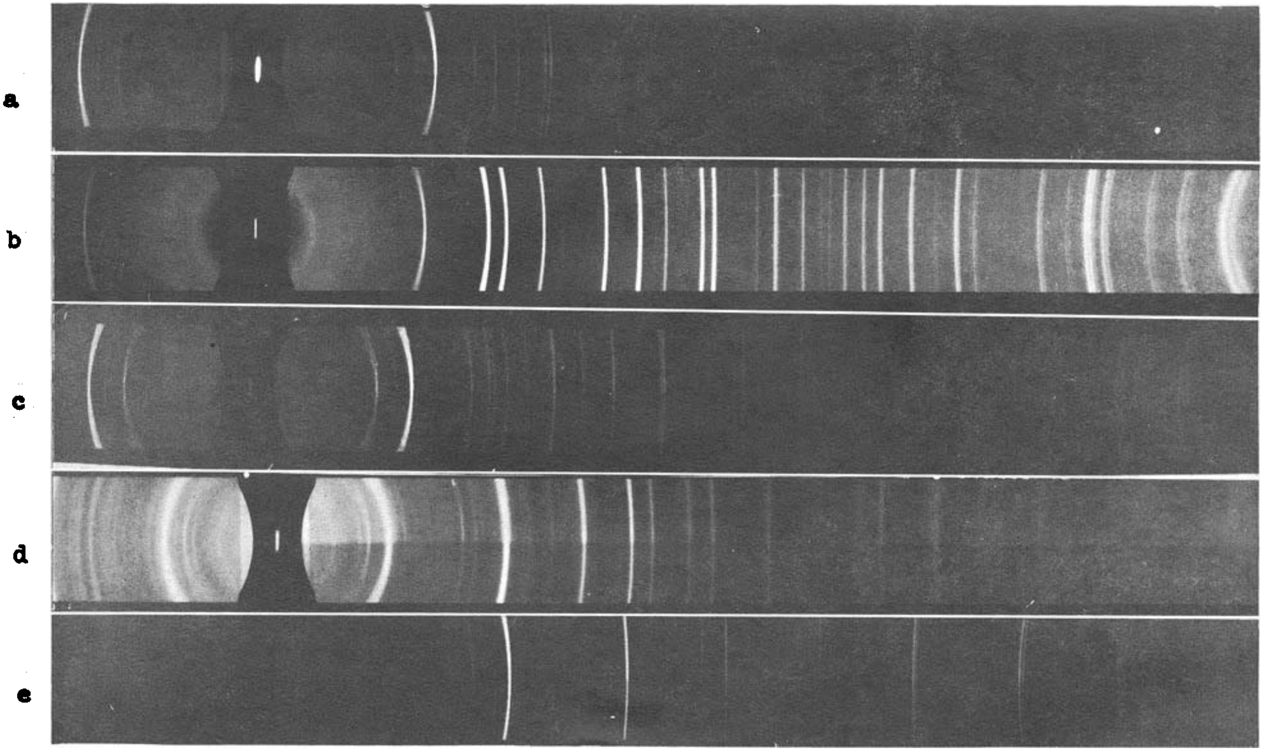
FIG. 6—*Functional diagram of X-ray-diffraction unit.*

thin pencil of parallel rays. The collimating tube may be an integral part of the camera. The pencil of X-rays is intercepted by the sample located on the central axis of the camera. A large percentage of the beam penetrates the sample and is caught and dissipated in the beam trap. A small fraction of the primary beam is diffracted to the outer circumference of the camera and strikes the photographic film at definite positions depending upon the angles of diffraction. The magnitude of these angles of diffraction is determined by the atomic arrangement within the crystal compound producing the diffraction. After sufficient exposure, the photographic film is developed and patterns are produced, those shown in Fig. 7 being typical. These are compared with patterns or data produced by standard compounds. When the position and intensity of lines from the pattern of an unknown compound match those from the pattern of the standard, the unknown material is identical with that of the standard. Identification therefore requires a series of standards or a set of authenticated diffraction data. The best single source of crystal data is the "Card Index File of X-ray Diffraction Data for Chemical Analysis," available from ASTM. Details of procedure, with additional literature references, are given in ASTM Identification of Crystalline Compounds in Water-Formed Deposits by X-Ray Diffraction (Method D 934) [*1*].

The X-ray diffraction method of analysis is essentially one of identification of crystalline compounds present in a deposit. It is sometimes referred to as the "powder diffraction method," a name that indicates the most useful form in which samples are prepared for analysis. Most crystalline, water-formed deposits do not occur as powders but must be finely ground for proper mounting and for crystal distribution. Sludges usually are very finely divided but may cement or harden on drying and may also contain flakes or larger particles which are truly part of the sample. The only limitations on the type of sample that can be used for powder diffraction are that it be crystalline, that it be susceptible to grinding, and that a sufficient amount be available for manipulation.

Although the X-ray diffraction method is not usually considered to be a micro-method, with special care an analysis can be made with less than 10 mg of sample. Exposure of a sample to X-rays may require from 1 to 4 h, and samples subject to change in the atmosphere in that length of time may be protected by enclosure in an airtight capsule during exposure.

In recent years, direct measurement techniques of X-ray diffraction have been introduced, employing counter tubes for detection of X-ray intensity. These instruments have distinct advantages. Ordinarily, they employ a somewhat larger sample, so that better integration of the overall composition of a sample is possible. Further, although only one sample may be run at a time, the method is considerably faster than photographic methods, because under most circumstances sufficient of the pattern can be run in a matter of 30 min to 1 h. For detection of the presence or absence of a certain phase, it is necessary to scan only over an area where a line unique to the



(a) Calcite, $CaCO_3$. *(d) Magnesium hydroxide, $Mg(OH)_2$.*
(b) Hematite, Fe_2O_3. *(e) Magnesium oxide, MgO.*
(c) Quartz, SiO_2.

FIG. 7—*Typical X-ray-diffraction patterns.*

compound being sought is located. For instance, a time 2 or 3 min is sufficient to determine the presence of quartz in a turbine deposit. The pattern obtained is more nearly quantitative than that from film. Accurate quantitative analysis, however, must depend on careful consideration of the absorption characteristics of the sample, whether one is using the photographic or direct-measurement technique. Because of the fact that a large, flat sample is used, direct-measurement techniques are somewhat prone to preferred orientation unless the sample is prepared very carefully. This property is sometimes an advantage in qualitative analysis, as it may markedly increase the intensity of the strongest line, thus allowing detection of smaller amounts. A good example of this is anhydrite, which can be detected in a sludge in concentrations as low as 1 percent because of this orientation, even though the anhydrite pattern is not exceptionally strong.

In the absence of substances in the sample that give high background, the sensitivity of the direct measurement technique is about the same as that of the photograph for those compounds which are well crystallized. With poorly crystalline substances, the advantage is decidedly with the direct-measurement, or diffractometer, technique because broad peaks whose intensity is not greatly above background are much more easily detected by variation in the background level on a chart than gradual differences in blackening on a photographic film. Thus, the sensitivity for poorly crystallized magnesium silicate in a boiler sludge is frequently appreciably greater with a diffractometer than with photographic methods.

The method does not ordinarily detect low percentages of compounds in a deposit. The minimum amounts that can be detected may vary from 1 to 30 percent, depending upon the efficiency of the compound as a diffractor and the absorption characteristics of other materials in the mixture. For example, 1 percent copper can be detected in magnesium hydroxide, whereas from 5 to 10 percent copper must be present for detection in an iron oxide sample. Copper is a good diffractor and magnesium hydroxide has low absorption compared with that of the iron oxides. Poorly crystallized compounds, such as frequently occur in the case of magnesium silicate, may escape detection when present in amounts as great as 30 percent.

Solid solutions frequently can be detected if the solute has appreciably changed the lattice dimensions of the solvent phase. Solids of the solid solution type are common with such sodium salts as are deposited in superheaters and drypipes.

Crystal size or degree of crystallization may be determined qualitatively from the uniformity and breadth of the diffraction lines in a pattern. It is frequently possible to differentiate between the poorly crystallized and the well-crystallized species in a mixture.

In both of the foregoing techniques, the diffractometer has a marked advantage over the photographic method. Photographic film is not entirely dimensionally stable, and it is therefore sometimes difficult to detect very slight solid solution. Also, in a camera that will allow reasonable exposure, the lines on the film are relatively small, and it is not possible to detect very slight variation in line width.

By scanning over the area of interest at slow speed with the diffractometer, peaks of sharp lines can be located within 0.01 deg, thus permitting detection of extremely slight solid solution. Further, by employing narrow slits and fast time constants in the instrument, it is possible to achieve extremely high resolution, of an order that would be almost physically impossible on a photographic film. This allows at least partial separation of diffraction lines of well-crystallized substances which are so slightly separated that they might appear as a single line on a film. Of course, if the lines are exactly superimposed, they cannot be separated even by high-resolution techniques.

There are, however, several distinct advantages to the photographic method. First, a pattern of high quality can be obtained on a very small amount of sample, such as 2 or 3 mg. Second, in a sample that gives a very complex pattern, such as one containing a large number of crystal phases, certain compounds found in deposits from water are prone to give somewhat spotty lines if they are not ground sufficiently fine. These spotty lines stand out quite well on the film, and permit separation of the pattern into two distinct types of lines, which frequently aids identification. Quartz, calcium sulfate, calcium carbonate, and analcite are compounds that often develop rather large crystals and are particularly likely to give spotty lines. The third advantage for film lies in the ease with which a number of X-ray patterns may be compared by placing the films edge to edge on a viewing box. This is done much more easily with films than with charts.

Because of its ability to give useful patterns with samples consisting of very small crystals or of crystals that are opaque to light, the X-ray method is generally more widely applicable to deposits than the petrographic microscope. The microscope, however, can give useful information about the state of aggregation, can detect amorphous materials which contribute little or nothing to the X-ray pattern, and permits identification of a single crystal on a whole slide of material, thus providing a sensitivity much greater than that of the X-ray method, provided the crystal is of sufficient size. Where both instruments are available, it is generally advisable to run the X-ray diffraction pattern first, thus giving a good average composition of the sample, and to use the petrographic microscope to detect glasses and amorphous materials—those substances present in too small amounts for X-ray detection—and information about the state of agglomeration of the sample.

The report of an X-ray diffraction analysis should give the name and formula for the crystalline species identified, together with an estimate of the relative amounts of the identified phases present, and any remarks regarding crystal size, solid solution, or other pertinent information that may have been obtained.

The equipment used in the photographic method consists essentially of a source of constant high-voltage electrical current, an X-ray diffraction tube in an appropriate mount, and a cylindrical camera. Suitable commercial units are manufactured at a cost of $7000 or more.

The diffractometer is considerably more complex, and consists of a source of highly stabilized high-voltage electrical current, the X-ray tube, a counter tube, an amplifier, ratemeter and recording circuits, and an adjustable goniometer for mounting the counter tube and the sample and providing for rotation of the counter tube about a focusing circle upon which are the X-ray tube, the sample, and the counter tube. Such equipment is available as commercial units starting at about $14 000.

X-Ray Spectroscopy

Secondary X-rays are generated when X-rays of sufficiently short wavelength are absorbed by matter. These secondary rays are characteristic of the elements present in the irradiated material. The X-ray spectrograph is an instrument for separating the X-radiations from the various elements of the absorbing material, and for detecting and recording their wavelengths and relative intensities. The apparatus used for such detection is not greatly different from the X-ray diffractometer, and most of the components of one instrument are used for the other.

The chief difference lies in the fact that the sample is the source of the X-radiation in X-ray spectroscopy, rather than the X-ray tube, as in diffraction. A single crystal, cut parallel to one of the principal planes, takes the place of the powdered sample in the diffractometer technique, and diffracts the various wavelengths of X-rays at different angles, thus allowing each wavelength to be separately detected by the counter tube.

X-ray spectra are very simple, consisting at the most of about 15 lines, not all of which are of significant intensity. These lines as a group vary in wavelength in a regular manner with the atomic number of the element. Complete X-ray spectra are therefore known for all elements. The wavelengths have been precisely calculated, and most of them have been very carefully checked experimentally.

The smaller the atomic number of the element, the longer the wavelength of the corresponding lines of the X-ray spectra. "L" series spectra are used in analysis for the heavy elements, that is to say, those heavier than barium, and the "K" series for the lighter elements. Elements of atomic number smaller than titanium give rise to radiation of sufficiently long wavelengths that their absorption in air is too great for good sensitivity. A helium atmosphere is therefore maintained from the sample, past the analyzing crystal, to the window of the counter tube. This has allowed detection of elements as light as sulfur. Softer radiation than this is absorbed strongly in the window of sealed counter tubes, and counting losses are consequently high. This has been solved recently by the use of a flow counter tube employing a thin organic film such as Mylar[2] and Formvar [2] as a window in the tube, and, since this tube is not gastight, allowing the counting gas to flow continuously through the tube. Elements as light as sodium have been detected by such counters, and quite useful intensities have been obtained for aluminum, silicon, phosphorus and, except for quite low concentrations, for magnesium. This method is useful over a very wide range of concentrations, from as low as a few parts per million in favorable cases up to 100 percent. Some elements influence the excitation of others in a manner that would be predicted from a knowledge of the laws of absorption of X-rays and the periodic table of the elements.

Optical Spectroscopy

Emission spectroscopy is a method of analysis for elements that depends on the fact that when atoms are excited by either thermal or electrical means, light is given off as discrate wavelengths as the atoms return to their normal state. If this light is defined by a slit, separated into its various wavelengths by a prism or diffraction grating, brought to a focus by a lens system and viewed with an eyepiece, recorded on film, or measured by photoelectric means, the elements that have given rise to the spectral lines can be identified by locating the characteristic wavelengths in published tables of spectra.

The common sources of excitation for spectrographic analysis are flame, d-c arc, a-c arc, and high-voltage spark. Each has special uses, and the advantage and limitations of each one will be discussed briefly.

The flame of a Bunsen or Meker burner is at a sufficiently high temperature to excite the atoms of only the alkali and alkaline earth metals and a few others, if the concentration is sufficiently high. Propane-air, propane-oxygen, acetylene-air, oxygen-acetylene, and oxygenhydrogen flames produce successively higher temperatures. The atoms of about 43 elements can be excited with acetylene-oxygen or hydrogen-oxygen flames. The sensitivity for many of these elements is not very high. The flame is a highly reproducible source, however, if fuel and air or oxygen pressures are carefully controlled; it is quite satisfactory for the analysis of solutions which represent ideally homogeneous samples. The flame spectrophotometer is actually a small direct-reading spectrograph.

The d-c arc, which is operated at a voltage from 50 to about 250, is an extremely sensitive source because it is capable of producing very high temperatures. The detection of a number of elements in parts-per-million concentrations in a solid sample is quite possible with this energy source. The reproducibility of this source is somewhat limited because of the tendency of the arc to wander. It is therefore considered highly satisfactory

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[2] These are registered trademarks of E. I. du Pont de Nemours & Co., Inc., and Shawinigan Products Corp., respectively.

for qualitative analysis because of its sensitivity, but it is probably not the best one for quantitative analysis.

The high-voltage a-c are, using a voltage of 1000 or more, is a steadier and more reproducible source than the d-c arc and, except for extreme cases, has adequate sensitivity for most of the elements. The chief drawback to this source is the dangerously high voltage, which requires safety interlocks and careful shielding for protection of the operator.

The high-voltage spark is a very reproducible source, using 10 000 to 50 000 V across the two electrodes, and a synchronous interrupter to extinguish the spark and prevent it from becoming an arc. The discharge is predominantly electrical in nature, rather than thermal, and in many cases it is cool enough that one can handle the electrodes immediately after exposure. A condenser and inductor are usually added to this circuit to produce some heating effect. Although the reproducibility of the discharge is quite high, because of the low temperature comparatively little material is consumed, and sampling problems are sometimes major. The spark source, however, is readily adapted to the analysis of solutions, where a completely homogeneous sample is possible.

The simplest type of dispersing instrument is the visual spectroscope, commonly called the Bunsen spectroscope. It consists of a focusing lens, a slit, a prism, and a telescope on a movable arm for viewing the spectra produced. In addition, a wavelength scale is usually sent through the prism from a side tube, and brought to focus in the telescope just above the spectrum of the sample to be studied. The spectroscope is limited to the elements that have lines in the visible part of spectrum, and is generally considered to be a qualitative instrument, although some estimate of amounts can usually be made. The instrument is simple and it has many potential uses, but it has the drawback of poor dispersion, which makes it difficult to resolve some lines that are normally close together. In addition, simultaneous observation of all parts of the spectrum is not possible.

The spectrograph employs either a prism or a diffraction grating as the dispersing device and, for general use, photographic film as the recording medium. For routine production control, where the same elements are normally being determined, it is entirely practical to replace the photographic film with a photoelectric device for recording the relative light intensities of the various elements to be analyzed. Generally, however, problem in industrial water treatment are sufficiently varied that the direct-reading spectrograph would be of limited use.

Metals, which conduct electricity, can be used as their own electrodes, but most of the materials encountered in industrial water treatment are nonconductors. Therefore, the sample is usually placed in a small core in a carbon or graphite electrode, which is generally made the lower electrode. The upper electrode is usually a plain carbon or graphite rod, ground to a blunt point. The cavity in the lower electrode may be formed with a center post, to decrease wandering of the arc, and may also be undercut, the narrow neck tending to increase the arc temperature by decreasing the conduction of heat down the electrode. Metal electrodes are occasionally used for special cases, but graphite is quite satisfactory for general work.

Very satisfactory electrodes can be made for the a-c arc and high-voltage spark by thoroughly mixing the powdered sample with graphite, often with a buffer also, and pressing into a pellet under high pressure. The pellet is placed in a metal holder, the other electrode being a tipped carbon rod. This technique is not wholly satisfactory for use with the d-c arc, because of the high temperature.

Fineness of the powdered sample is important. Since the sample usually melts in the d-c arc, a 200-mesh sample is adequately fine. For the a-c arc and high-voltage spark, however, where relatively little material is consumed, the sample should be at least 325-mesh, or should be fused with a flux to ensure uniformity. Alkali metal borates are satisfactory fluxes for most samples. Solutions are atomized into the flame or spark. In the latter case, a rotating graphite disk which dips into a container of the solution can be used; the spark is generated at the side of the disk opposite the solution container. One great advantage for the solution method is the ease with which synthetic standards are prepared, and the simplicity of the addition of an internal standard to the unknown sample to serve as a reference. This procedure increases accuracy by allowing the determination of concentration ratios rather than absolute values of concentration.

ASTM Committee E-2 on Emission Spectroscopy publishes a number of methods in a single volume for determination of impurities in various materials. Most of these, however, are not applicable to deposits from water because of the lack of a uniform matrix. Possible methods have been published elsewhere, and are currently being submitted to Committee E-2 for inclusion in future publications. These so-called "Universal Methods" are generally of somewhat lower accuracy than those for determining impurities in rather pure materials, but are of much wider applicability. It seems probable that many of these will be adaptable for use in deposits from water.

A complete spectroscope, with an adequate d-c arc source and various accessory materials, can be purchased for slightly under a thousand dollars. Spectrographic units, which include microphotometers for measuring the photographic film or plate, start in the neighborhood of $13 500, and may run as high as $45 000 (with computer interface and cathode ray tube display, up to $160 000), depending upon the complexity of the equipment desired.

The microphotometer is actually a dual instrument. It normally consists of equipment for projecting a reference film, on which the location of the sensitive lines of the various elements are indicated, beside that of the unknown spectrum for qualitative analysis. In addition, a densitometer portion permits determination of the photographic blackness, expressed as percent transmittance, for any given line. A comparison of photographic blackness with known samples is used to plot working curves for the various elements to be determined quantitatively, and the transmissions of the lines on the unknowns are converted to concentrations from these curves. The results of spectrographic analysis are recorded as elements, without indication of the state of combination. A number of standard reference books are available for all operations dealing with the spectrograph.

Electron Microscope

Many particles of sludge, as well as certain corrosion products, are too finely divided to be studied with an optical microscope. These small particles can often be profitably studied by electron microscopy. The electron microscope is similar to the optical microscope in many ways, but the entire optical path is in high vacuum. Electrons are generated by a hot filament, and are driven from the filament by a focusing cap at high negative potential, located immediately behind the filament. The electron beam is further focused by a series of electrostatic or electromagnetic lenses, correponding to the condenser in an optical microscope. The crystals, or other matter making up the sample, absorb electrons according to their thickness and the absorbing power of the atoms, and the shadow thus formed is viewed on a fluorescent screen, or photographed. The resolving power of the electron beam is very high, and magnification of the photographic plate may be used to bring out more detail.

The sample for examination should be dispersed as much as possible, as agglomerates of a large number of particles cannot be studied except at the edges. A thin film of a resin such as Formvar or collodion is perpared by placing a drop of solution of the resin on water and allowing the solvent to evaporate. The film is then picked up on a platinum screen, and the sample deposited on the film and allowed to dry.

A second technique that may be applicable is the replica technique, normally used to study metal surfaces. In this method, the resin is applied to the surface to be studied, allowed to dry and then stripped off, usually by immersion in water. The film retains the contours of the surface to which it was applied; thus it is thinner where there were elevations and thicker where there were depressions. The film is removed from the surface of the water on the platinum screen, as in the foregoing, and viewed with the microscope. The replica may be shadowed with chromium metal evaporated on the surface to improve contrast.

Much can be learned about the crystal shapes and the sizes of sludge particles, the type of material which acts to bind them together, and tendencies to twin, or branch, by study of electron micrographs. Most of these phenomena occur in crystals that are under 1 μm in size, and this makes study with the optical microscope nearly impossible. Because certain unique properties of a crystalline substance, such as refractive index, cannot be measured with the electron microscope, this instrument should not be considered a means of identifying a completely unknown substance. Rather, identification of the phases should be completed prior to the electron microscope study.

Molecular Absorption Spectroscopy

The identification of organic substances usually presents some problems not common in the inorganic field. Most of the substances occurring in water-formed deposits are either not crystalline, or they are sufficiently complex mixtures that the crystal phases would not be identifiable by an X-ray diffraction pattern. Many are soluble in the oils used for refractive index determination, which limits the use of the microscope. Although methods such as melting and boiling points, refractive index, elemental analysis, and similar techniques can be used in some cases to identify pure compounds, none of these is generally applicable to deposits, which usually are not pure.

Most organic compounds, and many inorganic as well, show sharp absorption bands in the infrared region of the spectrum. These absorption bands have their source in different modes of vibration and rotation within a molecule. The most useful analytical wavelength range is from about 2 to 15 μm, or slightly longer in the case of the halogens. The following types of linkage give bands in specific regions, which can be used to characterize the particular group: C—H (aliphatic), C—H (aromatic), N—H, O—H (phenolic), S—H, C—O, C=O (aldehyde), C=O (acid), C—C, C=C, C≡C, C≡N, C—Cl, C—Br, C—I. Each specific absorption band will shift somewhat, due to changes in adjoining groups, but the band will still be within the same general region.

The source of infrared radiation may be a lamp whose filament operates at a low temperature, thus giving more infrared and less visible light, or it may be a Globar (see footnote 2) element. The temperature of the source must be carefully controlled to prevent change in the distribution of spectral intensity.

The light from the source is passed through the sample, then broken up into its various wavelengths by a prism, usually of quartz or rock salt. Alternatively, a diffraction grating may be used, but care to prevent interference from overlapping orders must be taken. In the 2 to 15-μm range commonly used for survey work, a rock salt prism is generally employed, as the transmission of quartz drops off sharply beyond 3.5 μm. Rock salt is also the usual cell window for nonaqueous solution techniques.

After isolation of the desired wavelength band by a variable slit, the radiation falls on a detecting and measuring device, most commonly a thermocouple. Lead sulfide photocells are more sensitive detectors for wavelengths up to about 5 μm.

Scanning of the absorption spectrum is accomplished by rotation of the prism rather than by movement of the slit. The output of the detecting device is amplified and fed to a recorder.

A most useful survey device for completely unknown nonvolatile solid samples is the potassium bromide pellet technique. The sample is ground briefly with powdered potassium bromide and the mixture is placed in an evacuable die. A mechanical vacuum pump removes the entrapped air, and the mixture is then pressed at about 103 425 kPa (15 000 psi). The absence of air results in a solid pellet free of bubbles, which is used as the absorber. This technique is not fully quantitative, but does tell where the absorption bands lie.

More quantitative results are obtained by selecting solvents that do not absorb in the region of interest and running the spectrum in these solvents. Concentrations employed are of the order of 1 to 10 percent.

Gases also usually give characteristic infrared absorption bands, and these bands are the basis for continuous monitoring of gas streams.

A few typical applications to water-formed deposits are the detection of oil in turbine deposits and classification as to type, determination of the type and degree of degradation of amines, and possible identification of the source of stream pollutants.

Atomic Absorption Spectroscopy

Another type of absorption spectroscopy makes use of light absorption by atoms rather than by molecules. When atoms are diffused by atomization into a flame, these atoms absorb light of the same wavelength as is emitted at high temperature by that same element. The amount of light absorbed by the atomized atoms is proportional to the element concentration in the vapor of the sample flame.

For example, nickel is to be determined in a sample of water. The water sample is atomized into a wide vaporizing oxyacetylene flame. A beam of light containing radiation emitted from a nickel source is passed through the sample flame. The absorbance of the nickel radiation in passing through the flame-containing nickel atoms is measured by a photometer. The amount of nickel in the sample is determined by reference to a calibration curve showing the relationship of absorbance to concentration.

Solutions in the micrograms-per-litre range of concentration may readily be tested. Scales and solid deposits can also be analyzed with good agreement with wet chemical analysis. The solid samples are first taken into solution and the solutions are atomized into the flame in a manner similar to that for water samples. The method has the advantage of speed, high sensitivity, and relative freedom of interference of one element on another.

Complete atomic absorption spectrometers are priced to $3000 to $8000.

The foregoing descriptive material is intended to suggest some uses of instrumental methods to aid in the identification of water-formed deposits. Some of these methods are described in detail in various ASTM methods. Others are described more fully in the references.

Summary

The primary object of all sampling procedures is to bring the original specimen to the place of observation or analysis without alteration of composition, structure, or physical properties. Methods of microscopy, diffraction, and spectroscopy provide means for determining facts about the chemical and physical nature of the sample which are not available by other means. According to the type of information desired about the sample, there is a choice of methods, each of which is highly specific. The fields of principal application and limitations are compared in Table 1.

To indicate further the kind of information each method provides, a typical analysis report for each method is given in Table 2 on two samples of water-formed deposits.

TABLE 2—*Typical report form for results by different methods of identification for two different samples.*

Sample A		Sample B	
Chemical Analysis			
SiO_2	19.7	SiO_2	17.9
Fe_2O_3	26.6	Fe_2O_3	2.6
CaO	10.8	CaO	30.8
MgO	16.2	MgO	17.9
SO_3	0.1	SO_3	0.1
P_2O_5	12.3	CO_2	24.2
Cu	5.4	Loss on ignition	30.5
Loss on ignition	8.5		
Microscopical Analysis			
Considerable amount of iron oxide present in colored bands. Some hydroxyapatite and considerable amount of poorly crystalized compound, probably magnesium silicate. Small quantities of dendrites of metallic copper.		Large amount of highly birefringent calcite present. Magnesium silicate also present. Iron oxides present as a minor constituent.	
X-Ray Diffraction Analysis			
Hematite, serpentine, hydroxyapatite, and metallic copper all identified with probable percentages in the order named. Particle size for the serpentine and the hydroxyapatite very small.		Calcite and serpentine present in about equal amounts. Serpentine present in extremely small particle size while the calcite was present in two forms, one in crystals of quite large size and the other in crystals of very small size.	
Spectroscopic Analysis			
Constituents over 5 percent: Si, Fe, Ca, and Mg Constituents 0.5 to 5 percent: Cu Constituents 0.05 to 0.5 percent: Mn and Cr		Constituents over 5 percent: Si, Ca, and Mg Constituents 0.5 to 5 percent: Fe Constituents 0.05 to 0.5 percent: Zn, Al, and Mn	
Spectrographic Analysis			
Mn	0.13	Zn	0.43
Cr	0.07	Al	0.17
Ni	0.01	Mn	0.08
Cu	5.29	Pb	0.02

A typical report from the examination of water by the biological microscope is as follows:

Sample A—Organisms of the short rod-shaped variety were observed in clusters of 1 to 10 surrounded by a mucoid capsule. Considerable quantities of rust-brown hydrous ferric oxide surrounded the capsules. The organism is identified as an iron bacterium of the genus *Siderocapsa*.

Sample B—Sample contained a number of protozoa which moved quite rapidly across the field of vision of the microscope. Living diatoms of characteristic shape were present along with other isotropic, suspended, inorganic materials. Algae of both the green filamentous and the unicellular variety were present.

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Chapter 14—Chemical Analysis of Deposits

Many of the difficulties that arise during the industrial use of water are closely related to water-formed sludges, scales, and corrosion products. These water-formed deposits are the accumulations of insoluble material derived from the water, or are formed by the reaction of water with surfaces in contact with it. The composition of such deposits can be used to diagnose the reason(s) for deposition, to determine preventive treatment of either the water or its environment, and to effect their removal. A thorough and accurate analysis is an important beginning in this process.

The analysis of water-formed deposits must be versatile and comprehensive in order to handle the most complex sample. It must also be flexible enough to handle the simplest samples easily and efficiently. The usual quantitative analysis will yield the elemental composition of the major constituents of such deposits. When single elements or simple compounds predominate, such an analysis is probably sufficient. For more complex deposits, however, other tools must be used to determine accurately the combinations of these elements. These include emission spectroscopy, X-ray diffraction, X-ray fluorescence, electron probe microanalysis, flame photometry, atomic absorption, petrographic microscope, and the electron microscope. A method for atomic absorption and spectrographic analysis is outlined in ASTM Testing Water-Formed Deposits (Method D 2331) [*1*][1]; a procedure for identification by X-ray diffraction is dealt with in ASTM Test for Identification of Crystalline Compounds in Water-Formed Deposits by X-Ray Diffraction (Method D 934) [*1*]; X-ray fluorescence is covered in ASTM Analysis of Water-Formed Deposits by X-Ray Fluorescence (Method D 2332) [*1*]; flame photometry in ASTM Test for Sodium and Potassium Ions in Industrial Water and Water-Formed Deposits by Flame Photometry (Methods D 1428) [*1*]; and microscopy in ASTM Examination of Water-Formed Deposits by Chemical Microscopy (Method D 1245) [*1*]; These and other instrumental techniques are also discussed in Chapter 13.

It is often possible to determine the source or cause of water-formed deposits from the results of chemical and physical analyses. The treatment

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

for removal or prevention of such deposits can thus be accomplished scientifically instead of by trial and error.

Frequently the analyst must know the composition of the water involved if he is to make an accurate diagnosis of industrial water deposit problems. In addition, information on the type and composition of equipment through which the water passes, on the type of water treatment used, and on temperatures and pressure existing in the system, can be useful. With this information and the results of his own analysis, the chemist usually is able to suggest a cause and cure for the water-formed deposit when he reports its chemical composition.

Care must be exercised in selecting a representative sample for analysis, since the value of an analysis is related to the sampling technique employed. The analysis represents only that material actually analyzed, and, thus, the information gained depends upon precise knowledge as to where and how the sample was obtained. Sampling practice is dealt with in Chapter 13 and ASTM Field Sampling of Water-Formed Deposits (Method D 887) [*1*].

Preliminary Examination of Deposits

The method of preparing a sample for analysis depends to a great extent on the type of water-formed deposit: scale, sludge, corrosion product, or biological deposit.

Immediately after removing the deposit from the container, its characteristics should be recorded for later comparison with observations made during the field sampling. Photographs are a very good form of record. Pertinent information includes quantity, color, dimensions, hardness, magnetism, odor, contour, structure, and consistency. It is especially important to note whether the sample was received in place on its confining surface. In removing deposits from confining surfaces, great care must be exercised to avoid contaminating the sample with particles of the surface.

When significant differences in deposit structure are visible, such as laminations or colored bands, it may be desirable to divide these portions and analyze them separately. Separations can be made with a sharp blade, preferably under a low-power microscope. A separate bottle should be used for each portion.

The entire sample or a representative portion should be freed from water and oil so that it may be properly pulverized. If the material is very wet, it is best to decant off the excess liquid (mother liquor) or remove the solid material by filtration, and first to air-dry the sample or to dry it at a low temperature such as 35°C to prevent loss by spattering. If the air-dried sample smears or agglomerates when tested for pulverization, the sample should be extracted with organic solvents, such as chloroform, and redried at 105°C. If important to the solution of the problem, the solvent may be evaporated and this extractable matter examined.

Drying at 105°C and organic extraction constitute the first treatments if mother liquor is absent. The dried material finally should be ground in a mortar and quartered down to a sample of 10 or 15 g. This sample should be further ground to pass a U. S. Standard Series, 149-μm (No. 100) sieve and then should be bottled and tumbled to ensure thorough mixing. The bottle should be labeled with all information necessary to identify its contents completely.

Preliminary tests on the sample will often reveal sufficient information for the analyst to make a direct approach to the analysis rather than to follow the scheme discussed later. A spectrograph may be used for a quick determination of the elemental major, minor, or trace constituents.

X-ray diffraction equipment operated by skilled personnel can be extremely useful for identifying compounds. Such equipment is not always accessible and as a substitute, the petrographic microscope is very useful for the initial examination. A simpler microscope, although limited in its applicability, is useful if a petrographic model is not available.

If sufficient information accompanied the sample of water-formed deposit, shrewd guesses can be made about its likely composition. Preliminary tests for these suspected constituents may be accomplished by means of spot tests [*2*] and by simple qualitative tests. For example, carbonates will react with acid to liberate carbon dioxide; iron can be dissolved in acid and precipitated with ammonium hydroxide; sulfide can be detected by heating with acid and noting the odor of hydrogen sulfide; and oil can be detected by extracting with chloroform, evaporating, and examining the residue. Standard analytical texts will include complete lists of such qualitative tests.

Analysis of Deposits

Any analytical scheme can be only a guide, and the analyst must use his skill and ingenuity in carrying out or modifying such a scheme. It is impossible to draw a blueprint that will fit rigidly all water-formed deposits that may confront the analyst. The amount of sample available may dictate that only a few tests be made. Preliminary examination may show that only a few tests are needed for determination of the important constituents.

Frequently, direct determinations for single constituents can be made without going through a sequential analysis. Copper can be selectively extracted with ammoniacal persulfate and the amount of copper determined photometrically from the color of the extract. Silica can be dissolved from the sample by molten sodium hydroxide and the extracted silica determined colorimetrically with the molybdate-blue procedure. These and other relatively rapid determinations of one or more constituents are given in ASTM Method D 2331.

The analysis scheme shown graphically in Fig. 1, and the separate steps are discussed in the following paragraphs.

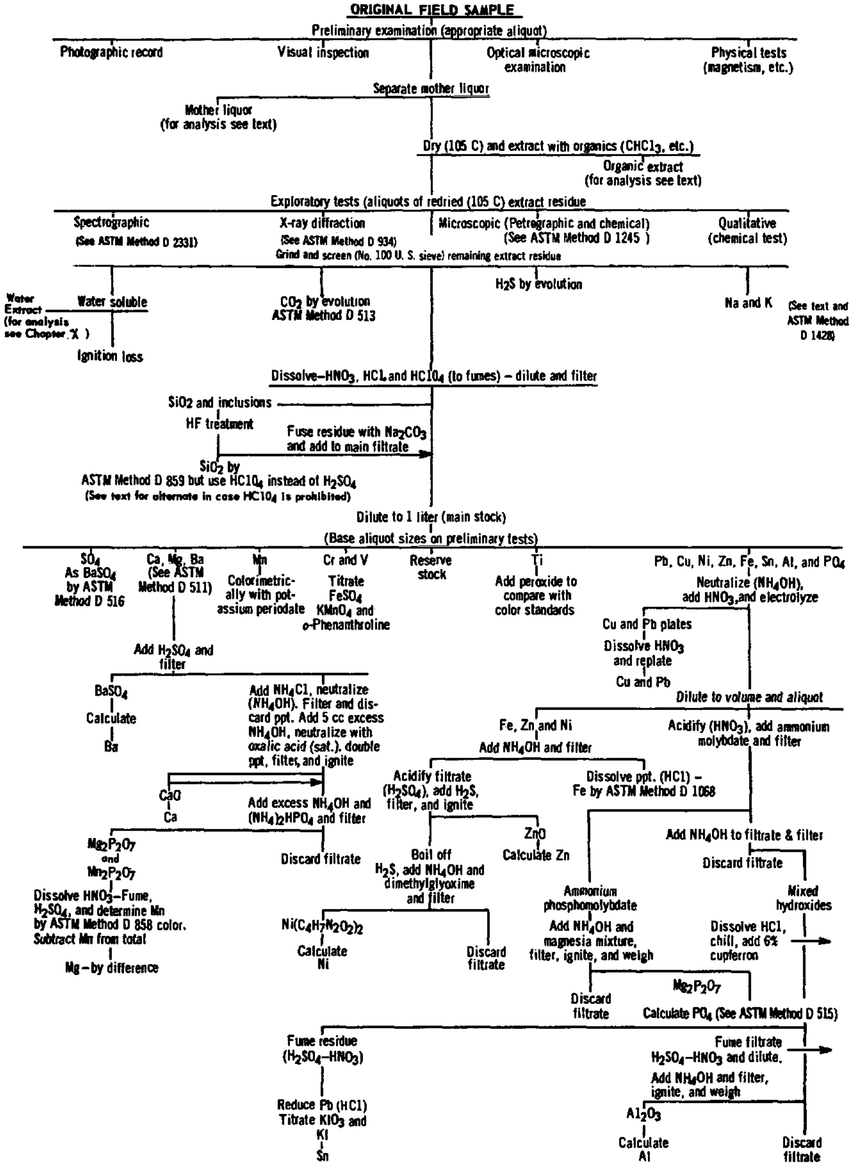

FIG. 1—*Outline of a typical scheme of analysis.*

Treatment of Extracts

Mother liquor separated from a field sample frequently will include solids that led to formation of the deposit. Soluble constituents such as chloride, sulfate, nitrate, and metal ions can be detected by standard analytical procedures such as the ASTM methods Ref *1*.

Extracted organic matter sometimes can be identified as lubricant, fuel oil, rust preventive, or paint residue. However, heat and pressure associated with deposit formation often will decompose the original organic matter and yield decomposition products that are useless in fixing the original source of organic contamination. Such tests as saponification number, iodine number, viscosity, and additive identification sometimes are useful. Infrared spectrophotometric examination may also give useful information about the organic constituents.

Water-Soluble Matter

This test should be made immediately ahead of the ignition-loss test, and on the same sample, to remove hydrates and certain other components that might confuse the ignition-loss value. If appreciable water-soluble matter is present, it should be examined for the usual water-soluble ions: chlorides, bromides, fluorides, sulfides, sulfates, phosphates, nitrates, silicates, and metal ions. If any are found in significant amounts, they should be determined quantitatively. Normally the water-soluble content of a waterside deposit will be low, but certain deposits, like calcium hydroxide, can cause difficulty even though they are reasonably soluble.

Ignition Loss

Ignition loss will include such items as organic matter, carbon, sulfur (sulfite and sulfide), carbon dioxide from carbonates, and, on rare occasions, nitrogen oxides or ammonia. Certain hydrates not removed by the water solubility test also may be decomposed. The results of the ignition-loss test are difficult to interpret, for while some constituents are being driven away, others are being oxidized to higher weight values. For example, reduced forms of iron oxide and copper can increase in weight on ignition.

The principal merit of ignition is in helping to confirm the presence of constituents indicated by other tests. If a large amount of free copper is found in preliminary inspection, a proportionate increase in weight on ignition will be expected. On the other hand, if a large amount of organic copper is observed in the extraction test, then a large loss of weight on ignition would be expected.

Often, heating to a lower temperature than the usual 900 to 1000°C will provide useful information. Carbonaceous samples, for example, should be heated to a maximum temperature of 500°C. The report of analysis should give the ignition temperature and length of ignition time.

Hydrogen Sulfide by Evolution

A qualitative test for hydrogen sulfide, using sulfuric acid and lead-acetate test paper, should be made first. If this test is positive, a standard evolution method should be followed [*3*].

Carbon Dioxide by Evolution

A qualitative test for carbon dioxide should be made first by adding mineral acid and passing any evolved gas into a solution of either calcium hydroxide or barium hydroxide. If this test is positive (cloud produced), the quantitaive determination can be made either gravimetrically [*4*], using the standard Ascarite absorption tower, or volumetrically as given in the ASTM Test for Total Carbon Dioxide and Calculation of the Carbonate and Bicarbonate Ions in Industrial Water (Method D 513) [*1*], using modifications of a method originally developed for carbon dioxide in industrial waters. The modifications permitting determinations to be made on solid samples are only minor, and the method is more rapid than the gravimetric method.

Sodium and Potassium

Sodium and potassium salts usually will be found with the water-soluble portions (mother liquor or water extract) but in some cases they may occur in complexes which remain behind in the silica residue and return to the master solution with the fusion thereof. The quantitative determination can best be made using a direct measuring-type flame photometer. Method C in ASTM Methods D 1428 provides the detailed procedure.

Treatment of the Main Analytical Sample

Solution of water-formed deposits is generally best effected with a mixture of mineral acids, including hydrochloric, nitric, and perchloric. Complete solution of certain silicate complexes may be impossible by this means, but these will be broken down by treatment of the silicate residue with hydrofluoric acid and subsequent treatment with sodium carbonate. If laboratory regulations prohibit use of perchloric acid, initial solution can be brought about with nitric and hydrochloric acid or with nitric-sulfuric acid. In the first instance, repeated dehydration may be required to separate the silica. In the second case, analysis for certain constituents will be affected by the sulfuric acid. For example, it will add sulfate ion and precipitate barium. Separate samples must be used for such constituents when this method of solution is used.

If a large amount of phosphate present in the original sample is subjected to fuming with nitric, hydrochloric, and perchloric acids, considerable phosphate will be separated with the silica, and some of it may be lost as phosphoric acid if too much sulfuric or perchloric acid is used in the hydrofluoric acid treatment of the silica residue. The silica residue may also include barium sulfate and tin, as well as sodium and potassium from silica complexes. These will be returned to the original sample, however, with the sodium carbonate fusion.

The final filtrate from the silica determination is divided into several aliquots as shown in Fig. 1. The size of these aliquots should be based on preliminary exploratory tests so as to yield the best volume for each determination. It will be noted that perchloric acid is recommended in place of sulfuric acid in the hydrofluoric acid treatment. This eliminates introduction of sulfate ion.

The analyses of several aliquots of the analytical scheme are discussed in the following in the order of their occurrence in Fig. 1.

Sulfate

Sulfate is determined by precipitation as barium sulfate as given in ASTM Test for Sulfate in Industrial Water and Industrial Waste Water (Method D 516) [*1*]. If the iron content is high, preliminary precipitation and filtration to remove excess iron will reduce to a minimum the contamination of the barium sulfate precipitate.

Calcium, Magnesium, and Barium

Calcium and magnesium are determined in series, after removing iron and aluminum, by adding ammonium chloride and neutralizing with ammonium hydroxide. Other metals need not be removed because the double precipitation of calcium will reduce occlusions to insignificant proportions, while the phosphates of such ions as copper, nickel, and zinc are largely soluble in ammoniacal solution, though they are insoluble in neutral solution.

The calcium is precipitated as calcium oxalate. This can be ignited and determined as calcium oxide or dissolved in sulfuric acid and titrated with standard permanganate. Magnesium is precipitated as magnesium ammonium phosphate and ignited to magnesium pyrophosphate. This residue will also include manganese pyrophosphate as well as traces of heavy metals. The presence of manganese accounts for treatment of the residue and determination of magnesium by difference. It also is practicable to calculate the manganese pyrophosphate from the manganese determination. If extreme accuracy in the magnesium determinations is desired, or if the original deposit contains very large amounts of copper, nickel, zinc, and lead, the analyst may wish to remove these interferences by treating the solution with hydrogen sulfide, filtering off the sulfide precipitate, and boiling the filtrate to remove hydrogen sulfide before following the scheme shown in Fig. 1. Alternatively, the heavy metals usually present in water-formed deposits may be separated by the mercury cathode.

Manganese

Since the primary solution is a perchloric acid medium, manganese can be determined colorimetrically by the standard potassium periodate method described in various texts.

Chromium and Vanadium

An experienced technician can do these two determinations simultaneously by the indicated scheme. The chromate and vandanate ions oxidize a part of the ferrous ion and the excess ferrous ion is titrated with potassium permanganate to disappearance of the red *o*-phenanthroline color. The vanadium is then oxidized by the permanganate. Titration is complete when the pink color from one drop of permanganate persists for 30 s. The permanganate consumed in the latter part of the titration is equivalent to the vanadium. The chromium is determined by difference from the residual ferrous ion calculated to have been used to reduce the vanadium.

If the vanadium content is relatively high, greater than 0.5 percent, the *o*-phenanthroline end point is difficult to determine. In this case, it is more practical to titrate the chromium and vanadium completely with permanganate in the same manner, then to reduce the vanadium with ferrous sulfate, oxidize the residual ferrous sulfate (but not the vanadium) with ammonium persulfate, and finally titrate the vanadium with permanganate. It also is possible to determine vanadium by electrometric titration with ferrous sulfate.

Fortunately, vanadium is a rather unusual waterside deposit constituent, so that precise analyses for it generally are not required.

Titanium

The standard method of oxidation with peroxide and determining titanium by comparison with color standards is satisfactory for most boiler deposit work. Vanadium produces a similar color and will yield essentially a quantitative error. If the vanadium content is know, it can be subtracted. Again, the absence of vanadium from most water-formed deposits makes this error relatively unimportant.

Lead, Copper, Nickel, Zinc, Iron, Tin, Aluminum, and Phosphate

This large group of constituents is handled together because primary removal of copper and lead, followed by removal of phosphate, eliminates pertinent interferences from the schemes for the remaining constituents.

Plating copper and lead from perchloric acid solution generally results in a dark copper plate containing traces of lead. This can be overcome by dissolving the plated metals in nitric acid and redepositing them.

It is practical, but unnecessary, to separate copper and lead with hydrogen sulfide and then to dissolve the precipitate in nitric acid and plate the metals in the same manner. This method also separates tin as a sulfide but it will remain dissolved in the acid electrolyte after plating. The hydrogen sulfide must be driven off by heating before completing the scheme.

Zinc may be determined gravimetrically as the oxide or colorimetrically by the use of Zincon.[2]

The nickel dimethylglyoxime residue can be measured either gravimetrically or colorimetrically by standard procedures.

The phosphorus is removed early in the sequence to prevent interference. It can be determined gravimetrically or volumetrically as ammonium phosphomolybdate or gravimetrically as magnesium pyrophosphate. All are standard analytical procedures.

The cupferron reagent used to separate iron and tin from the mixed hydroxides decomposes slowly and should be freshly prepared for use. Stability of cupferron is sometimes enhanced by adding 50 mg of acetophenetidide per litre of 6 percent aqueous solution. If a small bag containing ammonium carbonate is suspended in a bottle containing the dry cupferron reagent, its quality can be maintained for a longer period.

Iron cupferron precipitate is only slowly attacked in the cold by 2 *N* hydrochloric acid (used to wash the precipitate prior to washing with ammonium hydroxide), but hot acid decomposes it. For this reason the precipitation must be done in the cold. Nitric acid should be absent when cupferron is used as a precipitant. For this reason the mixed hydroxides are dissolved in hydrochloric acid.

It is also practical to determine iron and titanium as mixed oxides by ashing the cupferron precipitate. If the precipitate is bulky, it should be wet-oxidized with nitric and sulfuric acids and then reprecipitated with ammonium hydroxide. Direct ignition is satisfactory for small precipitates. The iron oxide can be corrected for the titanium oxide determined earlier. Iron may also be determined colorimetrically by *o*-phenanthroline, with which titanium does not interfere.

Precautions must be taken in determining aluminum as an oxide, since aluminum oxide is a desiccant and will increase in weight if not kept in the proper atmosphere. Large amounts of aluminum may be determined by sodium fluoride-sulfuric acid titration, using phenolphthalein or a pH meter for detection of the end point.

Expressing Results

The results of analysis are generally reported in terms of basic oxides and acid anhydrides, as shown in ASTM Reporting Results of Examination and Analysis of Water-Formed Deposits (Method D 933) [*1*]. This procedure does not provide for reporting definite molecular combinations. The expression of analytical results in terms of basic oxides should not be taken as implying that any of the oxides are present in the sample as such. This method of reporting results is only an arbitrary procedure of long usage.

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[2] "ZINCON" is a trade name of The La Motte Chemical Products Company for their 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene.

When definite combinations are desired, it is better to rely upon microscopic or X-ray diffraction evidence than on hypothesis. ASTM Method D 933 gives definite rules for reporting results by these techniques. When such apparatus is not available, however, probable compounds can be calculated from the analytical data.

Conclusions

The preceding information on analysis of deposits is not intended to be exhaustive. The discussion and tables of compounds likely to be found in water-formed deposits (Table 1 and Chapter 13) should be used as a guide by the analyst in determining his course of procedure. There may be occasions when preliminary qualitative tests indicate the presence of elements not included in the scheme discussed herein. In such cases, the analyst will perforce have to use his ingenuity and modify the procedures to effect the necessary separations and choose methods which will adequately determine the elements so indicated. Many of the methods discussed in Chapter 11 for the analysis of industrail waters may be applicable to the determination of certain constituents of water-formed deposits, and the analyst is advised to study that chapter carefully.

TABLE 1—*List of compounds reported to be found in water-formed deposits.*

Acmite	$Na_2O{\cdot}Fe_2O_3{\cdot}4SiO_2$
Ammonium bicarbonate	NH_4HCO_3
Analcite	$Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$
Anhydrite	$CaSO_4$
Ankerite	$CaCO_3$(Fe, Mg, Mn)CO_3
Aragonite	$CaCO_3$
Atacamite	$CuCl_2{\cdot}3Cu(OH)_2$
Azurite	$2\ CuCO_3{\cdot}Cu(OH)_2$
Barite	$BaSO_4$
Bayerite	$Al_2O_3{\cdot}3H_2O$
Bloedite	$Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$
Boehmite	$Al_2O_3{\cdot}H_2O$
Bornite	Cu_5FeS_4
Brochantite	$CuSO_4{\cdot}3Cu(OH)_2$
Brucite	$Mg(OH)_4$
Bunsenite	NiO
Burkeite	$Na_2CO_3{\cdot}2Na_2SO_4$
Calcium oxalate monohydrate	$CaC_2O_4{\cdot}H_2O$
Calcium phosphate (dibasic)	$CaHPO_4$
Calcium pyrophosphate	$Ca_2P_2O_7$
Calcium sodium phosphate	$CaNaPO_4$
Calcium sulfate	$CaSO_4$
Calcite	$CaCO_3$
Calcium aluminate	$3CaO{\cdot}Al_2O_3{\cdot}6H_2O$
Cancrinite	$4Na_2O{\cdot}CaO{\cdot}4Al_2O_3{\cdot}2CO_2{\cdot}9SiO_2{\cdot}3H_2O$
Celestite	$SrSo_4$
Cementite	Fe_3C
Cerrucite	$PbCO_3$
α Chalcocite	$\alpha\ Cu_2S$

TABLE 1—*Continued.*

β Chalcocite	$\beta\ Cu_2S$
Chalcopyrite	$CuFeS_2$
Copper	Cu
Copper aluminate	$CuAlO_2$
Corundum	$\alpha\ Al_2O_3$
Covellite	CuS
Cristoballite	SiO_2
Cuprite	Cu_2O
Delafossite	$Cu_2O \cdot Fe_2O_3$
Dolomite	$CaCO_3 \cdot MgCO_3$
Fayalite	$2FeO \cdot SiO_2$
Ferrous bicarbonate	$Fe(HCO_3)_2$
Ferrous sulfate monohydrate	$FeSO_4 \cdot H_2O$
Ferrous sulfate quadrahydrate	$FeSO_4 \cdot 4H_2O$
δ Ferric Oxide	$\delta\ Fe_2O_3$
β Ferric oxide monohydrate	$\beta\ Fe_2O_3 \cdot H_2O$
Fluorite	CaF_2
Foshagite	$5CaO \cdot 3SiO_2 \cdot 3H_2O$
Forsterite	$2MgO \cdot SiO_2$
Gaylussite	$CaCO_3 \cdot Na_2CO_3 \cdot 5H_2O$
Gehlenite	$3CaO \cdot Al_2O_3 \cdot 2SiO_2$
Gibbsite	$\gamma\ Al_2O_3 \cdot 3H_2O$
Glauconite	$K_2(MgFe)_2Al_6(Si_4O_{10})_3(OH)_{12}$
Goethite	$\alpha\ Fe_2O_3 \cdot H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Gyrolite	$2CaO \cdot 3SiO_2 \cdot H_2O$
Halite	$NaCl$
Hematite	Fe_2O_3
Hemihydrate	$CaSO_4 \cdot \frac{1}{2}H_2O$
Hemimorphite	$Zn_4(OH)_2SiO_7 \cdot H_2O$
Hydromagnesite	$4MgO \cdot 3CO_2 \cdot 4H_2O$
Hydrotalcite	$MgCo_3 \cdot 5Mg(OH)_2 \cdot 2Al(OH)_3 \cdot 4H_2O$
Hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
Hydroczincite	$2ZnCO_3 \cdot 3Zn(OH)_2$
Iron	Fe
Lazurite	$3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2Na_2S$
Lead	Pb
Lepidocrocite	$\gamma\ Fe_2O_3 \cdot H_2O$
Libethenite	$4CuO \cdot P_2O_5 \cdot H_2O$
Maghemite	$\gamma\ Fe_2O_3$
Magnesia	MgO
Magnesium chloride hydrate (basic)	$MgCl_2 \cdot 5Mg(OH)_2 \cdot 8H_2O$
Magnesium hydroxyphosphate	$Mg_3(PO_4)_2 \cdot Mg(OH)_2$
Magnesite	$MgCO_3$
Magnetite	Fe_2O_3
Malachite	$CuCO_3 \cdot Cu(OH)_2$
Meta halloysite	$Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$
Meta thenardite	Na_2SO_4I
Montmorillonite	$Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot nH_2O$
Mullite	$3Al_2O_3 \cdot 2SiO_2$
Muscovite	$KAl_2(Si_3Al)O_{10}(OH_2F)_2$
Natrolite	$Na_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 2H_2O$
Nontronite	$H_4(Al, Fe)_2Si_2O_9$
Noselite	$4Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot SO_3$
Oldhamite	CaS
Olivine	$2(Mg, Fe)O \cdot SiO_2$
Para sepiolite	$2MgO \cdot 3SiO_2 \cdot 2H_2O$

(*Continued*)

TABLE 1—*Continued.*

Paratacamite	γ $CuCl_2 \cdot 3Cu(OH)_2$
Pectolite	$Na_2O \cdot 4CaO \cdot 6SiO_2 \cdot H_2O$
Periclase	MgO
Portlandite	$Ca(OH)_2$
Pyrrhotite	FeS
Quartz	SiO_2
Sepiolite	$2MgO \cdot 3SiO_2 \cdot 2H_2O$
Serpentine	$3MgO \cdot 2SiO_2 \cdot 2H_2O$
Siderite	$FeCO_3$
Smithsonite	$ZnCO_3$
Sodium disilicate	β $Na_2Si_2O_5$
Sodium metasilicate	Na_2SiO_3
Sphalerite	β ZnS
Syngenite	$K_2SO_4 \cdot CaSO_4 \cdot H_2O$
Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$
Tenorite	CuO
Teschemacherite	NH_4HCO_3
Thenardite	$Na_2SO_4(V)$
Thermonatrite	$Na_2CO_3 \cdot H_2O$
Troilite	FeS
Trona	$3Na_2O \cdot 4CO_2 \cdot 5H_2O$
Vermiculite	$(Mg, Fe)_3(Al, Si)_4O_{10}(OH)_2 \cdot 4H_2O$
Vivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$
Wedellite	$CaC_2O_4 \cdot 2H_2O$
Wilkeite	$Ca_{10}O[(Si, P, S)O_4]_6$
Willemite	Zn_2SiO_4
Witherite	$BaCO_3$
Whitlockite	β $Ca_3P_2O_8$
Wollastonite	β $CaSiO_3$
Wustite	FeO
Xonotlite	$5CaO \cdot 5SiO_2 \cdot H_2O$
Zinc A	$ZnO \cdot xH_2O$
B	$ZnO \cdot yH_2O$
E	$ZnO \cdot zH_2O$
Zincite	ZnO
Zincosite	$ZnSO_4$

References

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Chapter 15—Sediment in Streams and Other Water Bodies

All streams and other water bodies contain sediment in variable quantity and character. Methods for measurement of these sediments are affected by the sediment mode (suspended or deposited), by the characteristics of the water body, and by the spacial and temporal variations of the sediments.

The purpose of this chapter is to indicate some of the needs for sediment measurements, describe some of the more common sediment environments in which it may be necessary to make measurements, and provide general references to the commonly used methods for making these measurements.

Many activities in the conservation, development, and utilization of land, mineral, and water resources affect sediment movement and thereby may create sediment-related problems. For example, a change in the runoff regime from a drainage basin may concentrate or disperse sediment in the stream channel and, in turn, affect the flow capacity of the stream. Because of the complex interrelationships that affect sedimentation phenomena, a knowledge of climate, the physical attributes of drainage basins, the hydraulic and hydrologic characteristics of streamflow, and the quantitative and qualitative aspects of sediment is required to solve sediment problems.

One might think that the solution to most sediment problems would be to stop landscape and channel erosion. This is not only impossible, but would severely upset the natural balance so that a host of new problems would emerge. Experience has shown that erosion should be carefully controlled to fit the situation. Intensive sediment movement (perhaps 100 t/ha) from a small construction site may be tolerated for a few weeks, especially if the sediment is deposited before it reaches a stream; but a relatively small amount of top soil (perhaps 1 t/ha/year) from a cropland with adsorbed herbicides may be intolerable if it reaches a stream.

Experience gained over the years has led to a greater understanding and appreciation of sediment problems; however, recent lawsuits attest to the fact that man's activity has caused, and will continue to cause, detrimental environmental changes resulting from the transport of fluvial sediment. Life scientists have become increasingly aware of the effect of sediment on the flora and fauna of streams and other water bodies. As an example, bottom sediments contaminated by industrial or municipal wastes may be dispersed by dredging operations, and thereby made available to enter the food chain through fish and other aquatic life. Numerous references can be found showing that bottom sediments in rivers are capable of adsorbing pesticides, trace metals, and other toxic chemical constituents.

Glymph [*1*][1] indicates that we have recently begun to appreciate the water-quality implications of sediment as a pollutant in the same context as industrial wastes, effluents from sewage treatment plants, and other kinds of pollutants. Rutherford [*2*] has asked the pertinent question: How much longer can the strained soil colloids near commercial, industrial, and other waste-producing areas continue to extract and store pollutants through ionic exchange before they become totally clogged, and how fast are these soils becoming unwanted sediments in nearby water bodies? These aspects of sedimentation require new levels of sophistication for determining sediment yields and sediment properties in small basins to form the basis for cost-effective sediment and pollution management programs.

The scope of water-related sediment problems varies widely in intensity and in time and space. The most prevalent problems, however, range from the hour-by-hour impacts on small streams of sediments that are eroded from cropland or construction sites during rainstorms to continuous impacts on large streams of sedimentation phenomena that affect aesthetics, stream-channel and reservoir capacity, and the disposition of sorbed pollutants. Although visual inspections may be helpful, a solution to a sediment problem usually requires scientific measurements that serve to define the quantitative and qualitative character of sediments suspended in, transported by, and deposited from natural and man-made streams and water bodies.

Modeling experts have made some progress, though sometimes with conflicting results, in outlining predictive equations in sedimentation. However, it seems that there is only a remote possibility for development of a complete set of such equations. Therefore, numerical simulation techniques using current and pertinent basic data offer the most practical basis for predicting specific fluvial sediment phenomena.

Because of the impact of an ever-changing environment on sediment movement, it is expected that there will be an increasing need for sediment measurements to obtain information on its quantity and characteristics which can be correlated with these environmental changes. Sediment data are also needed to help verify the effectiveness of sediment-control measures. Most sediment measurements are made to satisfy one of three general program objectives:

1. To obtain general information from a network of sediment-measuring stations which provide unbiased comprehensive information about sediment concentration and movement.
2. To obtain special information relative to specific problems so water managers can better choose among alternative actions.

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

3. To disclose and describe process relationships between water, sediment and environment.

It is appropriate to point out that when sediment data have potential for multiple use, including extrapolation in time or space, they should be cataloged and available to potential users. Therefore, this discussion is intended, first, to provide a better understanding of the essential requisites for valid sampling and data-collection programs in which sediment is one of the constituents of interest, and second, to foster the use of suitable standardized equipment for the purposes of improving the accuracy of sediment data and providing data truly comparable from one source to another.

Characteristics of Sediment Environments

Land Surface

The sediment environment at the land surface includes all areas not in stream channels or inundated by water and, thus, represents immensely diverse conditions. The immediate source area for much of the sediment in stream channels and other water bodies is from the land surface. Sedimentation, or, more specifically, the transport and deposition of sediment, is a staged process. Particles detached and entrained in a given event may move downslope on the land surface only a short distance, or may become part of the stream load.

A well-developed soil mantle indicates that the long-term erosion phase of the sedimentation process has been slower than the soil-forming processes. This condition requires the presence of good vegetative cover on the land surface. Generally, well-developed soil consists of fine particles mixed with relatively high proportions of organic material.

Disturbance of areas with well-ceveloped soils, such as row-crop cultivation or construction, usually causes a complex change in the sediment environment. Disturbances of the surface environment which do not result in increased runoff, or in significant concentration of flow, may only minutely increase sediment yield. To the extent that the disturbance mixes the soils, the character of the water-sediment mixture in runoff will be more varied in particle size and chemical composition than would be expected for undisturbed soils.

Disturbances which increase runoff or channelize water generally cause the sediment yield to increase dramatically. The range of particle sizes in transport broadens, with an attendant change in the chemical composition from the soil being eroded. New channels or gulliers, or both, form which may permanently alter the rate and character of sediment movement from the particular landscape.

On any catchment, the sediment-contributing area is usually less than 1 percent of the catchment. The sediment sources and the rate of yield change with the amount of disturbance, and both tend to increase with an increase in the intensity of storm events.

Regardless of conditions on an existing land surface, erosion and entrainment occur mainly in response to rainfall events. Rainfall events naturally vary in magnitude, the larger events occurring less frequently. There may be no sediment-producing rainfall events in any given year or there may be tens or hundreds of such events. Typically, one would expect anywhere from a few events to 30 or 40 annually. These discrete rainfall events, which may last for only a few days or even a few hours in a year, collectively make up the annual sediment yield from a land surface.

Streams

Although the land-surface environments are the basic sources of supply for stream sediment, the stream channel itself may be a sediment source. As noted, the processes of erosion and deposition on the landscape cause a highly variable quantity of sediment to be available for movement by streams. In discussing sediment available to streams, it is useful to classify sediment as either fine or coarse.

Fine Sediment—Fine sediment (< 0.062 mm) is easily suspended by natural stream turbulence, and hence travels through a stream system with about the same velocity as the water. The quantity of fine sediment moving at a given stream cross section depends on the amount of erosion in the basin and the routing of the particles by the flow to this section. The quantity moving is only indirectly dependent on the flow rate of the stream. The exact concentration of fine sediment in transport during stormflow is unpredictable with respect to time, and frequently increases by a factor of 100 to 1000 times that of "normal flow." Thus, sediment measurement techniques require a program to obtain a sufficient number of observations to define the large temporal variations in concentrations.

Coarse Sediment—Coarse sediment (> 0.062 mm) usually is found in appreciable quantities in the bed of a stream and may be transported both as suspended load and as bedload. The mode and rates of transport depend on the properties of the fluid, the sediment, the hydraulics of flow, and the characteristics of the channel geometry. Thus, it follows that coarse-sediment discharge often can be roughly related to water discharge at a given stream transect (cross section).

The movement of coarse particles consists of a series of steps interrupted by periods of no motion, when the particle is a part of the bed material. A particle moves and becomes a part of either the suspended load or the bedload whenever lift and drag forces or impact from another moving particle, or both, overcome the resisting forces and dislodge it from its resting place. The magnitudes of the forces vary according to the fluid properties, the velocity and turbulence of the flow, the physical character of the particle, and the degree of exposure of the particle. The degree of exposure depends largely on the size and shape of the particle relative to other particles in the bed mixture, and to the position of the particle relative to relief features on the bed such as permanent obstructions or bedforms, or both. Because of these factors, even in steady flow, the discharge of coarse sediment can be expected to fluctuate significantly with time at any point, and even vary substantially across the stream at any instant.

In order to define the coarse-sediment discharge at a transect, measurements must be made at a number of different lateral locations. Also, because of the close relationship between coarse-sediment discharge and the flow forces, at any given time, particles that move as bedload at one transect may or may not move as suspended load at another transect. As a result, the bedload portion of the total-sediment discharge observed at one transect is not necessarily representative of that at some other transect.

Suspended-Sediment Discharge—All particles in suspension, both fine and coarse, that have a density greater than that of water tend to settle. As a result, because the upward and downward turbulent currents are necessarily equal, there is a tendency for the flux of sediment through any horizontal plane to be greater downward than upward. This tendency is naturally counteracted by the establishment of a vertical concentration gradient of such a steepness that the concentration of upward moving parcels of water-sediment mixture are just sufficiently greater than the concentration of downward moving parcels to produce a net upward flux that just balances the flux due to settling. Because of their higher fall velocities, the coarser the particle, the steeper the gradient. Usually, the concentration of particles smaller than 0.062 mm will be uniform throughout the entire depth.

Due to the spatial variations in the coarse and fine suspended-sediment concentrations and in flow velocities, the discharge of suspended sediment at any given instant must be determined from

$$Q_s = \int_A C\, U\, dA \tag{1}$$

where

Q_s = "instantaneous" suspended-sediment discharge through a section of area A,

U = velocity of sediment particles through an elemental area dA, and

C = suspended-sediment concentration in the elemental spatial volume $Ut'dA$, in which t' is one unit of time used to express U.

In the practical application of Eq 1, U is considered to be equal to the flow velocity and C is considered to be constant during any given sampling period associated with its determination. Integrating the Eq 1 over time yields the quantity of suspended-sediment discharge during any specified duration, T. That is

$$S = \int_T Q_s\, dt = \int_T \int_A C\, U\, dA\, dt \tag{2}$$

where S is the quantity of suspended sediment discharged through area A during the elapsed time T.

Lakes, Reservoirs, and Ponds

Lakes, reservoirs, and ponds are relatively still bodies of water which serve as sinks for sediments. Those with outlets usually trap much but not all of the sediment carried to them. Factors affecting the sediment environment include the trap efficiency, the presence of suspended material, and the character of the bottom sediments. The major variables that determine the character of the sediment in this type of environment are the source and character of the inflow, the size and shape of the water body, the volume of the water body relative to the rate of outflow, the age of the water body, and the time of year.

Lakes or reservoirs with one or more major inlet streams develop deltas composed of coarse materials deposited as foreset beds. As a delta develops, the extension of the river channel tends to form topset beds on the delta. Fine materials are mostly deposited far into the impoundment as bottomset beds. Wide fluctuations in water levels, such as those occurring in flood-control and irrigation reservoirs, significantly affect the deposition patterns in many reservoirs. Most natural lake bottoms show the results of hundreds or thousands of years of the sedimentation processes. Lake currents and the character and timing of the sediment-laden inflows will be reflected in the particle size and deposition patterns of bottom sediments.

To provide reliable information, sampling programs must have well-defined goals and must take into account the factors controlling the distribution of sediment in the lake, reservoir, or pond.

Estuaries

Significant differences in the sediment environment are found in different types of estuaries. In estuaries where the tidal volume of seawater flowing into and out of the estuary is very large relative to the volume of river flow, sufficient mixing usually occurs so that the vertical distribution of salinity is uniform with depth and only a longitudinal salinity gradient exists. Under these circumstances, the flow is not vastly different from rapidly varying unsteady flow in rivers, and sedimentation processes are roughly similar to those that occur under like flows in a river.

In the so-called partially mixed estuary, which is the most prevalent type of major estuary along the Atlantic and Pacific coasts of North America, the volume of freshwater inflow is sufficiently large relative to the volume of seawater flow that a complex pattern of salinity (and therefore density) gradients develops. This produces a net vertical circulation in which seaward from a point on the channel bottom—termed the null point or the point of zero net flow—there is a predominance of landward flow of relatively dense saline water along the bottom, and a predominance of seaward flow of less dense relatively freshwater near the surface, even though the body of the flow alternates direction periodically in accordance with the tide. This generally produces a characteristic feature termed a "turbidity maximum. The turbidity maximum manifests itself as a bell-shaped longitudinal suspended-sediment concentration distribution that progressively develops in magnitude and then abates and translates landward and seaward with each flood and ebb.

In addition to suspended-sediment distributions engendered by vertical circulation patterns, larger estuaries typically develop horizontal circulation patterns, due to the Coriolis effect, major ocean circulation patterns, and sometimes prevailing wind patterns. These horizontal circulation patterns frequently cause a predominence of flow in certain channels during the flood period and a predominence of flow in other channels during the ebb. These patterns may produce extreme lateral variations in suspended-sediment concentration and disposition of bottom sediments.

As a result of the different hydraulic and sediment characteristics in estuaries, sampling techniques and requirements vary from one estuary to another. The common characteristic of all estuaries is that at any given time the concentration, composition, and transport direction of the suspended sediment is different in some degree from every other point in the estuary, and that at every point in the estuary these quantities vary continuously throughout time. Consequently, a measurement at a single point or cross section cannot be used to represent either the transport of suspended sediment in the entire estuary nor the transport through any other point or cross section in the estuary. These conditions dictate the necessity to define precise sampling goals and, likely, to limit the usability of a given set of samples to the specific purpose for which it was collected.

Conduits and Outfalls

The physical and chemical composition of the sediments entering a stream from conduits or outfalls could include a wide variety of fluvial sediments, and, in the case of many industrial operations or municipal water treatment plants, metals, other inorganic material, or organic material. In contrast to natural streams, the distinguishing characteristics of flow in conduits and outfalls is that it is the waste or effluent of industrial or municipal processing, or the outflow of an artificial watershed such as a storm sewer system. In either case the conditions that determine the flow, the type of sediments, and their concentrations are controlled mostly by man's activities. Sampling programs and sampling methods will be effective only if the components of sediment inputs and hydraulic conditions are understood and considered.

Methods of Measurement

A wide number of samplers and procedures have been developed and are commonly used for sampling sediment in streams and other water bodies. In general, the requisites for sampling sediment that is in motion are substantially different from those for sampling stationary deposited sediment. Prior to documentation of specific instructions by ASTM, specifications of samplers and sampling procedures are given in Chapter 3 of a *National Handbook of Recommended Methods for Water-Data Acquisition* prepared by a working group of representatives from Federal agencies interested in aspects of sediment measurement. The chapter also includes instructions for sample handling and preservation, laboratory analysis, methods for making reservoir surveys, methods for documenting stream channel changes, and quality control for the sediment measurement program.

References

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[*2*] Glymph, L. M., 1975, "Evolving Emphasis in Sediment-Yield Predictions," Present and Prospective Technology for Predicting Sediment Yields and Sources, U. S. Department of Agriculture, ARS-S-40, Washington, D. C., pp. 1-4.

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Chapter 16—Radioactive Nuclides in Water

Before the summer of 1945, it could be fairly stated that the problem of radioactive contamination of water did not exist. True, some radioactive springs were known, but these aroused little interest, except for possible use of the supposed healing properties of the water. The successful testing of an atomic bomb in the New Mexico desert on July 16, 1945, changed this situation. Fogging of some packages of photographic film was traced to radioactive debris from this bomb. The radionuclides had got into the process water and then into the wrapping paper. This is the first known damage to a commercial product from radioactively contaminated water.

Radioactivity may be defined as the spontaneous emission of penetrating energetic radiation from certain atomic nuclei. The early workers in the field soon classified the radiation into three types, called alpha (α), beta (β), and gamma (γ) rays, on the basis of their ability to penetrate matter. They were also able to establish their nature, finding that alpha and beta rays were high-speed particles, while gamma rays were electromagnetic waves similar to X-rays. The results of these early studies can be tabulated as shown in Table 1.

The emission of these radiations is associated with a nuclear disintegration, which is the rearrangement of the constituents of the nucleus into a more stable configuration with an associated release of energy. The rate of emission is characteristic of the radioactive material (also called radionuclide), and is described by the time required for half of the unstable nuclei

TABLE 1—*Types of radiation: nature and penetration ability.*

Type	Penetration		Nature
	Air	Solids	
Alpha	few centimetres	few micrometres	fast-moving helium nuclei
Beta	metres	several millimetres	very rapid electrons (+ and -)[a]
Gamma	many metres	several centimetres	electromagnetic radiations of very high energy

[a] All the beta radiation from naturally occurring materials consists of negative electrons; the emission of positive electrons (positrons) by certain man-made materials was discovered in the 1930s.

to complete their rearrangements and emissions: the half-life. After the lapse of one half-life, since the number of unstable nuclei has been reduced to one-half the original number, the emission rate (or activity) is also reduced to one half of its initial value. The quantity of radioactive material is measured by the rate of disintegration; that amount of a nuclide in which 3.7×10^{10} atoms disintegrate per second is defined as a curie. Ordinarily, subdivisions of this unit, milli-, micro-, or even micromicrocuries, are used. These are 10^{-3}, 10^{-6}, and 10^{-12} curies respectively. The term picocurie, is currently used as a synonym for micromicrocurie.

The energy released in a nuclear disintegration is large, usually of the order of a million times as much as is involved in ordinary chemical changes. When alpha particles or gamma rays are emitted, these carry off substantially all the energy release. In beta emission, however, the available energy is divided between the beta particle and a neutrino, which is not ordinarily observable. The division of the energy varies in individual disintegrations, so that a particular beta particle may have an energy from zero up to the maximum available, the average being about one third of the total energy released. Consequently, beta radiation has a continuous energy spectrum, while alpha and gamma radiations are characterized by line spectra.

The unit of energy most used in radioactivity is the electron volt, the energy gained by an electron in passing through a potential difference of 1 V. It is equal to 1.6×10^{-12} ergs. Alpha particles have energies of a few million electron volts (MeV); beta and gamma radiations may have energies from zero up to a few MeV.

The three types of radiations interact with matter in somewhat different ways. Both of the charged particles (alpha and beta) react primarily by electrostatic interaction with the electrons of the material, transferring energy to each electron that they approach sufficiently closely. Quantitatively, the actions differ considerably, with the heavier, slower-moving alpha particle interacting with many more electrons per unit path length. The interaction of gamma radiation with matter is essentially statistical in nature, with each individual gamma photon transferring no energy until it interacts, usually with an electron, whereupon it transfers all or a large part of its energy. The gamma radiation has no definite range, but is statistically reduced in quantity as it passes through matter. This gamma interaction has been compared to the process of firing machine gun bullets at random into a forest, in which each bullet is unaffected until it strikes a tree, when it loses all or part (if it ricochets) of its energy. The extent of the interaction of the three types of radiation with matter is illustrated in Table 2.

The primary effect of the interaction of any one of the three types of radiation with matter is the transfer of energy to electrons, resulting in the production of ions or of excited molecules. Secondary changes in matter include such phenomena as the darkening of photographic film, the initiation of chemical changes, and biological effects. The extent of such

TABLE 2—*Interaction of radiation with matter.*

	Range, cm		Energy Transfer, MeV/cm		Tenth-Thickness,[a] cm	
Radiation; Energy, MeV	Air	Aluminum	Air	Aluminum	Lead	Aluminum
Alpha, 5	3.5	0.0018	1.43	2800	. . .	. . .
Alpha, 7	5.9	0.0033	1.19	2100	. . .	. . .
Beta, 0.5	125	0.06	0.0040	8.3	. . .	. . .
Beta, 3.0	1320	0.64	0.0023	4.7	. . .	. . .
Gamma, 0.1	. . .	. . .	. . .	. . .	0.037	5.1
Gamma, 1.0	. . .	. . .	. . .	. . .	2.9	13.8

[a] Thickness needed to reduce intensity to 10 percent of incident intensity.

effects is dependent on the dose, or amount of energy absorbed by the material. The unit of energy absorption is the rad, which is equivalent to the absorption of 100 ergs/g of material.

Biological systems in particular are affected by radiation. Destruction of cells by large doses is the basis for radiation therapy for cancer. The effects of excessive exposure in man vary from skin burns through nausea, anemia, loss of resistance to infection, and even death. Smaller radiation doses may cause more subtle damage, leading to cancer and to genetic mutations. While information about the potential damage from low levels of radiation is unfortunately inexact, "acceptable risk" levels are established by the International Commission on Radiological Protection (ICRP) and the National Committee on Radiation Protection and Measurements (NCRP).

Because of their ionizing, photographic and, especially, biological effects, the quantities of radioactive materials in commercial products, in air, in water, and in foods, must be rigidly controlled. For each radionuclide, a concentration may be determined, based on its physical, chemical, and metabolic characteristics, such that no organ of the body will receive more than the "acceptable risk" exposure given above. The ICRP and NCRP also establish these maximum permissible concentrations.

Naturally Occurring Radionuclides

Heavy Element Series

Although radioactive contamination has been a problem for only a short time, radioactive materials have always been part of the environment. The major sources of natural radioactivity are uranium and thorium ores. These contain a great variety of radionuclides, differing in chemical nature, half-life, and type and energy of radiations, but linked genetically into three series, each stemming from an element of very long half-life. The three series are listed in Table 3.

Some of these elements can be dissolved, in ratios depending on their

TABLE 3—*Natural radioactive series.*

Atomic Number	Element	Atomic Weight	Historical Name	Radiation, Half-Life		Remarks
			URANIUM-RADIUM SERIES			
92	Uranium	238	uranium I	α	4.5×10^9 yr	
90	Thorium	234	uranium X-1	β	24 days	
91	Protactinium	234m	uranium X-2	β	1.2 min	
91	Protactinium[a]	234	uranium Z	β	6.7 h	
92	Uranium	234	uranium II	α	3×10^5 yr	
90	Thorium	230	ionium	α	8×10^4 yr	
88	Radium	226	radium	α	1600 yr	
86	Radon	222	radon	α	3.8 days	
84	Polonium	218	radium A	$\alpha(\beta)$	3 min	β 0.03 percent
82	Lead	214	radium B	β	27 min	
85	Astatine[a]	218		α	2 s	
83	Bismuth	214	radium C	$\beta(\alpha)$	20 min	α 0.04 percent
84	Polonium	214	radium C′	α	$<10^{-6}$ s	
81	Thallium[a]	210	radium C″	β	15 min	
82	Lead	210	radium D	β	~20 yr	
83	Bismuth	210	radium E	$\beta(\alpha)$	5 days	$\alpha \sim 10^{-5}$ percent
84	Polonium	210	radium F	α	138 days	
81	Thallium[a]	206		β	4 min	
82	Lead	206	radium G	stable		
			THORIUM SERIES			
90	Thorium	232	thorium	α	1.4×10^{10} yr	
88	Radium	228	mesothorium 1	β	5.7 yr	
89	Actinium	228	mesothorium 2	β	6.1 h	
90	Thorium	228	radiothorium	α	1.9 yr	
88	Radium	224	thorium X	α	3.6 days	
86	Radon	220	thoron	α	1 min	
84	Polonium	216	thorium A	$\alpha(\beta)$	0.16 s	β 0.01 percent
82	Lead	212	thorium B	β	10.6 h	
85	Astatine[a]	216		α	3×10^{-4} s	
83	Bismuth	212	thorium C	$\beta(\alpha)$	60 min	α 33.7 percent
84	Polonium	212	thorium C′	α	3×10^{-7} s	
81	Thallium[b]	208	thorium C″	β	3 min	
82	Lead	208	thorium D	stable		
			URANIUM-ACTINIUM SERIES			
92	Uranium	235	actino-uranium	α	7×10^8 yr	
90	Thorium	231	uranium Y	β	26 h	
91	Protactinium	231	protactinium	α	3×10^4 yr	
89	Actinium	227	actinium	$\beta(\alpha)$	22 yr	α 1.2 percent
90	Thorium	227	radioactinium	α	19 days	
87	Francium[c]	223	actinium K	β	21 min	
88	Radium	223	actinium X	α	12 days	
86	Radon	219	actinon	α	4 s	
84	Polonium	215	actinium A	$\alpha(\beta)$	2×10^{-3} s	β $<10^{-3}$ percent
82	Lead	211	actinium B	β	36 min	
85	Astatine[a]	215		α	10^{-4} s	
83	Bismuth	211	actinium C	$\alpha(\beta)$	2 min	β 0.32 percent
81	Thallium	207	actinium C″	β	5 min	
84	Polonium[a]	211	actinium C′	α	25 s	
82	Lead	207	actinium D	stable		

[a] Minor component, <1 percent.
[b] Minor component, 33.7 percent.
[c] Minor component, 1.2 percent.

individual solubilities, whenever water runs through formations containing them. In addition, since element 86 (radon) is an inert gas, it can move through the soil and so reach water not in contact with the radioactive formation. Because of its relatively long half-life, radon-222 can move through the ground for much greater distances than radon-220 or radon-219. In radioactive springs, radon-222 and its immediate daughters, radium A through radium C′, are usually the most conspicuous components. The radium-226 content of ordinary surface- or groundwaters will generally be less than 0.5 pCi/litre, while the radon-222 content of the same water may be as high as 100 pCi/litre. In some spring waters, radon contents may be in the range of microcuries per litre, with radium levels as high as thousands of picocuries per litre.

Each of the foregoing radioactive series owes its occurrence in nature to the existance of a long-lived parent, uranium-238, thorium-232, and uranium-235, respectively. All the other elements in the series have short half-lives, geologically speaking, and would no longer be present except for continual formation.

Other Long-Lived Materials

Radioactive series do not occur in other parts of the periodic system, and the only radionuclides existing are those few species of geologically long half-life. The most important of these is potassium-40, which comprises 0.012 percent of natural potassium, and thus contributes radioactivity to all potassium-containing systems. For each milligram of potassium, there will be almost two radioactive disintegrations per minute (dpm). Water itself will therefore be radioactive in proportion to its potassium content, plus a contribution from biological material. The second most important natural activity of this type in water is rubidium-87, which forms almost 28 percent of all natural rubidium. Because of the low abundance of rubidium in the earth's crust, as compared to potassium, rubidium activity is relatively unimportant in freshwaters. Both potassium and rubidium contribute significantly to the radioactivity of seawater, as shown in Table 4. Additional minor radioactive elements of long half-life are included in Table 4.

Cosmic-Ray-Produced Nuclides

A few radioactive materials of short half-life exist in nature from continuous production by cosmic-ray bombardment of the atmosphere. These nuclides are also listed in Table 4. The most important of these are carbon-14 and hydrogen 3 (tritium). Carbon-14 is formed by the action of cosmic-ray neutrons on atmospheric nitrogen, while tritium is formed directly in the splitting of atoms struck by the high-energy cosmic ray particles. Both of these are oxidized, to carbon dioxide and water, and enter the biosphere and hydrosphere. None of the other radioactive nuclides

TABLE 4—*Other naturally occurring radionuclides.*

Nuclide	Half-life, years	Abundance, %	Specific Activity, dpm/g[a] of element	Total in Sea, MCi[b]
Hydrogen-3	12.3	varies	varies	200
Beryllium-7	53 days	varies	varies	
Carbon-14	5730	varies	0 to 15	270
Potassium-40	$\sim 10^9$	0.012	1800	460 000
Vanadium-50	4×10^{14}	0.25	0.1	
Rubidium-87	5×10^{10}	27.85	50 000	8400
Indium-115	6×10^{14}	95.7	11	
Lanthanum-138	1×10^{11}	0.09	52	
Cerium-142	5×10^{15}	11.07	0.12	
Neodymium-144	5×10^{15}	23.87	0.26	
Samarium-147	1×10^{11}	15.1	8200	
Lutetium-176	$\sim 10^{10}$	2.6	~12 000	
Rhenium-187	$\sim 10^{10}$	62.9	~270 000	
Platinum-190	6×10^{11}	0.012	0.8	
Platinum-192	$\sim 10^{15}$	0.78	~0.03	
Bismuth-209	over 10^{18}	100	<0.004	

[a] dpm = disintegrations per minute.

[b] One megacurie = 10^6 Ci.

formed by cosmic-ray bombardment exists in large enough quantities to be of any real importance.

Radionuclides in Reactor Coolants and Moderators

This subject is discussed in Chapter 18.

Radionuclides from Chemical Processing of Ores, Reactor Fuels, and Blanket Materials

Ores

The primary natural materials useful in nuclear energy are uranium and thorium. Uranium-235 is the only natural fissionable material; uranium-238 and thorium-232 are the raw materials for manufacture of artificial fissionable materials. The first steps in nuclear technology are thus the mining and refining of these materials. Uranium and thorium are each the progenitor of long series of radioactive elements, any or all of which may be present in the ores.

Of all the daughter elements, those of relatively long half-life include thorium-230 (ionium), radium-226, and lead-210 (radium D) in the uranium-radium series, and radium-228 (mesothorium 1) and thorium-228 (radiothorium) in the thorium series. The long-lived protactinium-231 and actinium-227 occur in uranium, but since they are derived from relatively scarce uranium-235 (0.71 percent), they are less important. In removing the desired uranium or thorium from ore, the other radioactive elements present will be left behind. Depending upon the process, these elements may occur in various chemical forms with different solubilities. Those of long half-life will persist much longer than any conceivable control measures and their treatment must be absolutely foolproof. The more soluble materials, of course, may eventually reach and contaminate waters. Of all the nuclides listed in the preceding paragraph, radium-226 is the most harmful in a water environment by reason of its biochemical properties, its long half-life, and the energetic radiations of it and its immediate daughter products. The present maximum permissible concentration of this material in uncontrolled waters is only 4×10^{-9} μCi/ml (about 9 disintegrations/min/litre), or 4×10^{-12}g/litre. Obviously, extreme precautions are necessary to limit losses to this small amount.

Reactor Fuel and Blanket Materials

A wide variety of radionuclides is liberated from fuel elements when these elements are processed chemically. Conventional processing at the present time involves complete dissolution of the elements, separation and purification of the heavy metals, especially uranium and plutonium, and discharge of the waste to storage. The radioactive elements present in fuel elements include both fission products and neutron-activated elements.

Fission products of the heavy metals include all the elements from about atomic number 30 (zinc) to about atomic number 64 (gadolinium). The elements as first formed have excess neutrons and rapidly change by radioactive decay into more stable elements emitting beta and gamma radiation. After a reactor has been operating for some time, it will contain a large variety of radionuclides of both short and long half-lives. If a fuel element is then removed from the reactor and stored, the short-lived materials will change into either stable or longer-lived isotopes, so that most of the radioactivity will then be in the form of materials of long half-life. Some of the more important of these materials are listed in Table 5.

All reactor fuels, and especially all reactor blanket materials (materials placed around the reactor core to form additional fissionable material from neutrons that would otherwise escape), will contain a number of artificial heavy elements, also listed in Table 5.

On dissolution of a fuel element, all these fission products and heavy elements are free from confinement, and pass into the liquid. The volatile materials, such as inert gases and halogens, pass off as vapors. If released to the atmosphere, they can settle out or be washed into surface waters by rain, thereby becoming potential contaminants of the water environment. The fission products remaining after processing constitute an intensely radioactive aqueous waste, which at present is stored indefinitely. The product

TABLE 5—*Nuclides in reactor technology.*

		MaximumPermissibleConcentration(Occupational)			
		Water		Air	
Nuclide	Type	μCi/ml[a]	μg/litre	μCi/ml[a]	μg/litre
Strontium-89	fission product	7×10^{-5}	3×10^{-6}	2×10^{-8}	7×10^{-10}
Strontium-90	fission product	8×10^{-7}	4×10^{-6}	2×10^{-10}	1×10^{-9}
Ruthenium-106	fission product	1×10^{-4}	3×10^{-5}	2×10^{-8}	6×10^{-9}
Iodine-131	fission product	6×10^{-5}	5×10^{-7}	6×10^{-9}	5×10^{-11}
Cerium-144	fission product	1×10^{-4}	3×10^{-5}	2×10^{-9}	6×10^{-10}
Radium-226	natural	4×10^{-8}	4×10^{-5}	8×10^{-12}	8×10^{-9}
Thorium (natural)	natural	5×10^{-7}	5000	3×10^{-11}	0.3
Thorium-234	natural	2×10^{-4}	9×10^{-6}	1×10^{-8}	4×10^{-10}
Uranium (natural)	natural	2×10^{-6}	3000	3×10^{-11}	0.05
Uranium-233	artificial heavy	3×10^{-6}	0.3	3×10^{-11}	3×10^{-6}
Plutonium-239	artificial heavy	3×10^{-6}	0.05	2×10^{-12}	3×10^{-8}
Americium-241	artificial heavy	3×10^{-6}	9×10^{-4}	4×10^{-11}	1×10^{-8}

[a] International Committee on Radiological Protection, *British Journal of Radiology*, Supplement No. 6, Table C. VIII, Dec. 1954.

phase, chiefly heavy metals, is also strongly radioactive; it requires special methods of handling to avoid contamination of the environment. Partly because of the hazard, and partly because of the very high value of the products, control is normally so thorough that only negligible quantities of product are lost as wastes.

The extraordinary precautions necessary in handling these materials may be judged from the quantities considered permissible in an industrial environment (Table 5); if discharged to an uncontrolled area, these values should be reduced by a factor of 10.

Radionuclides in Reactor Coolants and Moderators

In addition to the naturally occurring radioactive species discussed in the preceding section, a large number of artificially produced radionuclides are known. Most of these originate in the fission of heavy atoms or as a result of the bombardment of stable materials by nuclear particles, especially neutrons ("activation"). Since a nuclear reactor functions by the fission of uranium or plutonium and is an extremely strong source of neutrons, radioactive isotopes are formed in large quantities.

In most reactors, the fission chain reaction is principally propagated by neutrons of low (thermal) energies. The primary high-energy fission neutrons are slowed to thermal energies (moderated) by repeated interactions with light elements, of which hydrogen is the most effective. Water, the cheapest hydrogenous material, is a very common moderator. Water also is frequently used for heat transfer in reactors.

Natural Water

Water itself, when exposed to a neutron flux, does not yield any important radioactivities. There is a rather intense radiation from nitrogen-16, a product of the interaction of neutrons with oxygen-16, but this material has such a short half-life (7) that any system suitable for containing the reactor will be adequate to protect against it. But many materials present in natural waters will yield radionuclides of relatively long half-life under neutron irradiation. The potential hazard from these materials must be considered in plant operations, and, if discharged, their concentrations must be kept below values at which they might be detrimental to the environment.

The largest American installation using natural water as coolant is the reactor complex at Hanford, Wash. The effect of the reactor operations on the Columbia River has been studied extensively, including the radionuclide content of the water, and of fish and other biological forms in the river. Although a large number of radionuclides are formed in the water during its passage through the reactors, most of these have such short half-lives that they very soon become insignificant. Radioactive forms of manganese, arsenic, copper, sodium, phosphorus, zinc, chromium, and iron are prominent in the reactor cooling water, and many others are formed in lesser amounts.

In addition to the radionuclides formed by neutron irradiation of stable elements in the water, there is always the possibility of fission product leakage from the fuel elements into the cooling water. While careful design and painstaking workmanship confine such leakage to trivial amounts, some fission products can be identified in the water. The most important of these are iodine, strontium, barium, and the rare earths. Generally speaking, fission products are of greater biological significance than the induced activities, and very elaborate instrumentation is provided to detect leakage before it becomes a problem.

A rather special case of potential formation of radionuclides in a natural water is the operation of nuclear-powered vessels. Here, although the coolant moderator is usually very carefully purified water in a closed system, the designer must consider the possibility of reactor neutrons passing through the hull to activate sodium and other elements in the water in which the ship floats. Sufficient neutron shielding to prevent this is therefore included in the reactor plant.

Treated Waters

In most water-moderated or water-cooled reactors, extremely pure demineralized water is used. This may be ordinary (light) water or deuterium oxide (heavy water). In many systems the water is continuously purified by ion-exchange demineralizers.

There are several reasons for using such rigorously purified water in reactors. One advantage of pure water is that only a small amount of radioactivity is formed in it. In absolutely pure water, only the unimportant 7-s isotope nitrogen-16 would be formed. In practice, this ideal is unattainable, but the purer the water, the closer it can be approached. Another advantage is neutron economy. Not only is every radioactive atom in the water a nuisance, but its formation has required one neutron. Such unproductive consumption of neutrons is expensive in reactor technology.

In spite of extreme purity and the use of highly corrosion-resistant alloys, a minute amount of corrosion occurs in every system. Continuous bombardment by the large neutron flux inside the reactor core induces very significant activity even in these tiny amounts of corrosion products. The nature of the alloys involved determines the character of the induced activities. The most important induced radionuclides in stainless steel systems include isotopes of chromium, manganese, iron, cobalt, and nickel.

A second source of radionuclides is material specifically added for corrosion control. Practically all the common materials of this type, such as chromate, phosphate, and silicate, become radioactive in the reactor. A special case is the production of tritium by neutron bombardment of lithium, the lithium being added as hydroxide for pH control. Tritium, a pure beta emitter of low biological effect, is considered a less serious problem than the radioactive sodium or potassium that would result if hydroxides of these elements were used.

Just as in natural water systems, there could be some minute leakage of fission products from the fuel elements into the treated coolant water. Here also, the fission products are more hazardous than the induced activities, and their concentration in the water must be rigidly controlled.

Treated water systems, because of the high cost of the water, are invariably closed, recirculating systems. Although the contaminated primary coolant is retained within the shielded enclosure, some bleed-off and makeup is usually necessary. Uncontrolled discharge of the radioactive waste water to the environment is not permissible; therefore, waste tanks are usually provided in which the water (*a*) is stored for decay, (*b*) is monitored before discharge, and (*c*) is fed into the environment at a controlled rate so that permissible levels are not exceeded.

Canal Coolants

In addition to reactor coolant and moderator, water is used in the "canals" in which fuel elements are stored prior to processing. These fuel elements, containing an enormous quantity of radioisotopes, require considerable cooling to dissipate the residual heat of the radioactive decay. The gamma radiation from these elements is very intense, so that they must be heavily shielded to permit plant personnel to work in the vicinity. Water about 7.6 m (25 ft) deep serves both of these purposes satisfactorily. The fuel elements, after a sufficient cooling period, are removed by remote-control tools.

Canal waters become contaminated by transfer of the radioactive primary coolant adhering to the fuel element when it is removed from the reactor; in the case of a leaking element, there is alslo some contamination from fission products. The total contamination from both of these sources is ordinarily minor, but provision must be made for draining any contaminated canal water to waste tanks and replacing it with freshwater.

Radionuclides from Fallout

Fission Products

The most widespread type of radioactive contamination at present is fallout from nuclear weapons testings These tests have produced a considerable atmospheric content of fission products of intermediate and long half-lives, which gradually settle to the earth. In addition to settling under their own weight and as a result of atmospheric currents, large quantities of these materials are brought down by rain and snow.

In the United States during October 1958, it was unusual to find a rain or a surface water that contained no detectable fission-product activity. Levels of activity in rain may range from a few to thousands of picocuries per litre, while in surface waters they will generally be of the order of tens of picocuries per litre. In the period during and shortly after a weapons test series, rain activity may reach the order of hundreds of thousands and surface water activities hundreds of picocuries per litre. These increases are primarily due to fission products of short half-life, which do not persist in the atmosphere. Levels in groundwaters are ordinarily much lower than these, depending largely on the speed with which the groundwater is replenished by rain and surface water.

When rain containing fission product activity falls on the ground, much of the activity is transferred to the soil, mostly by adsorption on soil particles or on atmospheric particulates washed down with the rain. As a result, the fraction of radioactive material reaching streams or other bodies of water is relatively small, except where large water areas are exposed to direct rainout. Although water contamination is less than it would be if these mechanisms were not operative, this cannot be counted as a clear gain since much of the radioactivity remaining in the soil becomes available to plants, and so enters the food chain with the possibility of eventual ingestion by humans. Where rainfall is collected in cisterns for drinking water, much of the radioactivity is removed by adsorption on the collection surfaces, and by settling out and adsorption on the walls of the cistern.

The fission products cover a wide range of chemical elements. Consequently, their behavior in water is characterized by large variations. Some, such as zirconium, being very insoluble in most aquatic environments, settle out more or less rapidly with particulate material, thus becoming concentrated in silts and sludges. Others remain in solution for a much longer time and hence can be carried much farther in streams. Still others enter into the biological cycle and become distributed in a manner depending upon the biota present in each stream.

As a result of the processes described in the preceding paragraph, combined with normal radioactive decay, the total activity of a body of water may decrease rapidly after contamination. This decrease, however, does not necessarily imply a proportionate decrease in the biological hazard of this water, which depends strongly upon the radionuclide composition of the contamination. Removal of even large amounts of a relatively nonhazardous component does not have much effect on the potential biological damage.

Induced Activities

In addition to the fission products which are formed in fairly definite proportions in the actual nuclear explosion, radioactive materials are formed by irradiation with the neutrons produced in the explosion. The nature and quantity of these induced radioactive nuclides depend on the exact circumstances of the explosion, which determine the exposure to neutron fluxes. Thus, in a high-altitude burst, only those materials present in the bomb and in the air could be irradiated, while in a burst close to the ground, all the elements present in the soil would be potential sources of induced activity. In a subsurface explosion at sea, such materials as the sodium in the water would become radiocative under the resultant neutron bombardment.

The amount of fission product radioactivity formed during an explosion is so large that normally the induced activity would not be noticeable in the early stages; however, as the fission products of short half-life disappear, those induced activities of longer half-life would become relatively more prominent. A number of these induced radionuclides are concentrated by biological systems and in many cases they have detected in fish or other specimens taken from the water.

Table 6 lists some of the more important fission products and induced radioisotopes that have been found in fallout.

Radiotracers in Water

The number of potential applications of radiotracer studies in aqueous systems staggers the imagination; only a few can be selected as examples. For the sake of simplicity, tracer studies in which the water itself is the subject will be chosen.

Selection of Tracer Materials

The prime requirement of any tracer is that it shall actually trace the process under investigation. To illustrate, marbles are entirely unsatisfactory

TABLE 6—*Radionuclides found in fallout.*

Long-lived fission products	
Strontium-89	Ruthenium-106
Strontium-90	Cesium-137
Yttrium-91	Cerium-141
Zirconium-95	Cerium-144
Niobium-95	Promethium-147
Ruthenium-103	Samarium-151
Short-lived fission products	
Molybdenum-99	Iodine-133
Technetium-99m	Iodine-135
Tellurium-132	Barium-140
Iodine-131	Praseodymium-143
Iodine-132	Neodymium-147
Induced activities	
Carbon-14	Cobalt-57
Calcium-45	Cobalt-58
Manganese-54	Cobalt-60
Iron-55	Zinc-65
Iron-59	

in tracing stream flow, oranges are reasonably satisfactory (at least so far as surface flow is concerned), and fluorescein dye in solution is usually suitable. The same principles apply with radiotracers. In flow studies, presumably the best radiotracer for water would be tritiated water; reasonably good results could be expected with tracers which react with the stream environment to a very small degree, while tracers that tend to precipitate out, enter into the biology of the stream, or be removed by ion-exchange properties of the silts, would give poorer, less conclusive results.

After it has been established that one (or several) tracers are suitable, a number of other characteristics of the radioactive material become important. These characteristics include ease of detection and measurement, suitable half-life (long enough for the experiment but not so long as to interfere with subsequent experiments or use of the water), low radiological hazard, availability, and low (or at least reasonable) cost.

Hydraulic Tracing

A fairly large number of radionuclides have been used in tracing flow. Tritium would be ideal except for the difficulty of measuring its extremely soft beta radiation. Excellent results have been obtained with bromine-82, but there is the objection that the material has a half-life of only 36 h. It is therefore most useful in studying small artificial systems, such as settling basins and the like. Another halogen that has been used successfully in such applications is iodine-131.

In longer studies, a nuclide of greater half-life usually is needed. Iodine-131 is sufficiently long-lived for many experiments, but the maximum permissible concentration of this material in public waters is so low that its use is thereby restricted. One of the best nuclides for flow tracing in nature is rubidium-86, which has a half-life of 19 days, emits readily detectable beta and gamma radiation, and is relatively insensitive to precipitation or other sedimentation. Scandium-46 has also been used under conditions such that it would remain in solution or at least form fine, essentially nonsettling particles. In following the movement of silts, scandium-46 and gold-198 have proved suitable.

Biological Tracing

The discussion here will be confined to studies of the movement of radioisotopes in the biota of a stream. This is particularly important in understanding the fate of radionuclides introduced into a stream. The outstanding opportunity for this type of study has been in the Columbia River, where use of the river water as reactor coolant has resulted in the presence of a wide spectrum of irradiated radioelements in the stream. Many of these materials are concentrated strongly by algae and other plankton; much of this concentration appears to be a surface or adsorption phenomenon. As one examines other forms higher in the food chain, the number of elements concentrated (and often the degree of concentration) becomes less, partly because of rejection of these elements in the diet or in digestion, partly by disappearance of nuclides of short half-life. Thus, in the Columbia River, the nuclides most generally present in fish are phosphorus-32 and strontium-89, in contrast to the reactor effluent activities, which consist largely of arsenic, manganese, and copper.

Some laboratory experiments have been performed on the uptake of certain nuclides by fish and other aquatic forms. Most of the work has been concentrated on fission products, particularly strontium and cesium. The results of these studies, oversimplified, may be summarized by saying that many elements are taken up by the more primitive feeders, such as algae and mollusks. Forms feeding upon these primitive forms generally take up less of the insoluble elements, except in the contents of the digestive tract. A number of nonfission-product nuclides, particularly zinc, cobalt, and iron isotopes, are taken up by mollusks, and surprisingly large quantities of zinc have been found in fish.

Disposal of Water Containing Radioactive Nuclides

Low-Activity Wastes

It is difficult to make hard-and-fast statements about the disposal of water containing radioactive materials. As is the case with other wastes, disposal varies with the nature and quantity of the material, and with the ability of the environment to accommodate the waste. Since the term "radioactive material" covers such a wide variety of nuclides of different physical, chemical, and biological properties, the disposal of wastes will inevitably be a matter of individual determination in each case.

A large majority of users of radionuclides can dispose of their wastes with only the most elementary precautions. The Atomic Energy Commission has established regulations for the sewer disposal of radionuclides by its licensees. The average research user of isotopes need only measure the activity of his waste to make sure that its concentration when discharged will be acceptable. Beyond this, he must only make sure that the activity is prevented from depositing on plumbing, where it might become a hazard.

Even where an isotope user must dispose of quantities too large for direct discharge, simple treatment methods often suffice, for example, storage of materials of short half-life. In this case the waste is retained until radioactive decay reduces the activity to a level that will permit safe discharge. Where storage would be impractical, as in the case of high activity or long half-life, the radionuclide may often be removed from the waste water by coagulation, precipitation, or ion-exchange techniques. The concentrated nuclide in solid form can then be stored if convenient, or disposed of by burial. The decontaminated water, after its radioactivity has been shown to be at a safe level, can be discharged.

Waste water containing radionuclides at somewhat higher levels, say of the order of a few millicuries per gallon, is rather common in the nuclear industry. Here it is considered "low level" even though its activity may be much higher than would be considered "low" outside the industry. Such wastes often originate in laboratory or decontamination operations, or in operations involving the draining of a small volume of highly radioactive material. Normally such wastes require treatment prior to discharge. The treatment may be impoundment for decay, coagulation or precipitation, or ion exchange. A somewhat more stringent treatment, suitable for use with higher concentrations of radionuclides, is concentration by evaporation, suitable precautions being taken to minimize carry-over of spray in the condensate. This converts the waste into two parts, a condensate ready for monitoring and discharge, and "bottoms" of high-level waste. Electrodialysis with ion exchange membranes, which has been suggested as an alternative treatment to evaporation, must still be considered an experimental method although theory and preliminary investigations have been somewhat promising. Since these treatments will not affect all nuclides to the same extent, the discharge of the treated water must be regulated in accordance with its nuclide composition as well as its total radioactivity content.

Wastes may be discharged to the environment only after necessary treatment, when required, and after monitoring to make sure that the radioactivity actually is at an acceptable level. Discharge may be through sewer systems, when convenient, or directly into streams or other bodies of water. Discharge into the ground is often practiced in controlled areas. In this case, the ion-exchange capacity of the soil often provides a form of storage so that somewhat higher levels of activity can be discharged than would be acceptable for direct stream discharge. Adequate monitoring is required where ground disposal is used, to insure that the groundwater will not be adversely affected.

High-Activity Wastes

High-activity wastes may be defined as those containing radionuclides at a concentration of the order of curies per gallon. Most of these wastes originate in the chemical processing of irradiated reactor fuels. Their treatment is made difficult by their chemical properties (acidity, salt content, and so on) as well as by their radioactivity. Generally speaking, these wastes cannot be discharged. They must be stored, and treatment and disposal is only a way of making the storage as inexpensive as possible. The wastes may be stored in tanks, or disposal may be concealed as in discharge to the ocean or into geological formations, or they may be converted into a solid, nonleachable form. In all these cases, however, there is reliance on the material staying where it is put, and not being allowed to leak into the environment.

The only reliable, tested method for large quantities of high-level wastes is permanent tank storage. The waste is usually concentrated by evaporation to the greatest extent possible, the condensate being discharged as a low-level waste. The concentrated bottoms are then transferred to special tanks. These tanks must be corrosion-resistant and must provide for removal of the heat produced by radioactive disintegration. Although storage is stated to be "permanent," this cannot yet be considered definitely established, because the nuclear industry is less than thirty years old and retention for centuries is required. It is definitely established, however, that this treatment is expensive.

A treatment successfully used on small quantities of highly radioactive wastes is conversion into a solid such as concrete. One way of doing this is to add enough cement to the waste that it will set. The cement is usually allowed to set in drums, which are then buried either in the ground or in the deep sea. A modification of this method which offers much promise, and which has been tested on a small scale, is conversion of the waste into a glassy or ceramic material. The waste is calcined to alumina or zirconia and leached. The leached radionuclides may be taken up on clay be adsorption or ion exchange, and the clay is then fired to change its crystal structure in such a way that the radionuclides cannot be desorbed or leached. The ceramic pellets could presumably be stored much more cheaply than tank storage, because of the two factors of reduced volume and noncorrosive nature.

Another form of treatment that has been proved in the laboratory involves separation of the long-lived nuclides strontium-90 and cesium-137 on barium sulfate and potassium alum, respectively. These two nuclides may then be stored rather cheaply because the volume has been markedly reduced. An aqueous phase suitable for discharge is obtained by solvent extraction of the residual fission products from the waste water. These fission products present a much simpler storage problem because of their shorter half-lives.

Ultimate Disposal

The term "disposal at sea" really has two meanings. In one, it is contemplated that the material remain sealed indefinitely out of contact with the seawater; in the other, the material is introduced into the deep sea but is not sealed from it, and reliance is placed on the slowness of mixing in the sea to limit the spread of radioactivity into the human environment. Unfortunately, our present knowledge of the sea is not adequate to permit full confidence in slow mixing. Rates of transport, and especially of biological transport, are still very uncertain. Therefore, all present disposal at sea is actually sealed storage. Sealed containers, usually concrete-filled steel drums, designed to withstand the pressures and corrosion of the sea, are discharged into depths of 1000 fathoms or more. Presumably the drum and eventually the concrete will be corroded away, but it is hoped that this process will be slow enough that even the longer-lived dangerous nuclides will have decayed to insignificant levels.

Because of the cost of tank storage and of transportation for burial at sea, there is much interest in underground disposal. This is different from discharge into the soil as utilized for low-level wastes. The concept with high-activity wastes is utilization of sealed geological formations as permanent storage. A number of types of geological formations have been considered; at present the most promising appear to be salt domes.

Sampling and Measurement of Radioactive Water

Sampling

In sampling water for determination of its radioactivity, whether this be for gross or for radionuclide assay, the normal principles of sampling apply. Since no analysis is better than the sample, it is necessary to make certain that the sample drawn is actually representative of what is needed, both in space and time. The possibility that the analyst may require a continuously composited sample, even one composited proportionally to flow rate, should not be disregarded. Where adequate mixing is not assured, a number of samples from different points and various depths may be taken, either for individual analysis or for compositing. The principles involved in this aspect of sampling will not be mentioned further, because they have been covered in detail in Chapter 9.

Sampling for radioactivity determinations, however, does have one requirement not commonly found in other sampling. This is the need to prevent loss of the radioactive material to the sampler or container. When, as is often the case, the amount of nuclide is only of the order of 10^{-12} g, or even less, normal adsorptive losses on container walls may amount to an important percentage of the activity. Glass or plastic materials appear to give somewhat less difficulty of this kind than do metals. Where necessary, addition of carrier materials or chelating agents or acidification may be employed to minimize adsorptive losses.

Often, no adsorptive losses are found in sampling streams or other natural waters. It appears that in such waters the easily adsorbable materials are already on the surfaces of whatever suspended solids may be present. Therefore, treatment to prevent adsorption may result in undesired transfer of radionuclides from the suspended to the dissolved phase.

Measurement

Only the most general survey of the problems of measurement of radioactivity in water is in order here. Specific details are the subject of numerous papers and books. As it is often necessary to measure extremely small amounts of radioactive material in water, the problem of sensitivity or detectability becomes paramount.

Detectability is limited by the random nature of the radioactive disintegration process. The result is a statistical uncertainty in the number of counts observed, setting an inherent lower limit to the precision of the determination. At low enough levels, there is a question of whether there actually were any counts in a given period beyond what might be due to the background, that is, the counts caused by cosmic rays and by naturally occurring radionuclides in and around the instrument. Three techniques are available to get enough counts to permit a definite answer to this question: start with a large sample, detect as many of the radiations as possible, and suppress the background. It is not often convenient to collect or process samples larger than a litre or so, and sample size is often further restricted by solids content. This will be further considered in the discussion of methods of sample preparation.

High efficiency of detection is chiefly a function of the instrument type, although it is also affected by sample preparation. As far as the instrument is concerned, three factors are paramount. First is geometry, or fraction of radiation emitted toward the detector. This is primarily determined by sample and detector size, and by the distance between them. Next comes absorption, which refers to failure of part of the radiation to penetrate the sample solids, the air or other material between the sample and detector, or the wall of the detector itself. Third is the actual detector efficiency, or the fraction of radiations entering the detector which causes a response. Highest overall efficiency occurs when a sample is placed inside a detector able to respond to each disintegration. Such 100 percent efficiency is customarily attained only with gaseous samples, although it can be approached with solid samples in special 4-pi counters.

Background suppression is most commonly attained by surrounding the detector with lead or other heavy shielding to block gamma radiation from reaching it. Lead is used in thichnesses up to about 100 mm (4 in.); iron up to 200 mm (8 in.). Even such quantities of shielding will not block cosmic rays; these can only be eliminated by adding additional detectors which inactivate the counter momemtarily when a cosmic ray passes through them. For lowest background levels, careful choice of the materials of the detectors and shielding is important. Thus iron normally contains less radioactive material than lead, and so is more suited for critical shielding applications.

Instrumentation Types

Three principles of detection are used in measurement: gas ionization, scintillation, and photographic darkening. The last is omitted as not strictly an instrumental technique, although it is very widely used in such applications as personnel monitoring by film badges and in autoradiography. Each of the other two techniques may be used to provide an average, pointer-type indication, or to count individual events.

A second classification of instruments is by the type of radiation they are designed to measure. Since alpha particles are characterized by small penetrating power and high energy dissipation, alpha detectors must be made with extremely thin windows for the entrance of the radiation, or (more usual) with provision for the sample to be introduced into the detector. Only moderate amplification is provided to take advantage of the high energy dissipation, permitting low response for other types of radiation, including cosmic rays. In scintillation alpha detectors, discrimination against other radiations is provided by using a very thin zinc sulfide scintillating screen which gives only very small light pulses with beta and gamma radiation.

In the detection of beta particles, window requirements are less stringent than for alpha particles. The ordinary Geiger-Müller tubes may have glass or metal walls with a thickness of 30 mg/cm^2, or mica windows from 1 to 4 mg/cm^2 thick. For the highest efficiency, the sample may be introduced into the detector, as for alpha particles. In fact, the same instrument may be used to detect alpha particles or beta (plus alpha) particles merely by changing the voltage so as to provide higher or lower amplification. Scintillation beta detectors commonly have an organic scintillator, such as an anthracene crystal. The scintillator molecules may be dispersed in plastic to make detectors of varying sizes and shapes.

Gamma rays are characterized by large penetration through matter; therefore the detectors should have as much mass as possible. High atomic number increases the response. Ionization chambers may contain gas under high pressure, while gamma Geiger tubes usually have cathodes of silver, bismuth, or other heavy metal. Windows may be made heavy (300 mg/cm^2 or more) to reduce response to beta particles. The detection of gamma radiation by scintillation counters has reached a high state of development. Most detectors use sodium iodide crystals (thallium-activated). The heavy salt provides a large mass, and gamma absorption is enhanced by the large percentage of iodine, with its high atomic number.

Some less-common instruments of more specialized type may be mentioned briefly. The 4-pi counter is designed to permit detection, with 100 percent efficiency, of alpha or beta particles. Sample preparation requirements are so stringent that they limit use of the instrument to calibration, rather than to routine work. In liquid scintillation counters, the sample is dissolved in an organic solution of a scintillator, so that all the radiations can produce scintillations. This instrument has been especially developed for the special cases of measuring the very weak radiations from carbon-14 (0.15 MeV) and from tritium (0.018 MeV).

Sample Preparation

Sample preparation techniques are intimately connected with the type of radiation and with the instrumentation available. Alpha particles travel only a few micrometres in water and beta particles only a few millimetres; thus any detector measuring these in unprocessed water will be observing only a very thin film immediately surrounding it. Such an instrument will therefore respond only to relatively high radionuclide contents. Gamma rays, on the other hand, have a much larger range in water, and large unprocessed samples can be used. Even in this case, the material at large distances from the detector will have poorer geometrical efficiency.

For alpha and beta measurements, and for many gamma measurements, separation of the radioactive material from the water is required. The most common technique for this is evaporation of the water and transfer of the residual solids to a dish or planchet suitable for the counter being used. Removal of the water does not completely eliminate self-absorption loss. Even with a sample as thin as 5 mg/cm^2, an appreciable part of the beta radiation and as much as 50 percent of the alpha radiation are lost.

Chemical separation is required where a specific radionuclide must be determined in a mixture. This technique must also be used if the solids content of the water is so high that simple evaporation is inapplicable.

Hazards

The present thinking on radiological hazards is best summarized by the staff reports of the Federal Radiation Council. The most important points are that the total accumulated radiation dose should be kept as low as possible, and in any case shall not exceed 5 rems for each year beyond age 18, nor shall the dose in any 13-week period exceed 3 rems. Where exposure is restricted to skin, extremities, bone or thyroid, somewhat higher doses are permitted.

Hazards to workers with radioactive materials may be external and internal. External hazards arise as a result of the worker being close to a source of ionizing radiation. Measurement of radiation levels in the vicinity of radioactive material is relatively simple in most cases. The primary concern in this situation is with the highly penetrating gamma rays, since it is a simple matter to shield out the beta particles. Alpha emitters are of no concern as external sources, since this type of radiation is unable to penetrate the nonliving exterior layer of the skin. The permissible dose from the external sources of ionizing radiation is discussed in the *National Bureau of Standards Handbook 59*, as amended April 15, 1957.

Several kinds of measuring devices are in general use as monitors of radiation levels. One of the most useful is the film badge, routinely worn during working hours. This is simply a holder for X-ray film. At the end of a predetermined period, which may be a week or more, the films are removed from the badge, developed, and the accumulated radiation dose determined by comparison with films exposed to known doses. The film badge is widely used because of its simplicity, reliability, and permanence as a record. The film badge usually includes devices to permit identification of the type of radiation; by varying the thickness and nature of the covering of the film it is possible to distinguish beta particles, soft gamma rays, harder gamma rays, and neutrons.

Survey meters are commonly used for more rapid indication of radiation levels. One type (ionization chamber) indicates the radiation level by measuring the ion current in a gas space between two electrodes. This current is proportional to the ionization produced by the radiation. A second type employs a Geiger tube and gives an indication proportional to the counting rate. This type, while considerably more sensitive, is less directly related to dose rate and is not operable in high radiation fields. Both types may come with shutters thick enough to stop beta particles and thus differentiate between beta and gamma radiation.

Two special forms of these instruments deserve special mention. One is the dosimeter, which is a small ionization chamber that can be carried in a pocket. Before use, the electrodes are charged to a definite voltage, and the total accumulated dose can be read at any time by measuring the decline in voltage. The other form is the alpha survey meter, usually an ionization chamber or proportional chamber equipped with a very thin window through which alpha particles can pass. The primary function of this instrument is the measurement of alpha contamination of surfaces.

Three factors are paramount in the control of external radiation hazard: shielding, distance, and time. Storage in suitable shields reduces radiation from sources to an acceptable level. Well-designed shielding during actual work with nuclides can minimize the radiation dosage. The radiation level decreases as the square of the distance from a point source, and many operations can be carried out safely by remaining at a sufficient distance from the source. Remote handling tools, simple or complicated, are important in such cases. When it is impossible to reduce the radiation level in an operation to a low level, the duration of exposure may be controlled, either by performing the operation rapidly, or by using several sets of workers to complete it.

Internal hazard through ingestion or inhalation of radioactive material is more subtle. The most important factors in its prevention are good working habits, particularly careful planning, and good housekeeping practices. Not only should the quantities of nuclides used in an experiment be kept as small as possible, but nuclides of low physiological hazard should be used whenever there is a choice. All operations that may produce airborne radionuclides should be carried out in an adequate hood. Good housekeeping practices include working in trays, regular monitoring and cleanup of surfaces, careful washing when leaving the laboratory, and prohibition of eating, drinking, or smoking in the laboratory.

Monitoring of workers for internal contamination is most often done by analysis of urine, or less often of feces. If a worker is aware that he has ingested radioactive material, he should induce vomiting. Treatment beyond this is strictly the function of the physician, who should be called immediately.

The Federal Radiation Council has divided the possible intake by humans of four of the more hazardous radionuclides into the three ranges and appropriate responses listed in Table 7. The upper levels of Range II correspond to the radiation protection guides for population groups. The maximum permissible body burdens for other radionuclides and the maximum permissible concentrations of radionuclides in water are given in *National Bureau of Standards Handbook 69*. For drinking water supplies, the *Public Health Service Drinking Water Standards*, 1962, states that they shall be approved when radium-226 and strontium-90 concentrations do not exceed 3 and 10 pCi/litre, respectively, or if the total human intake from all sources is within the limits recommended by the Federal Radiation Council for control action. In the known absence of strontium-90 and alpha emitters,

TABLE 7—*Graded scale of action in response to transient intakes.*

	Range of Radionuclide Intake, pCi/day			
Scale of Action	Ra-226	I-131	Sr-90	Sr-89
Range I: Periodic confirmatory surveillance as necessary	0 to 20	0 to 10	0 to 20	0 to 200
Range II: Quantitative surveillance and routine control	2 to 30	10 to 100	2 to 200	200 to 2 000
Range III: Evaluation. and application of additional control measures as necessary	20 to 200	100 to 1 000	200 to 2000	2 000 to 20 000

the water supply is acceptable when the gross beta concentration does not exceed 1000 pCi/litre.

Sources of Information

Because of the novelty of the subject of radioactivity to many of the readers of this Manual, information on the literature of this field may be useful. It is not possible to make an exhaustive compilation of sources; accordingly, the following materials have been listed in the belief that they form a useful survey. Very possibly, equally good materials have been omitted through lack of acquaintance with them.

Books

For the novice in the field, books undoubtedly give the best introduction to a subject. The first three books listed are excellent surveys of radioactivity and atomic energy, at a level comprehensible to the nonspecialist:

Friedlander, G., Kennedy, J. W., and Miller, J. M., *Nuclear and Radiochemistry*, 2nd ed., Wiley, New York, 1964.

Lapp, R. E. and Andrews, H. L., *Nuclear Radiation Physics*, 3rd ed., Prentice-Hall, New York, 1963.

Glasstone, S., *Sourcebook on Atomic Energy*, 3rd ed., Van Nostrand, Princeton, N. J., 1967.

The next book can be recommended as a classic in the field, although somewhat old. It is particularly strong with respect to naturally occurring radionuclides:

Rutherford, E. R., Chadwick, J., and Ellis, C. E., *Radiations from Radioactive Substances*, Cambridge University Press, 1951.

The next group includes somewhat less general texts, each good in its field, which is generally indicated by the title:

Murray, R. L., *Introduction to Nuclear Engineering*, 2nd ed., Prentice-Hall, New York, 1961.

Glasstone, S., *Principles of Nuclear Reactor Engineering*, Van Nostrand, Princeton, N. J., 1955.

McCullough, C. R., *Safety Aspects of Nuclear Reactors*, Van Nostrand, Princeton, N. J., 1957.

Sharpe, J., *Nuclear Radiation Detectors*, Methuen, London, England, and Wiley, New York, 1955.

Taylor, D., *The Measurement of Radioisotopes*, Methuen, London, England, and Wiley, New York, 1951.

Smyth, H. D., "A General Account of the Development of Methods of Using Atomic Energy for Military Purpose Under the Auspices of the United States government" (1940–1945), U. S. Government Printing Office, Washington, D. C., 1945 (better known as the "Smyth Report").

Glasstone, S., Ed., *The Effects of Nuclear Weapons*, U. S. Government Printing Office, Washington, D. C., 1957 (much information on fallout).

Coryell, C. D., and Sugarman, N., Eds., *Radiochemical Studies: The Fission Products*, McGraw-Hill, New York, 1951.

Wahl, A. C., and Bonner, N. A., *Radioactivity Applied to Chemistry*, Wiley, New York, 1951.

Compendia

Intermediate between books and the periodical literature are reports of conferences, groups of papers, and similar compendia. A few of these may be listed:

National Nuclear Energy Series—a record and summary of Manhattan District and early Atomic Energy Commission research. McGraw-Hill, New York.

Proceedings, International Conference on the Peaseful Uses of Atomic Energy, the record of the 1955 Geneva Conference. 16 volumes, United Nations, New York, 1956.

Proceedings, Second International Conference on the Peaceful Uses of Atomic Energy, the record of the 1958 Geneva Conference, 34 volumes, United Nations, New York, 1959. (An edited series of 12 volumes is available from Pergamon Press, New York.)

Progress in Nuclear Energy, nine series each covering a specific area. Probably will appear annually. Pergamon Press, New York.

A further group of useful publications of this general type include:

Semi-annual Reports to Congress, U. S. Atomic Energy Commission, U. S. Government Printing Office, Washington, D. C. Each of the later reports is subtitled according to its principal subject. These include:

Sixth Semi-Annual Report, "Atomic Energy and the Life Sciences."

Eighth Semi-Annual Report, "Control of Radiation Hazards in the Atomic Energy Program."

Thirteenth Semi-Annual Report, "Assuring Public Safety in Continental Weapons Tests."

Twenty-first Semi-Annual Report, "Radiation Safety and Major Activities in the Atomic Energy Programs."

Twenty-fifth Semi-Annual Report, "Atomic Industrial Progress and Second World Conference."

Annual Reports, United Kingdom Atomic Energy Authority, H. M. Stationery Office, London, England.

"The Nature of Radioactive Fallout and Its Effects on Man," hearings before the Special Subcommittee on Radiation of the Joint Committee on Atomic Energy, 85th Congress, U. S. Government Printing Office, 1957.

"Industrial Radioactive Waste Disposal," hearings before the Special Radiation Subcommittee of the Joint Committee on Atomic Energy, 86th Congress. U. S. Government Printing Office, 1959.

Reports of the National Academy of Sciences—National Research Council, Washington, D. C.:

"The Biological Effects of Atomic Radiation"

"The Disposal of Radioactive Waste on Land"

Symposium on Radioactivity in Industrial Water and Industrial Waste Water, ASTM STP 235, American Society for Testing and Materials, 1959.

Recommendations of the National Committee on Radiation Protection and Measurements (NCRP), published as Handbooks of the National Bureau of Standards. U. S. Government Printing Office, Washington, D. C. The handbooks include:

Handbook 49, "Recommendations for Waste Disposal of Phosphorus-32 and Iodine-131 for Medical Users," Nov., 1951.

Handbook 51, "Radiological Monitoring Methods and Instruments," April, 1952.

Handbook 52, "Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water," March, 1953.

Handbook 53, "Recommendations for the Disposal of Carbon-14 Wastes," Oct., 1953.

Handbook 54, "Protection Against Radiations from Radium, Cobalt-60, and Cesium-137," Sept., 1954.

Handbook 58, "Radioactive Waste Disposal in the Ocean," Aug., 1954.

Handbook 59, "Permissible Dose from External Sources of Ionizing Radiation," Sept., 1954 (amended April 15, 1957).

Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure," June, 1959.

Kinsman, S., et al, "Radiological Health Handbook," Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

"Glossary of Terms in Nuclear Science and Technology, USA Standard N1.1-1967, American Society of Mechanical Engineers, United Engineering Center,. 345 E. 47th Street, New York, N. Y. 10017, 1957.

Periodical Literature

The periodical literature in nuclear energy is so voluminous that only a brief glimpse into the field can be given. In addition to the usual journal publications, a vast number of government reports (including U. S. Atomic Energy Commission, U. K. Atomic Energy Authority, and similar groups) are available. For this reason, the abstract literature in this field is especially important. Fortunately, the first journal listed below does an outstanding job of covering the report literature, in addition to providing adequate coverage of the journals. The other abstract coverage listed is generally somewhat more specialized than Nuclear Science Abstracts.

Abstracts, Reviews, and Bibliographies

Nuclear Science Abstracts, NSAB-A
Public Health Engineering Abstracts

Journal, American Water Works Association, JAWWA, Abstract Section
Chemical Abstracts, CHABA, (outstanding coverage of journal literature)
Sewage and Industrial Wastes, SIWAA: Annual Review of Literature on Radioactive Wastes
Analytical Chemistry, ANCHA: Reviews (usually each April)
Water Pollution Abstracts
TID Bibliographies, U. S. AEC, especially:
  TID-4563, "Special Sources of Information on Isotopes"
  TID-3511, "Bibliography on Uses of Radioactive and Stable Isotopes in Industry"
  TID-3050, "Bibliography of Selected AEC Reports of Interest to Industry"
AERE Bibliographies, United Kingdom Atomic Energy Authority, especially:
  AERE-Lib (L1) "Sources of Information in Atomic Energy."
  AERE-Inf/Bib 96 "A List of Reports and Published Papers by AERE Staff" (with Supplements).
"Publications on Atomic Energy," H. M. Stationery Office, London, England, 1956.
"Selected Readings on Atomic Energy," U. S. Govt. Printing Office, Washington, D. C., 1955.

General Journals

Nucleonics, NUCLA (particularly valuable for nuclear news)
International Journal of Applied Radiation and Isotopes, IJARA (applications of radionuclides in industry, medicine, and science; radiation techniques; radiochemistry)
Science (contains technical articles of general interest)
Nature (generally similar to *Science*)
Analytical Techniques, Including Instrumentation:
Analytical Chemistry, ANCHA
Analytica Chimica Acta, ACACA
Analyst
Reviews of Scientific Instruments

Water Journals

Journal, American Water Works Association, JAWWA
Sewage and Industrial Wastes, SIWAA
Water Pollution Research

Miscellaneous

Transactions, American Geophysical Union, TAGUA, (hydrology; meteorology; natural activity)
Radiation Research, RAREA
Industrial and Engineering Chemistry, IECHA (especially radiation waste treatment)
Health Physics

Chapter 17—Nuclear Water Technology

The first application of nuclear reactor systems to commercial power generation was at the Shippingport Atomic Power Station, which began operating in December 1957. This station operates as part of the Duquesne Light Company grid, supplying power to the Pittsburgh, Pa. metropolitan area.

Today, 21 years later, nuclear power stations satisfy a significant portion of our electrical power requirements. As of December 1970, there were in the United States 104 civilian power reactors operating or on order, having a combined electrical generating capacity of 86794 MWe (megawatt electrical). Of these, stations generating a total of 8000 MWe were operational. The total U. S. electrical generating capacity in operation at this same time was approximately 341 000 MW. Forecasters indicate that, by the last decade of this century, nuclear power will represent 40 percent of the approximately 1 400 000-MWe electrical generating capacity that will be installed by that time and will generate over 50 percent of the electricity used.

Most of the power reactors in service or under construction today are thermal reactors using various coolants and moderators. Great Britain played a pioneering role in the development of gas-cooled (carbon dioxide) and graphite-moderated reactors and is the largest manufacturer of gas-cooled reactors. Canada has specialized in heavy water-cooled and moderated reactors. However, the majority of plants in use or under construction in the United States and elsewhere use light water for both coolant and moderator. The two types of light-water reactors are pressurized water reactors (PWR) and boiling water reactors (BWR).

The few fast reactors in operation or under construction today are basically demonstration plants. While they cannot compete economically with thermal reactors at the present time, they are considered to be the reactor type of the future. Fast reactors use either materials with high mass number (liquid metals like sodium, for example) or gases as a coolant.

In this chapter, boiling water reactors and pressurized water reactors using natural water coolant, those most widely used for power generation, are discussed.

Pressurized Water Reactor Power Plant

A typical pressurized water reactor system (PWR) is shown in Fig. 1. Heat generated by the fissioning fuel in the nuclear core is removed by water (reactor coolant) circulating at high pressure through the primary circuit. The water in the primary circuit both cools and moderates the reactor. The primary water is kept under pressure to keep it from turning to steam.

The heat is transferred from the primary coolant to the secondary system coolant (also light water, but unpressurized) in a shell-and-tube type heat exchanger, or to a steam generator turning the secondary coolant to steam. Typical operating conditions are summarized in Table 1. The steam produced in the steam generator is at a lower pressure and temperature than the primary coolant. Therefore, the secondary portion of the cycle is similar to that of the moderate-pressure fossil-fueled plant.

Boiling Water Reactor Power Plant

In a BWR power plant (Fig. 2), the nuclear core is contained in a pressure vessel. Light-water coolant is circulated through the core, but, since it is unpressurized, is turned directly to steam. The steam is separated from the bulk coolant and delivered directly to a turbine and then to a condenser. The

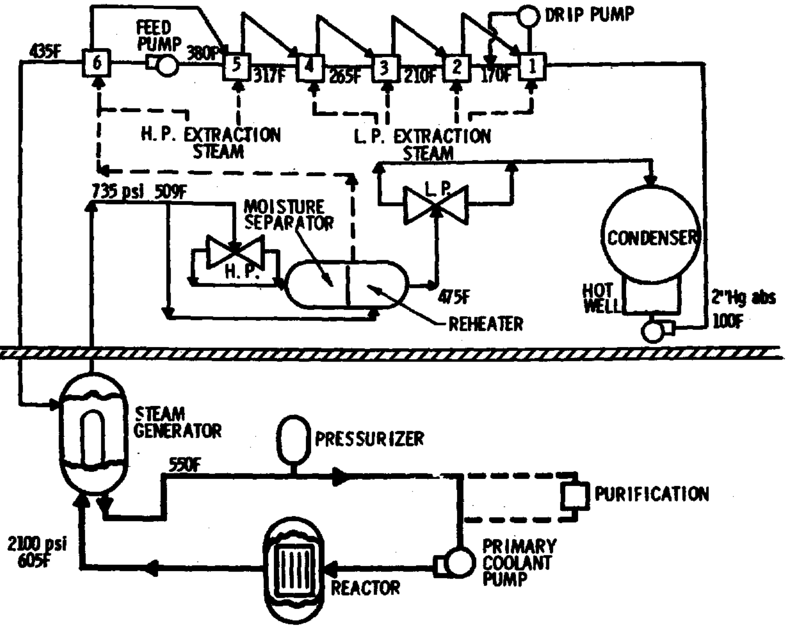

FIG. 1—*Typical pressurized water reactor (1 psi = 6.895 kPa).*

TABLE 1—*Typical operating conditions for PWR systems.*

Primary System	PWR	BWR
Temperature	288 to 321°C (550 to 610°F)	285 to 313°C (545 to 596°F)
Pressure	13 790 to 15 514 kPa (2000 to 2250 psig)	6895 to 10 342 kPa (1000 to 1500 psig)
Secondary System		
Steam temperature	266 to 274°C (510 to 525°F)	none
Pressure	4826 to 6205 kPa (700 to 900 psig)	none

essential difference between the PWR and BWR is that the latter uses a direct cycle, that is, no heat exchanger.

Typical operating conditions for the BWR are given in Table 1.

Reactor Components

A power reactor is composed of a core or group of fuel elements, control rods, coolant, and moderator (Fig. 3). Heat energy is generated in the reactor core, which contains an array of fuel assemblies. Various typical PWR cores are rated from approximately 1500 to 3500 MWt (megawatt thermal) with corresponding electrical outputs of 500 to 1200 MWe. An 800-MWe core, for example, is approximately a right circular cylinder with an equivalent diameter of 345 cm (136 in.), an active height of 348 cm (137 in.), and is made up of 217 fuel assemblies. About 80 metric tons of uranium oxide (UO_2) are used in the reactor core. The core is completely open, shrouded only at the outer periphery.

Each fuel assembly is made up of 176 fuel rods supported within a rigid frame consisting of stainless steel upper and lower end fittings, Zircaloy fuel rod spacer grids, and five Zircaloy axial guide tubes which will accept a control element assembly (control rods). The overall length is about 394 cm

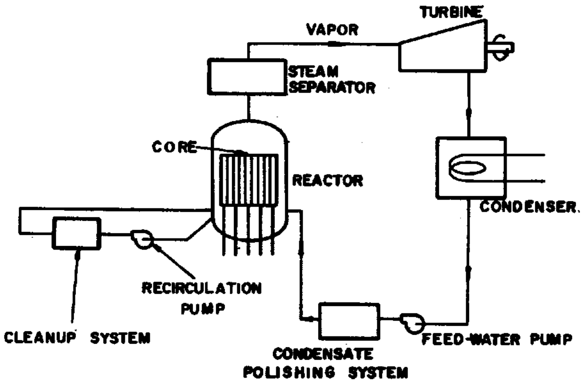

FIG. 2—*Schematic arrangement of boiling water reactor power plant.*

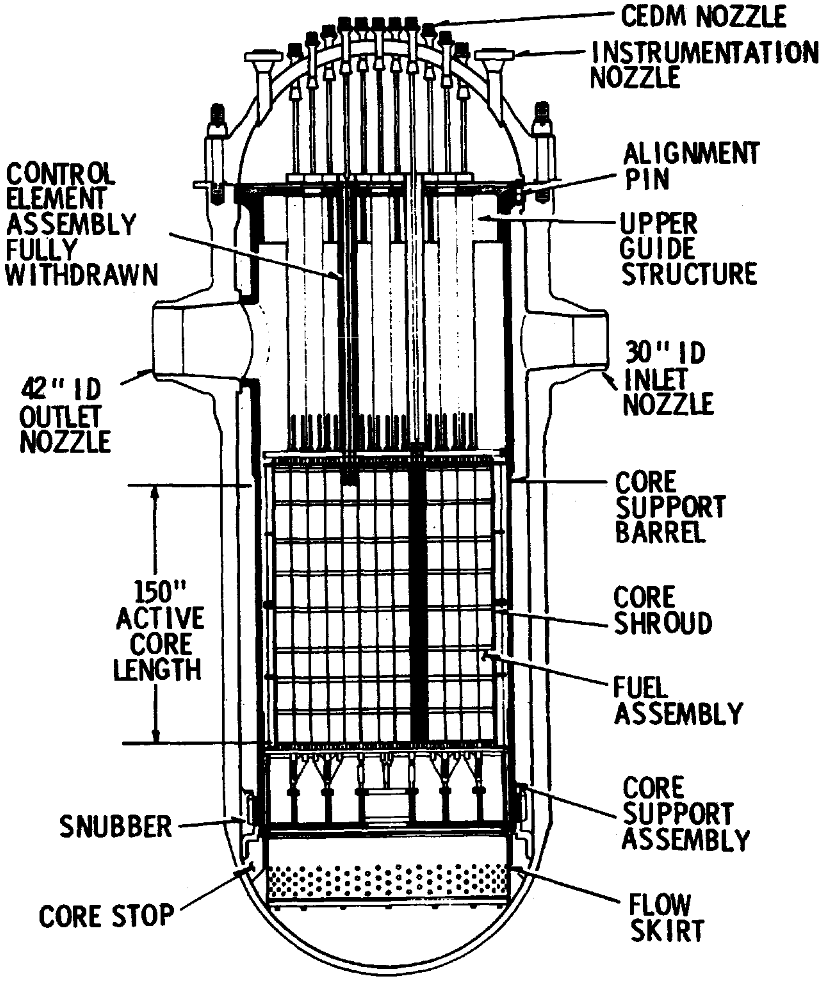

FIG. 3—*PWR reactor assembly* (*1 in. = 2.54 cm*).

(155 in.), and the cross section is approximately 8 in. (20 cm) square. Each assembly weighs about 585 kg (1300 lb) (Fig. 3).

Each fuel rod contains sintered uranium oxide pellets of approximately 10 mm (0.4-in.) diameter and approximately 15 mm (0.6-in.) long. The Zircaloy-4 cladding tube is approximately 0.66 mm (0.026 in.) thick. This material has good corrosion behavior in the reactor environment and has low neutron absorption cross sections. The tube length accommodates the fuel pellet column and a fuel and gas expansion space. A diametral gap between the pellets and the cladding provides for differential expansion between the cladding and fuel to limit clad strain.

Control rods are located in selected fuel assemblies and contain materials possessing high neutron absorption cross sections. Their relative position (depth) in the core regulates the rate of power generation. Control rod materials commonly used are boron as the carbide (B_4C) or the alloy silver-indium-cadmium (Ag-In-Cd) (Fig. 3).

The coolant, or core heat removing medium, is water. A typical 800-MWe PWR coolant system flow is approximately 19 m^3/s (300000 gal/min). Coolant temperature at the core inlet is 288°C (550°F) and at the core exit 316°C (600°F). In a pressurized water reactor, the coolant water also serves as the moderator.

Materials of Construction

The materials of construction listed in Table 2 are typical of modern water reactors and consists of 300-series stainless steel primary system surfaces, Zircaloy-clad fuel elements, and, in PWR's, Inconel-600 steam generator tubing. With the possible exception of core materials, conventional construction materials are used throughout the reactor coolant and steam-condensate cycle.

These materials are common to both systems. For BWR's and those PWR's that produce superheated steam, no copper alloys can be used for condenser or feedwater heater material; stainless steel only is employed. This is to prevent thermally insulating copper deposits from forming on fuel element surfaces (BWR) or steam generator (superheat section) tubing (PWR).

TABLE 2—*Materials exposed to coolant in a typical water reactor coolant system.*

Reactor vessel	
vessel cladding	weld-deposited SS[b]
vessel internals	304 SS
instrument and control rod drive nozzles	Ni-Cr-Fe alloy 600[a]
Fuel cladding and guide springs	Zircaloy-4
Control rod drives	304 SS and 410 SS
Pipe cladding-main loop pipes	304L SS
Surge and spray piping	316 SS
Steam generator	
bottom head cladding	weld-deposited SS[b]
tube sheet cladding	weld-deposited Ni-Cr-Fe alloy-600[a]
tubes	Ni-Cr-Fe alloy-600[a]
divider plate	410 SS
Pumps	
casing	316 SS
internals	304 SS
Pressurizer	
cladding	Type 304 SS[b] and Ni-Cr-Fe alloy 600
heaters	Ni-Cr-Fe alloy-600[a]

[a] Inconel-600.

[b] Equivalent to Type 304 SS as deposited.

Water Quality

High-purity water is needed in nuclear applications principally to preclude fouling of heat-transfer surfaces, prevent corrosion, and preclude the creation of radioactive materials through nuclear activation processes. Corrosion can impair material integrity or increase corrosion product concentrations, which result in activated residues on the primary system surfaces, filters, and in waste systems.

Water has many uses in a nuclear plant, and the end use dictates the quality requirements. The water used is largely recycled, but normal valve or gland leakage may contain radioactivity and must be collected and processed prior to reuse or discharge. Radioactive liquid waste processing employs a wide variety of water purification techniques. Water is also used for shielding in fuel storage pools, as a cooling fluid in reactor and auxiliary cooling circuits, and as the working fluid.

As in any power cycle, long-term reliability is a necessary goal. To achieve this goal, water quality control is established to opitimize the environment in which the system materials will operate. The main objectives of this control are:

1. To reduce the general corrosion of system materials.
2. To maintain material integrity of components and piping.
3. To assist in reactivity control of the reactor in PWR's.

The first two objectives are applicable to any power plant water treatment program regardless of whether conventional or nuclear fuel is used. The nuclear water technologist deals largely with the same problems as the conventional power plant chemist.

There are many similarities in water quality requirements between PWR and BWR power plants. In the primary system of a PWR or BWR, the presence of the reactor neutron flux results in unique chemical conditions not found in fossil-fueled plants. This flux has two major effects on water chemistry control:

1. Impurities can be made radioactive.
2. Radiation can induce or cause normally nonoccurring chemical reactions to take place.

Makeup Water Quality

To assure water quality in the reactor primary coolant, makeup water must be maintained to equivalent specifications. The typical water quality specification for reactor coolant makeup water is given in Table 3.

One example of a common impurity which can be introduced is the chloride ion. The potential for stress corrosion of austenitic stainless steels in the presence of chloride and oxygen is well documented. Since austenitic stainless steel is used extensively in construction of PWR systems, it is obvious chloride and oxygen must be rigidly controlled. The specifications for chloride and oxygen are as follows:

TABLE 3—*Reactor coolant makeup water chemistry.*

Specifications	Operating Limit
specific resistivity	0.5 megohm-cm
total solids	0.5 ppm
pH [25°C (77°F)]	6.0 to 8.06
dissolved N_2 and O_2	nondeaerated
halides	
chloride	0 to 0.15 ppm Cl
fluoride	0 to 0.1 ppm F

	mg/l
Chloride	<0.15
Dissolved oxygen [temperature 66°C (150°F)]	<0.10

In a PWR, hydrazine is employed during startup operations to ensure that oxygen is not present to induce the stress corrosion reaction. Oxygen reacts with hydrazine as follows:

$$H_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

The reaction rate is temperature dependent and is extremely rapid in the range of 66° to 121°C (150° to 250°F) (Fig. 4). A competing decomposition reaction also accelerates as the temperature increases. At approximately 204°C (400°F), hydrazine decomposes rapidly and chemical deoxygenation of water is no longer practical (see Fig. 5). At power, oxygen can enter the coolant system in aerated makeup water. This oxygen is immediately scavenged by dissolved hydrogen in a reaction induced by the reactor radiation.

PWR Water Coolant Chemistry

Water in the primary system of a PWR is employed for both cooling and neutron moderation. It is basically high-purity water to which chemical additions have been made to achieve specific properties. For example, boric acid is used in the coolant of modern PWR's to control long-term reactivity changes. Pressurized water reactors use control materials in three different forms:

Control Method	Purpose	Material	Reactivity Worth, approximate %
Control rods	power maneuvering	boron carbide silver-indium-cadmium	8.0
Burnable poison	power shaping, compensation for fuel burnup	boron/aluminum	5.0
Soluble poison	compensation for fuel burnup, shutdown	boric acid	10 to 15

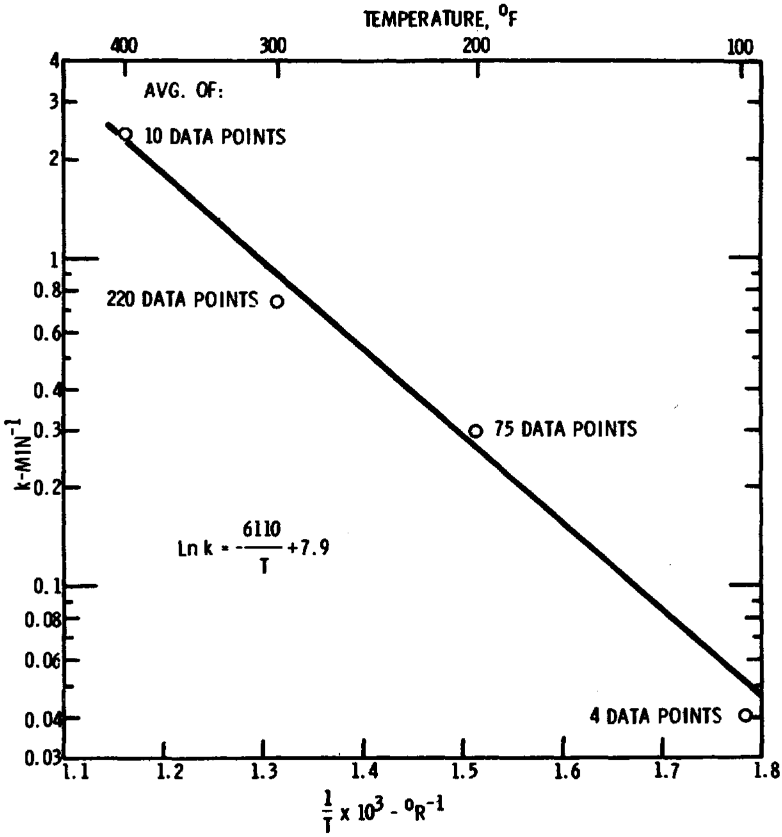

FIG. 4—*Effect of temperature on the N_2H_4:O_2 reaction rate constant.*

The control rods are adjusted according to the need to compensate for short-term changes, thus maintaining the power level. The movement of the rods is usually initiated by an automatic controller. Power maneuvering is accomplished by control rod movement also. A certain number of the control rods are always kept in the "full out" position to provide the means for fast reactor shutdown if needed.

Burnable poisons are employed as fixed poison rods in the fuel assemblies. They accomplish two purposes: (1) they compensate for fuel burnup, and (2) they help shape the power distribution within the core. Early in core life, when the new fuel contains more fissile material, the burnable poisons absorb neutrons, thus holding the reactivity and power down. By the end of cycle, when a large portion of the fissile material is gone due to fuel burnup, the burnable poisions are not present. Through reactions induced by neutron absorption, they are converted into neutral materials with small neutron absorption cross sections. Also in the beginning of the cycle, when new fuel is introduced into the core, the local variations in power density are relatively high. Judicious placement of the burnable poison rods makes more

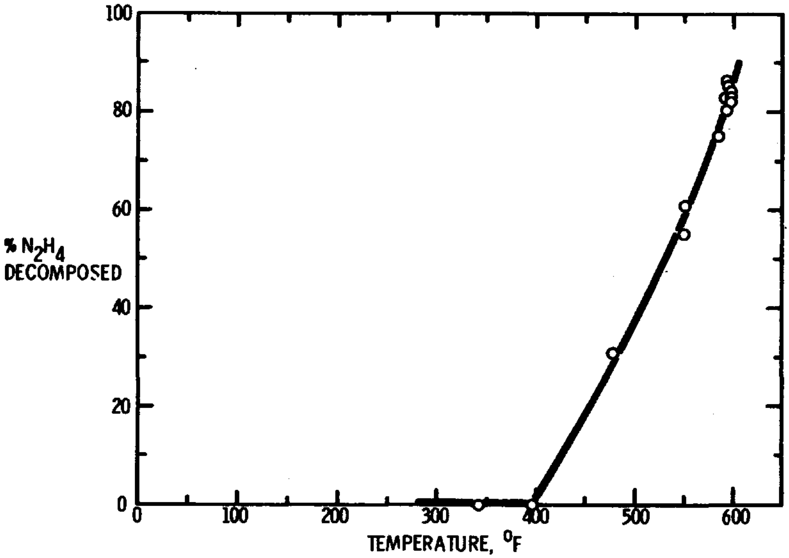

FIG. 5—*Effect of temperature on the decomposition of* N_2H_4 *for a reaction time of 0.8 min with initial* N_2H_4 *of 0.5 ppm in carbon steel and stainless steel tubing.*

uniform power generation possible. Since power output is limited by the hottest portion of the core, uniform power distribution results in higher power putput for the same core size.

Water reactors are characterized by large reactivity changes over a core lifetime, including both long-term changes due to fuel burnup and shorter-term changes associated with power maneuvering. When control rods are used to compensate for these changes, their changing pattern of insertion introduces substantial and time-varying distortions of the spatial power distribution in the reactor core. Unless the control rod system is designed and operated with great care, these distortions may correspond to highly nonuniform power density distributions. The adoption of "chemical shim" control (reactivity control by boric acid dissolved in the reactor water) for PWR's has largely bypassed this problem, and so has been a source of major improvement in power distribution. In principle, with chemical shim, there is no need for control rods in the core during power operation, although they must be held in the withdrawn position as a means of rapid shutdown.

In practice, however, the adjustment of the boric acid concentration—which is done by a "feed-and-bleed" system—is cumbersome and expensive if used for short-term reactivity adjustments. The system is used more beneficially for compensating the excess reactivity incorporated for fuel burnup. This amounts to 10 to 15 percent reactivity for a core employing a three-batch refueling scheme. Since the early PWR plants have been intended for base-load operation, the other control requirements during power operation are small, and these reactors will operate almost as "rodless" reactors.

The limitations of chemical shim control are quite apparent. In addition to the problem of short—term reactivity adjustment, they include a practical limit on total capability for reactivity compensation. The limit is imposed by the positive component of the moderator temperature coefficient of reactivity, which increases approximately in proportion to the boric acid concentration, and which may cause undersirable dynamic characteristics if it becomes large enough to outweigh the negative component and yield a net positive coefficient. The use of chemical shim is expected to remain an important feature of the PWR technology, but the importance of control rods is expected to increase with time. In order to control core reactivity, boric acid is controlled much like any additive or treatment chemical in power operations. Boric acid dissolved in the primary coolant controls only the slowly changing reactivity effects. The mechanism by which this occurs is the absorption of neutrons by the B^{10} isotope of natural boron. Natural boron contains approximately 20 atom percent B^{10}, which has a very thermal neutron cross section of approximately 3840 barns. The reaction is a follows:

1. $B^{10}\ (n,\ \alpha)\ Li^7$
2. $B^{10}\ (n,\ 2\alpha)\ H^3$

The second reaction, although substantially less probable, does produce tritium activity, which must be analyzed and accounted for in waste handling.

Reaction 1 results in Li^7 production of about 0.1 ppm/day at a boron concentration of 1070 ppm (B^{10} 200 ppm) in a plant having rated power of 2500 MWt. The effect of alkali metal input is to partially neutralize the boric acid and increase the coolant pH (water quality is discussed below).

In a pressurized water reactor, water has been shown to undergo various equilibrium reactions which are normally unexpected for the thermal conditions of the coolant. These reactions generally can be summarized as follows:

3. Water decomposition and formation

$$H_2O \rightleftharpoons H_2 + 1/2\ 0_2$$

4. Ammonia synthesis and decomposition

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

5. Nitric acid synthesis

$$2H_2O + 2N_2 + 50_2 \rightarrow 4HN0_3$$

6. Nitric acid reduction

$$2HN0_3 + 5H_2 \rightarrow N_2 + 6H_20$$

The kinetics of these reactions are quite rapid during reactor operation, and many intermediate products are postulated before formation of the end products. Since these reactions are dependent on the reactor flux, they are first order with respect to the reactor power level and the concentrations of reactants.

It is apparent from Reactions 3 through 6 that the presence of free hydrogen can shift the equilibrium of these reactions to preclude the excess decomposition of water or formation of nitric acid. For this reason, PWR's operate with an excess of hydrogen (added as hydrogen gas).

Hydrogen concentration control in the current generation of PWR's is accomplished by the chemical and volume control system (CVCS). This system, unique to pressurized water reactors, allows direct and continuous control of water quality in the primary coolant on a completely automatic basis.

The presence of boric acid fixes the lower pH specification of 4.5. Boric acid is slightly ionized at reactor operating temperatures so that it does not greatly influence the fluid pH. Therefore, the addition of very small amounts of strong or weak base constituents greatly influences the pH at high temperature (Fig. 6).

There are several benefits arising from operation at adjusted pH. First, the general corrosion of system materials is reduced, and second, core reactivity has been reported to be affected by changes in coolant pH in large commercial PWR's.

In general, the metal corrosion rates from typical PWR materials are low, and tests have shown that they stabilize after 200 days. Since an increase in pH reduces the corrosion rate, the coolant chemistry is adjusted to obtain this effect.

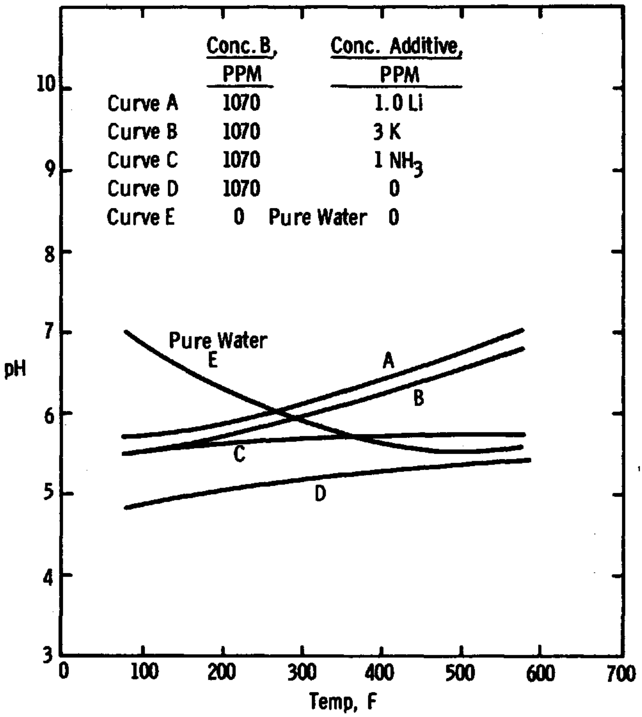

FIG. 6—*pH of various solutions (with and without boric acid) versus temperature.*

PWR Operating Chemistry

The effect of radiation-induced reactions on PWR coolant chemistry is illustrated in Fig. 7. In this figure, the coolant is high-purity light water (that is, with no alkalinity or chemical shim additives). The pH of the water, measured at 24°C, ranges between 7 to 8 and is due to the ammonia which has formed by Reaction 2 of the foregoing. Hydrogen gas has been added to the coolant. At Shippingport and other power reactors, hydrogen losses have been shown to be due to various system water losses and pressurizer vent valve steam phase leakage.

PWR plants generally use nondeaerated, but otherwise high-purity, makeup water. This introduces some oxygen and nitrogen into the reactor coolant. The dissolved oxygen is reacted (Reaction 3 given earlier) with excess hydrogen to form water. The nitrogen and hydrogen react to form ammonia (Reaction 4). The actual concentration of ammonia due to synthesis is determined by the reaction rate and rate of removal of ammonia by ion exchange resins which continuously purify a portion of the coolant.

The effect of these radiation-induced reactions on coolant chemistry when air (oxygen and nitrogen) is present in excess of the dissolved hydrogen

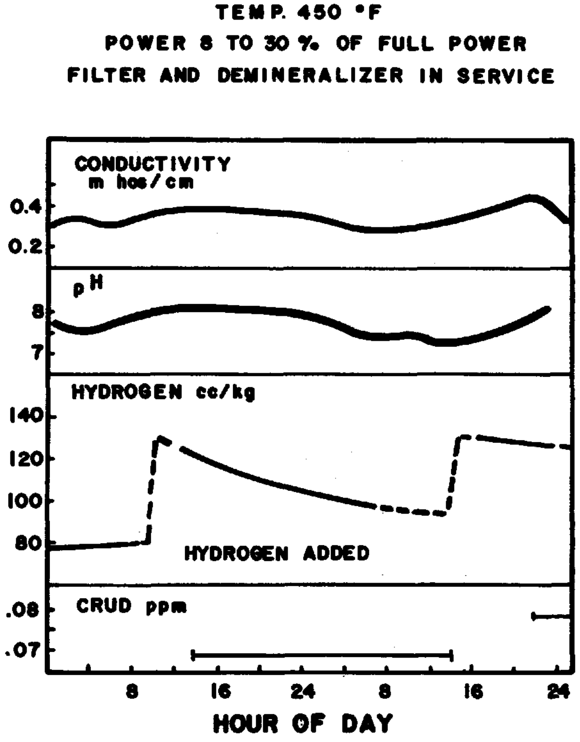

FIG. 7—*Radiation-induced changes in high-purity, light-water PWR coolant.*

concentration is shown graphically in Fig. 8. The reactor power was increased slowly during the test. Ammonia, which was present in the coolant from the previous operation, was neutralized as nitric acid was formed. As the nitrate ion concentration increased, the coolant became acidic, and chromate (Cr^{+6}) ions were detected.

The concentration of chromate ions increased during the period, indicating chemical attack on the system. After hydrogen was added, the reactions were reversed—that is, the nitrate and chromate ion concentrations decreased—and the coolant pH increased to approximately the initial condition.

Reactivity changes have been reported to be caused apparently by changes in coolant pH. These effects have been reported in Saxton and other nuclear power stations. The magnitude of change has been between 0.2 and 0.9 percent $\Delta K/K$. This result is of interest since it could stretch core operating lifetime by about 200 megawatt days/metric ton. The reactivity insertions experienced have not been abrupt, requiring about 6 to 24 h for completion. Figure 9 shows a typical reactivity response measured at Saxton. In this test sequence, a cation exchanger was placed into service to remove lithium

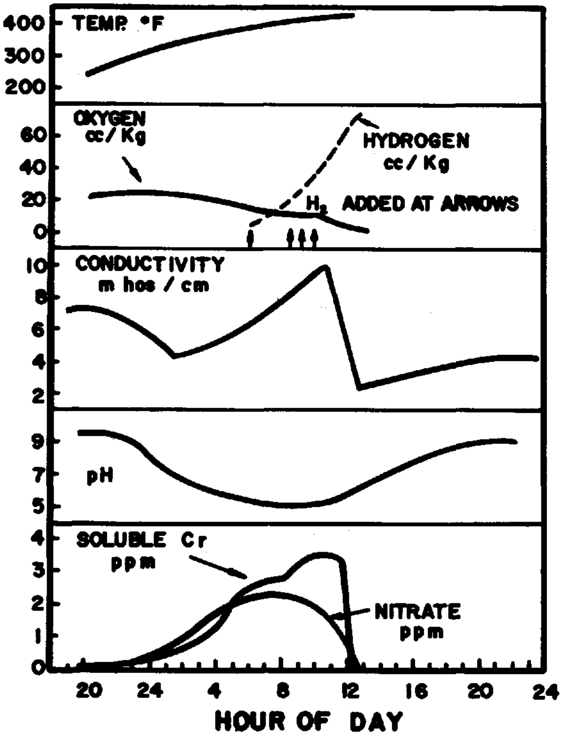

FIG. 8—*Plant start-up with air in loop (low power).*

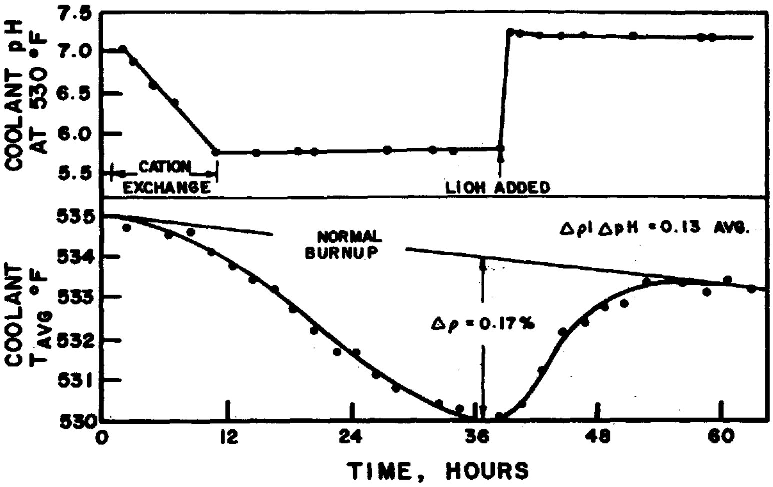

FIG. 9—*Change of reactivity with coolant pH at Saxton—20 MWt—no boron.*

(approximately 0.9 to <0.01 ppm), which had been used to maintain a high pH condition in the coolant. No boron was present during this test. Coolant average temperature began to decrease coincidentally with lithium removal (pH decrease). After the pH stabilized at approximately 5.75 (low pH), *T* average continued to decrease for 24 h. Following this operation, lithium hydroxide was added, and coolant *T* average began to rise and returned to the predicted burnup rate after 24 h.

Figure 10 shows the correlation of experimental data from field studies at Yankee. The data points represent operation over a wide variety of boric acid concentrations and include essentially zero boron.

Early speculations on the reason for pH-induced reactivity swings were that neutron poisons from either defective silver-indium-cadmium control rods or soluble boric acid were removed from core surfaces as a result of alkali additions to the coolant. Later observations indicated that (1) the magnitude of the effect was independent of boric acid concentration; (2) there was no evidence of the appearance or disappearance of neutron poisons during the reactivity change; (3) there was no effect at zero power; and (4) it was independent of the choice of alkali but related by magnitude and direction of pH change.

Tests now indicate that a more satisfactory hypothesis would involve the effect of coolant chemistry on the structure or distribution, or both, of corrosion product films on clad fuel surfaces. Changes in the properties of these deposits affect (1) heat-transfer characteristics, which in turn affect fuel temperature and, hence, reactivity due to the fuel Doppler effect; (2) the extent and nature of local boiling, thereby changing the local and core average voids, which would affect the void coefficient of reactivity; and (3)

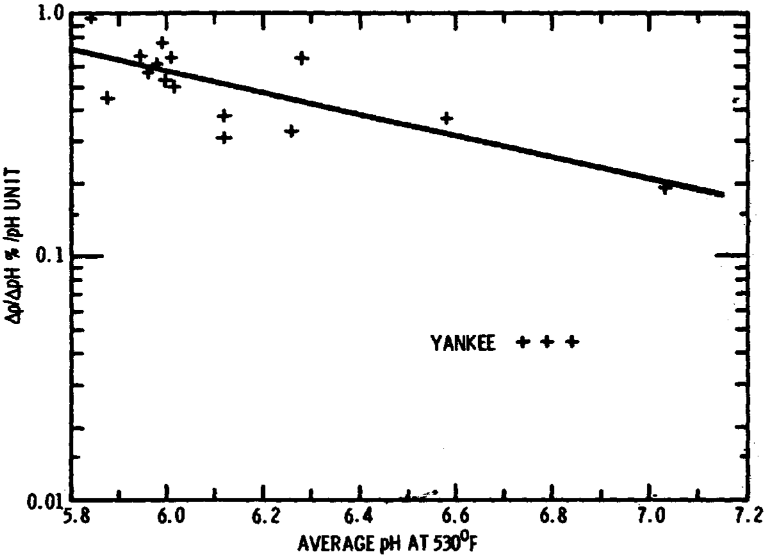

FIG. 10—*pH coefficient of reactivity versus coolant pH (277°C) (530°F).*

system hydraulic properties with associated changes in flow, that is, core ΔP, and temperature.

BWR Water Chemistry

The following two aspects of BWR chemistry make effects that occur in both the feedwater and primary coolant systems unique relative to fossil and PWR systems and significantly affect corrosion product chemistry:

1. No chemical additions are made to the feedwater or primary coolant to control pH or oxygen concentration.
2. The formation of hydrogen and oxygen, which occurs in the primary system because of the radiolytic decomposition of water, has a significant effect on the behavior of materials in the primary system and parts of the feedwater system.

The use of chemicals for coolant chemistry control raised significant questions regarding radiolytic decomposition of these chemicals, which would occur in the primary system and could lead to significant radioactivity and corrosion problems. For these reasons, and also because of the successful operation of the BWR in the absence of chemical additives, no consideration is given to changing feedwater or primary system chemistry by the addition of chemicals normally used in fossil or PWR systems.

The radiolytic decomposition of water in the primary coolant, which generates 0.0014 to 0.0028 standard cubic centimetres per second/megawatt thermal (0.03 to 0.06 standard cubic feet per minute/megawatt thermal) of the stoichiometric mixture of hydrogen and oxygen, controls the oxygen and hydrogen concentrations in the reactor water, steam, and turbine and feedwater heater drains. Oxygen concentration in the primary coolant varies from 100 to 300 ppb. Oxygen concentration in the steam, which approximately corresponds to that predicted by steam-water equilibrium in the primary system, varies from 10 to 30 ppb. Turbine and feedwater heater drains vary in oxygen concentration both with the rate of radiolytic decomposition in the primary coolant and also with temperature and pressure. Feedwater oxygen concentration varies from 10 to 30 ppb, depending on the effectiveness of condensate deaeration.

To serve as a basis for comparison with the plant operating data presented in the following, the General Electric BWR water quality requirements for feedwater and primary coolant are presented in Table 4. The limits in the table define the quality of the reactor water and feedwater for plant design and operational control when operating at rated pressure. Allowance for operation outside these limits for specific time periods is made for start-up and nonroutine occurrences.

BWR Feedwater Chemistry

In a typical BWR feedwater system, as shown in Fig. 2, all heater drains are cascaded to the hot well for treatment by the full-flow condensate deepbed demineralizer or filter-demineralizer. Corrosion products in the condensate result from corrosion or erosion of steam and turbine piping, turbine components, extraction steam piping, and feedwater heater shell, tubing, and drain lines. With the exception of a few plants still operating with copper-alloy feedwater heater tubing, the corrosion products resulting in the condensate from the aforementioned sources are limited primarily to soluble and insoluble compounds of iron. Low concentrations of corrosion products also result from the corrosion of the condenser tubing, which may be either a copper alloy or stainless steel. Upon passing through the full-flow condensate treatment equipment, ionic species are almost quantitively removed; insoluble species are removed with a variable efficiency, depending on their chemical and physical nature.

TABLE 4—*BWR water quality specifications.*

	Feedwater	Primary Coolant
Corrosion product concentration, ppb		
total	<30	NS[a]
copper	< 2	NS[a]
Conductivity, μmho/cm @25°C	< 0.1	<1.0
pH	6.5 to 7.5	5.6 to 8.6
Oxygen Concentration, ppb	<14[b]	NS[a]
Chloride Concentration, ppb	**[c]	<200

NS = not specified.

[b] <200 ppb oxygen in forward pumped plants.

[c] Sufficiently low to meet primary coolant specification.

Coolant Purification Systems

Both BWR and PWR power plants use sidestream purification systems to remove impurities from reactor coolant. In a PWR, the system serves several functions.

The Chemical and Volume Control System (CVCS) (Fig. 11) is essentially a sidestream loop on the primary coolant system (PCS). It permits continuous bleeding and feeding of water from the PCS, through purifying ion exchangers and filters, and into a gas-pressurized water reservoir called the volume control tank. Purified water from this tank is charged back into the reactor at the same rate as the letdown flow, thereby effecting reactor coolant volume stabilization. The simplicity of the bleed-and-feed process permits the addition of concentrated boric acid to increase boron concentrations or the replacement of the reactor coolant with makeup water free of boric acid to reduce boron concentrations. The hydrogen concentration in the coolant is controlled by maintaining a hydrogen overpressure on the volume control tank.

Hydrogen concentration control in the current generation of PWR's is accomplished by the CVCS. This system, unique to pressurized water reactors, allows direct and continuous control of water quality in the primary coolant on a completely automatic basis.

Auxiliary Cooling Water

As in any power plant, a closed circulating cooling water system is employed to remove heat from components and equipment. In nuclear plants, this system is used to cool control rod drive mechanisms, waste gas compression aftercoolers, coolant letdown system, nonregenerative heat exchangers, etc.

In general, these systems employ high-purity makeup water and use the standard chromate corrosion inhibitor treatment. Variations in this approach are used, but, to date, the majority use the chromate treatment shown in Table 5. While the discharge of chromates to the environment is strictly limited, leakage from these systems is extremely small and has not been considered a problem. The alternative treatments, using organic compound inhibitor systems or simple pH adjustment, are in some limited use and are considered effective.

Activation of the metal ion additives in these systems has not been experienced, since the neutron flux gamma dosages are small and residence time in even these low flux levels averages only about a few seconds.

Radioactivity

Nuclear steam supply systems employing pressurized water reactors are indirect-cycle systems. The primary coolant, which picks up radioactivity

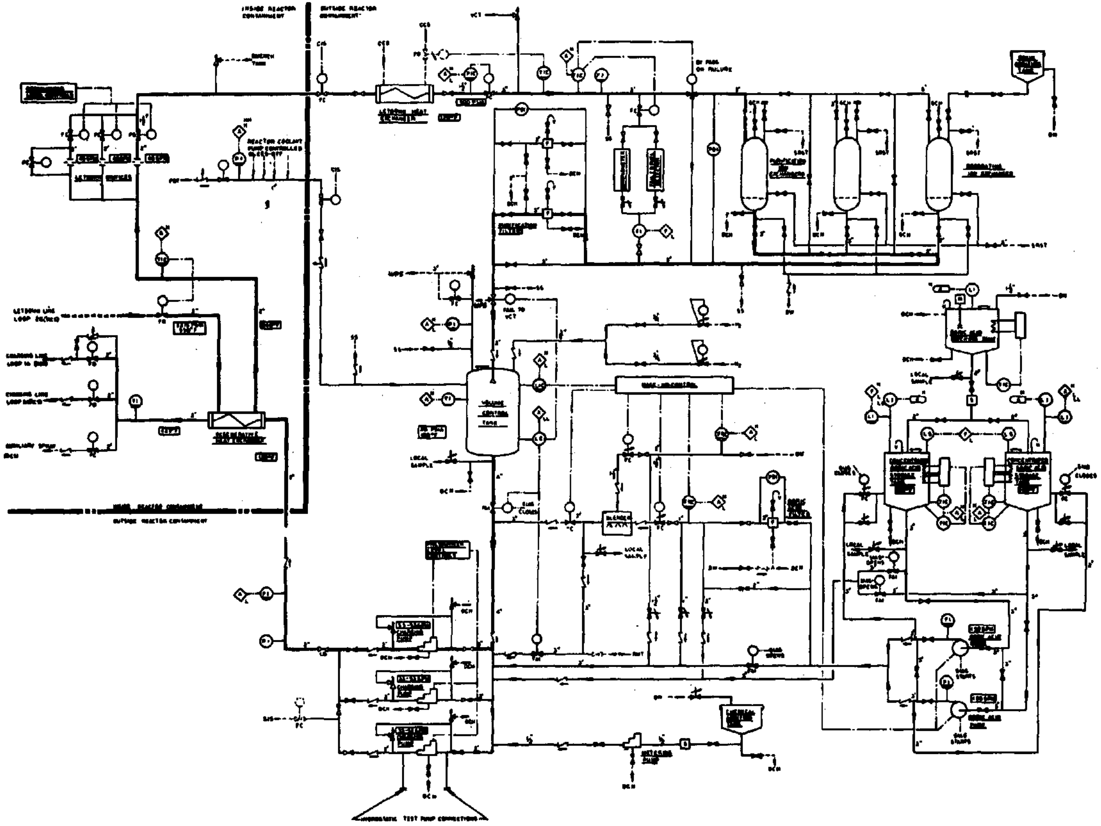

FIG. 11—*Chemical and volume control system flow diagram.*

TABLE 5—*Operating chemistry.*

BWR		PWR	
Chlorides	1.0 ppm	chlorides	0.15 ppm
pH	9.0 to 9.7 ppm	fluorides	0.1 ppm
Chromate (as CrO_4)	500 ppm	pH	8.0 to 8.5 ppm
		chromate	175 to 500 ppm

from a number of sources, is separate from the water which serves as working fluid for the steam turbine. The steam generator serves as a barrier between the two fluids.

Because of its closed-cycle design, control of radioactivity in a PWR is easily accomplished. Holdup in the system provides for decay of short-lived radioisotopes. Other fission products activities are continuously and efficiently removed from the water by the ion exchangers in the CVCS. BWR power plants are not of the closed-cycle design; however, off-gas systems are designed to reduce radioactive discharges to allowable, safe levels.

Fission Products

Fission products from two basic sources may be present in the reactor coolant. The first is uranium contamination on the surface or in the metal matrix of fuel cladding and core structural materials. This is essentially the background or base activity and has been present in all reactors. A second source of fission products arises when the cladding, which encapsulates the fuel, is penetrated or has minor leakage. This condition has been observed in reactors and does not impede safe continued operation of the plant.

The system design provides for operation of the core with a significant fraction of the fuel elements being defective. Routine monitoring of fission products provides the operator with trends in coolant activity and a history of the relationship between various activity species. The information on activity and ratios of activity of specific nuclides is useful for assessing changes in the source of fission products.

One method widely used for routine monitoring of fission products is the radiochemical analysis of I-131 and I-133. The relationship between these isotopes is a function of the release mechanism; that is, recoil from surface or a cladding interstitial uranium atom produces a different ratio than diffusion from a defective fuel rod. Both mechanisms may be operating and releasing fission products to the coolant simultaneously. However, the ratio between the two iodine isotopes would reveal which release mechanism was predominant.

If fuel cladding failure is suspected, confirmation can be obtained by observing the behavior of short half-life fission products during start-up power transients. This effect, called "water-logging," is the result of water entering the defective fuel rod during shutdown, and ejection of that water and its contained activity upon resumption of power operation.

This mechanism introduces high concentrations of short-lived fission products into the coolant at a rate much faster than would diffusion from the defected area. This diffusion mechanism would require a comparatively long time, and the short-lived fission products would be decayed. Figure 12 shows the peaking of I-131 at Connecticut Yankee during a start-up with defective fuel cladding.

Activation of Water

The isotopes N-13, N-16, N-17, and F-18 result from neutron activation of oxygen isotopes occurring naturally in the light-water moderator. The activity levels are a function of the reactor flux and system volume:

Nuclide	Half-Life	Reaction	Target Source
N-16	7.13 s	0^{16} (n,p)N-16	water
N-17	4.14 s	0^{17} (n,p)N-17	water
F-18	109.8 min	0^{18} (p,n)F-18	water
N-13	9.99 min	0^{16} (p,α)N-13	water

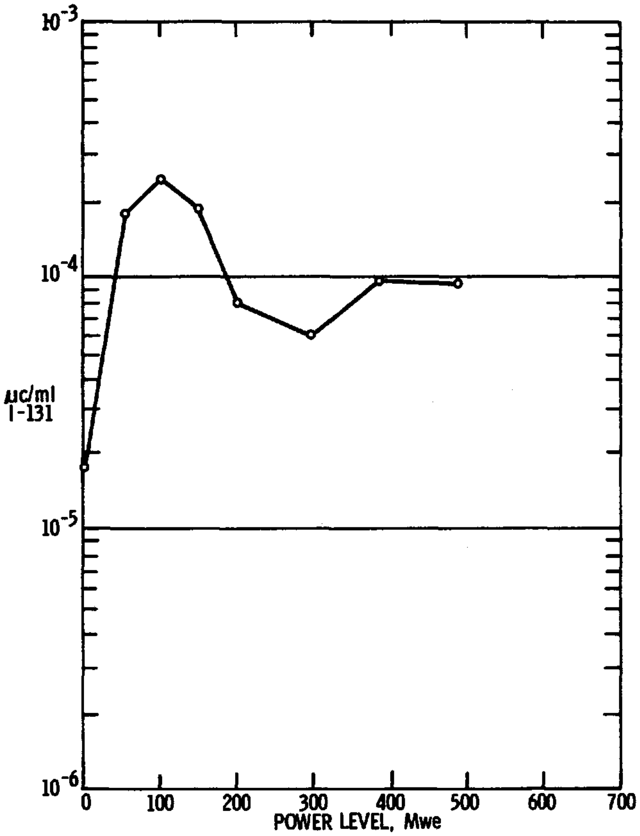

FIG. 12—*Connecticut Yankee reactor coolant I-131 concentrator versus power level, MWe.*

The level of N-16 activity determines the secondary shielding requirements for the reactor plant. This isotope ($T_{1\ 2}$ - 7.13 s) emits beta particles having maximum energy of 3.32, 4.39, and 10.49 MeV, and gamma rays of 6.18 and 7.1 MeV. The isotope N-17, which emits delayed neutrons, must also be considered when designing plant shielding and should be considered in the design of sample line delay times (transit time from reactor to sample point) to protect personnel during sampling operation.

A typical decay curve of radioactive reactor coolant contaminant activities in a PWR is shown in Fig. 13. The gamma activity, after a degassed sample has decayed about 15 min, is due principally to N-13 ($T_{1/2}$ = 9.99 min) and F-18 ($T_{1/2}$ = 109.8 min). The samples were taken with the reactor operating at steady-state full power. Normally, the fission product contribution to gross gamma activity is small.

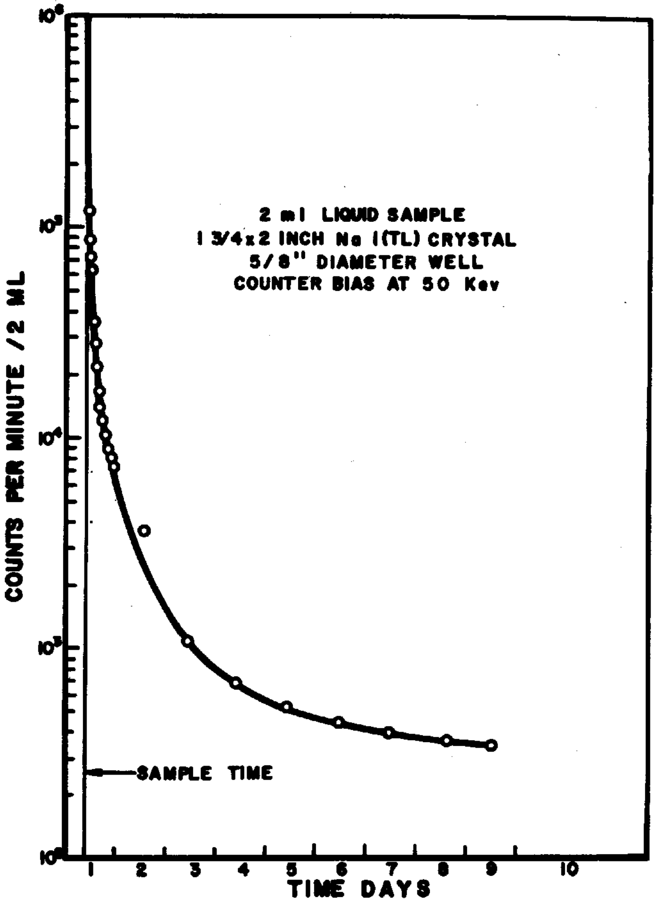

FIG. 13—*Decay of degassed reactor coolant (1 in. = 2.54 cm).*

Table 6 lists the major nonvolatile activities present is the Shippingport plant reactor coolant and gives the approximate percent of total gamma activity one hour after sampling. The activity is diminished very rapidly by a factor of 10 000 in a few hours until a long half-life residual of corrosion product activity remains. Volatile activities are the noble gas fission products Xenon and Krypton and Argon-41. Argon-40 enters the system with air dissolved in makeup water and becomes activated to Argon-41.

TABLE 6—*Shippingport Atomic Power Station nonvolatile gamma activity, Core 1 Seed 3.*

Nuclide	Half-Life	Activity at dpm/ml[a]	Sampling Time, μc/ml[b]	Percent of Total Gamma Radiation At 1 h
N^{13}	9.99 min	1.82×10^4	8.19×10^{-3}	0.3
W^{187}	24 h	2.22×10^3	9.00×10^{-4}	2.9
Na^{24}	15 h	1.92×10^3	8.64×10^{-4}	1.8
F^{18}	109.8 h	2.8×10^4	1.26×10^{-2}	21.3
Cs^{138}	32 min	1.03×10^4	4.68×10^{-3}	3.1
Mn^{56}	2.58 h	5.65×10^3	2.54×10^{-3}	4.5
Mn^{54}	313 days	3.43×10^2	1.09×10^{-4}	0.2
Cu^{64}	12.8 h	6.4×10^4	2.88×10^{-2}	39.2
I^{131}	8 days	4.2×10^1	1.89×10^{-5}	14.8
I^{133}	21 h	1.03×10^3	4.67×10^{-4}	
I^{134}	52 min	1.00×10^4	4.5×10^{-3}	
I^{135}	6.7 h	1.92×10^2	8.64×10^{-5}	
Percent of gross gamma activity at 1 h accounted for				88.1

[a] dpm = disintegrations per minute.

[b] μc = microcuries.

Activation of Impurities

The concentration of impurities in reactor coolant is generally kept extremely low by the strict control of makeup water quality, and by internal purification. However, the small quantities of impurities present do become activated and these can add to the system activities. The two most common isotopes are:

Nuclide	Half-Life	Nuclear Reaction	Target Source
Na^{24}	15 h	Na^{23} $(n, \gamma)Na^{24}$	impurity in water
Ar^{41}	1.83 h	Ar^{40} $(n, \gamma)Ar^{41}$	air in water

Activation of Coolant Additives

The major chemical constituent in a chemical shim coolant is boric acid for reactivity control. The nuclear reaction which provides for control produces a stable isotope Li^7. A second reaction produces tritium:

Nuclide	Half-Life	Reaction	Source of Nuclide
H^3	12.33 years	B^{10} $(n,2\alpha)$ H^3	boron in coolant

The chemical additives employed to increase the pH of the primary coolant ($LiOH$, KOH, NH_4OH) are used in very low concentration (10^{-4}M) so that their presence is not a major factor, even if activated. K^{41} is the only isotope which is easily activated:

Potassium hydroxide $K^{41}(n, \gamma)K^{42}T_{1/2} = 12.4$ h

Those plants which employ lithium hydroxide use lithium with the Li^7 isotope only to avoid the generation of tritium from the Li^6 isotope:

Lithium hydroxide $Li^6\ (n, \alpha)H^3T_{1/2} = 12.33$ years

Corrosion Product Activation

Some of the corrosion products generated by the primary system materials are released to the coolant and are transported to the core surfaces. This causes the metallic constituents to become activated, resulting in radioactive oxide deposits. Formation of corrosion products in a PWR results in a concentration of about 0.050 mg/litre in the circulating coolant.

Generally, the corrosion products correspond in composition to the system materials. In a modern PWR, the available surface areas in contact with reactor coolant and their respective corrosion rates are as follows:

Material	Corrosion Rate mg/D^2-month	Area, m^2	(ft^2)	%	Annual Metal Release, g/year
Stainless steel	2	2 340	(26 000)	10	5 860
Inconel-600	4	13 860	(154 000)	60	68 500
Zircaloy	small	4 860	(54 000)	30	small
		21 060	(234 000)	100	

Approximately 74 kg (165 lb) per year of metal or 92 kg (205 lb) of metal oxide are released.

The corrosion products are a function of system materials, and in the current generation of PWR's they are metal oxides having the following approximate composition:

Element	Weight Percent
Fe Iron	10
Chromium	30
Nickel	60

These corrosion and wear products are released from the surface of the plant piping and components and transported by the circulating coolant. A small percentage of these oxides is removed from the circulating coolant by the ion exchanger in the CVCS. The metal oxides we are concerned with are those which are deposited on the core where they become activated by core radiation, the degree of activation depending upon the residence time on the core. Initially, on a clean core surface, some of the corrosion products which strike the surface adhere to the zirconium oxide surface. As more oxide particles strike the surface, the deposit begins to build up. This continues unless the shear forces on the oxide particles, due to the coolant flowing past the particles, equal or exceed the forces causing the corrosion products to adhere to the surface. Therefore, the erodable or loose layer will be limited by the localized increase in coolant velocity through the core, the amount of corrosion products released to the coolant being a function of the change in velocity.

These activated metal oxides are then transported by the circulating coolant. Again, a small percentage will be removed by the CVCS ion exchanger, but some will redeposit on the plant surfaces as well as on the core. When they deposit on the plant surfaces, a radiation level increase on these surfaces will result and will be reflected in the radiation levels of the primary system. Subsequent operation will result in release of deposits back to the coolant which can again redeposit on the core to become further activitated. The nuclides which have the greatest contribution to these radiation levels are as follows:

Nuclide	Half-Life	Nuclear Reaction	Target Source
Cr^{51}	27.8 days	Cr^{50} (n, γ) Cr^{51}	steel and Inconel
Mn^{54}	313 days	Fe^{54} (n, p) Mn^{54}	steel and Inconel
Fe^{59}	45 days	Fe^{58} (n, γ) Fe^{59}	steel and Inconel
Co^{58}	71 days	Ni^{58} (n, p) Co^{58}	steel and Inconel
Co^{60}	5.26 years	Co^{59} (n, γ) Co^{60}	stellite, steel
Cu^{64}	12.8 h	Cu^{63} (n, γ) Cu^{64}	17-4 PH steel
Zr^{95}	65 days	Zr^{94} (n, γ) Zr^{95}	Zircaloy
W^{181}	130 days	W^{180} (n, γ) W^{181}	steel
W^{187}	24 h	W^{186} (n, γ) W^{187}	steel

The deposits of irradiated corrosion products found on components have not generally been a serious impairment to equipment maintenance. It does require that maintenance be planned and that contamination and personnel exposure be considered in this planning.

PWR Steam Generator Chemistry

Water chemistry of the working fluid of a PWR secondary cycle is similar to that employed in conventional moderate pressure boiler operations of 4826 to 6895 kPa (700 to 1000 psi). PWR systems use two types of steam generators: (1) the saturated-steam U-tube design, and (2) the straight tube generator which produces superheated steam. Cross sectional views of these generators are shown in Fig. 14.

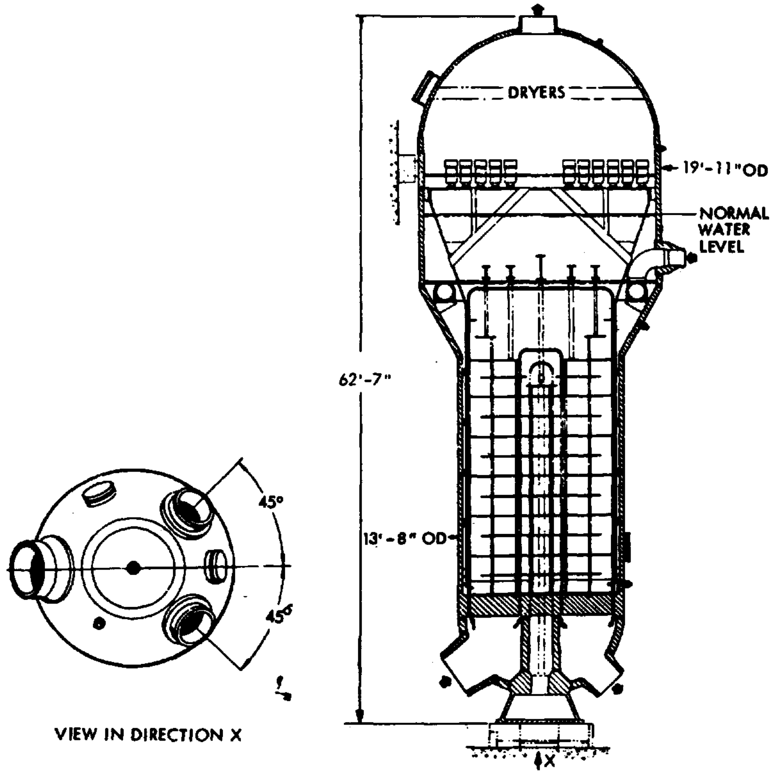

FIG. 14—*Steam generator for an 800-MWe PWR nuclear steam supply system (two required) (1 ft = 30.48 cm; 1 in. = 2.54 cm).*

Water conditions for the two types of units reflect necessary differences in water conditioning and auxiliary water treatment systems and equipment to ensure efficient long-term operation.

One of the unique conditions of PWR operation is that reactor coolant at a higher pressure than the secondary water may leak into the boiler if tubing integrity is breached. This can cause the introduction of primary system fluid containing boric acid and radioactive materials into the steam-condensate cycle. The special considerations concerning this situation are discussed later.

U-Tube Steam Generators

The U-tube steam generator is very similar in operating characteristics to a conventional, fossil-fueled, moderate-pressure, saturated-steam generator. The units operate at approximately 268 to 288°C (515° to 550°F) and approximately 5344 to 6895 kPa (775 to 1000 psi) throttle pressure. Water conditioning specifications and auxiliary treatment equipment are also similar to drum-type boilers operating at equivalent thermal conditions.

The unit pressure vessel is carbon steel and the boiler tubing is 19-mm (3/4 in.) diameter iron-chromium-nickel (alloy 600) having 40 to 50 mil wall thickness. Chemistry adjustment to the boiler and feedwater is done (1) to minimize corrosion of materials of construction, and (2) to ensure long-term tubing integrity. The selection of additives and control limits recognizes that the normal running, transient, and upset conditions may occur during plant operation and that may result in potentially deleterious conditions to the system.

Water conditions typically maintained with the steam generator are listed in Table 7. These conditions recognize that occasional deviations from normal may occur due to incursions of raw (cooling) water from surface condenser tube leakage.

The steam generator is protected from corrosion or fouling of heat-transfer surfaces, and steam purity is ensured by the control of chemical additives and blowdown. Specific corrective measures largely depend on the quality of raw water (whether brackish or freshwater, etc.) and the size or rate of the leak.

An operational philosophy with respect to in-leakage is outlined in Table 8 and is based on the objectives stated in the preceding paragraph.

When "solids" chemical treatment is employed, there is no need for condensate polishing equipment, since feedwater contaminants will concentrate in the generator or react with phosphates to form precipitates which can be removed by blowdown.

Feedwater

The steam generator acts as a concentrating device during operation. Soluble feedwater impurities which enter the steam generator become concentrated in the water since the steam leaving the drum does not carry off any appreciable amount. The recommended feedwater quality values given in Table 9 cover a number of dissolved and suspended constituents and are based on external or corrosion sources. For example, any contribution to

TABLE 7—*Steam generator chemistry limits.*

Impurity	Normal	Abnormal
Total dissolved solids	500 ppm max	1000 ppm max
Chloride	75 ppm max	250 ppm max
Total silica	10 ppm max	10 ppm max
Suspended solids	50 ppm max	100 ppm max
Dissolved oxygen	0.01 ppm max	0.01 ppm max
Chemical Additives for Corrosion Control		
Phosphate	15 to 25 ppm PO_4 [9.8 to 10.2 pH at 25°C 77°F]	15 to 40 ppm PO_4 [9.8 to 10.5 pH at 25°C (77°F)]
Sulfite	5 to 10 ppm SO_3	5 to 10 ppm SO_3

TABLE 8—*Criteria for maintaining steam generator water chemistry.*

Feedwater Conditions (Ingress Impurity Only)	Operational Limitations	Basic Steam Generator Water Chemisty	Chemistry Control
Total dissolved solids <0.5 ppm (normal)	none	TDS<500 ppm pH 9.8 to 10.2 PO_4 15 to 25 ppm Cl 75 ppm max	normal
Total dissolved solids 0.5 - 2.0 ppm (abnormal)	**LIMITED** schedule inspection and repair of condenser as soon as system load requirements permit.	TDS<1000 ppm pH 9.8 to 10.5 PO_4 15 to 40 ppm Cl 250 ppm max	immediately start chemical injection pumps to maintain required phosphate and pH conditions. Increase blowdown rate to limit total dissolved solids concentration.
Total dissolved solids <2.0 ppm (excessive)	**EMERGENCY** (*a*) immediately reduce load as necessary to permit isolation of damaged condenser section.	TDS<1000 ppm pH 9.8 to 10.5 PO_4 15 to 40 ppm Cl 250 ppm max	immediately start chemical injection pumps to maintain required phosphate and pH conditions. Do not continue to operate system if pH cannot be maintained above 8.0, or total dissolved solids below 1000 ppm.
	(*b*) prepare for orderly shutdown of the system if feedwater TDS concentration cannot be quickly reduced below 2.0 ppm.		if system goes into an orderly shutdown operation, prepare to establish chemical conditions for wet layup of steam generator and auxiliary equipment during condenser repair.

feedwater impurity concentration due to steam generator carry-over is allowed in addition to the contribution from an external source. Thus, if 0.2 percent moisture carry-over occurs with 500 ppm dissolved solids in the steam generator, then 1 ppm solids would be present in the feedwater due to carry-over, and the limit on total dissolved solids (TDS) for normal operation would then be 1.5 ppm instead of 0.5 ppm.

The TDS limit is specified to minimize steam generator fouling. Since TDS can, in general, be measured quickly by conductivity instrumentation, this category of impurities serves as a primary indicator of cycle contamination. The normal chloride concentration limit assures that long-term operation will not result in chloride-induced corrosion problems within the secondary cycle. The silica concentration limit assures that silica carry-over to the turbine by the vapor or steam solubility phenomena does not occur to any appreciable extent with respect to turbine fouling. The oxygen and pH specifications should limit the pickup of iron and copper from the feedwater cycle to those levels necessary for long-term steam generator cleanliness.

Secondary cycle operation is considered normal as long as feedwater TDS due to external sources is less than 0.5 ppm. Coupled with this is the requirement that pH value, oxygen level, and copper/iron levels are within the values given in Table 9.

Operation with feedwater TDS concentration between 0.5 and 2.0 ppm should be limited, and condenser repairs should be scheduled as soon as practical. Values of feedwater solids concentration due to external source contribution above 2 ppm are considered emergency levels. The unit load should be immediately reduced, the damaged condenser section isolated, and necessary repair work scheduled. The steam generator-turbine cycle should be shut down if feedwater concentration cannot be quickly reduced to values below 2 ppm.

TABLE 9—*Feedwater chemistry limits.*

Impurity	Normal	Abnormal
Total dissolved solids	0.5 ppm max	0.5 to 2.0 ppm (excessive is greater than 2.0 ppm)
Chloride	0.3 ppm max	1.2 ppm max
Total silica	0.02 ppm max	0.02 ppm max
Copper and total iron	0.05 ppm max	0.05 ppm max
Dissolved oxygen	0.01 ppm max	0.01 ppm max
Chemical Additives for Corrosion Control		
Feedwater pH [25°C (77°F)]		
(*a*) Feedwater system containing copper alloys of construction	8.8 to 9.2	8.8 to 9.2
(*b*) Copper free feedwater system	8.8 to 9.2 9.2 to 9.4	9.2 to 9.4
Hydrazine	0.02 ppm max	0.02 ppm max

Once-Through Steam Generator (OTSG)

The water quality specifications for the secondary system feedwater are given in Table 10. These specifications utilized conventional superheat experience. The OTSG requires high-purity water quality, and the steam plant contains condensate polishing equipment to maintain this high water quality. Several potential water chemistry problems were investigated to establish water chemistry specifications. They included the following:

1. The behavior of dissolved and suspended solids in the pressure/-temperature region of interest.
2. The effects of boric acid leaks in the steam and condensate cycle.
3. The removal of deposits.

Dissolved and Suspended Solids

Because of the lower operating pressure and temperature involved in the nuclear systems [6378 kPa and 299°C (925 psia and 570°F) full load], extension of data relating to the behavior of dissolved salts in this new environment was required. These data were obtained with a test boiler at the B&W Alliance Research Center. A portion of these tests was reported earlier. The data obtained were for the most commonly encountered materials, and those whose past behavior had varied from the most to the least soluble in high-pressure steam. The salts chosen were sodium chloride, sodium hydroxide, and sodium sulfate. Careful consideration was given to sampling procedures for superheated steam to obtain reliable data. The sampling procedures were established by earlier research.

It was found that sodium hydroxide and sodium chloride had solubilities as high as 75 ppb at 6378 kPa (925 psia). If these compounds are present in the feedwater in concentrations below 75 ppb, they will dissolve completely in the steam and pass through the steam generator. Since the turbine

TABLE 10—*Secondary feedwater specification.*

Total solids (dissolved and suspended)	50 ppb max
Dissolved Oxygen	7 ppb max[a]
Total silica (as SiO_2)	20 ppm max
Total iron (as Fe)	10 ppb max
Total copper (as Cu)	2 ppb max
pH at 25°C (77°F) (adjusted with ammonia)	9.3 to 9.5
Total hardness	[b]
Lead	0[c]

[a] Hydrazine is used to scavenge oxygen.

[b] No specification is listed owing to control analysis limitations. However, care should be taken to eliminate hardness constituents due to possible steam generator deposition problems.

[c] Lead contamination of the feedwater should be avoided in view of reported problems with nickel-chromium-iron alloy in oxygenated water containing lead. In specifying zero for lead, it is the intent that the level should be kept below the lowest values detectable by our acceptable referee methods.

operates wet after the first stage, these compounds will pass through the turbine and have no effect on performance of the system.

Tests showed that Na_2SO_4 had low solubility (5 ppb); therefore, if it is present in concentrations higher than 5 ppm, it may form deposits. However, tests showed that soluble salts are easily removed by rinsing with feedwater-quality water.

Primary-To-Secondary Leakage

In a PWR or closed-cycle power plant, reactor water can leak into the boiler water or working fluid if steam generator tube integrity is breached. Should this occur, primary water containing boric acid and radioactivity will enter the secondary system.

U-Tube Steam Generator

The concentration levels that result within the secondary cycle will depend on the primary coolant leakage rate, the boric acid and activity values in the primary coolant, steam generator blowdown rate, and employment of condensate demineralization.

The chemistry specifications outlined in Table 7 limit total dissolved solids to 1000 ppm during abnormal operation. This limit requires steam generator blowdown in the event of boric acid introduction. Since activity will be present in the steam generator, the blowdown fluid must be processed in the waste management system.

The room-temperature measurement of steam generator water pH will be depressed upon the introduction of boric acid, so that operation within the specified ranges given in Table 8 will not be possible. This is not adverse during operation, because boric acid does not significantly depress the pH of the higher-temperature steam generator water. As a control limit, however, the room-temperature pH measurement during operation with boric acid contamination must be maintained above 8.0. The upper limit of phosphate additive given in Table 7 for abnormal operation is 40 ppm. This concentration is sufficient to buffer the maximum amount of boric acid permissible within the 1000-ppm TDS limitation.

The volatile nature of boric acid results in carry-over of boric acid with the steam to the condenser hot well. The amount of carry-over has been determined to be about 8 percent for the secondary operating conditions of a U-tube steam generator. The boric acid volatility (or solubility) in the steam is dependent only on the steam pressure-temperature value. For every 1000 ppm of boric acid in the steam generator water, it is expected, therefore, that the steam will contain about 8 ppm.

Deposition of boric acid on turbine stages has not presented a problem in any operating plant to date. Some light deposition of boric acid on the last stages of low-pressure turbines has been observed, but these deposits have not affected turbine capability.

The feedwater will become contaminated with boric acid because of the volatility phenomenon. For instance, about 60 ppm of boric acid will be expected to be feedwater with 800 ppm boric acid in the generator, if condensate demineralization is not utilized. Feedwater impurity limits must, therefore, be raised to accomodate the presence of boric acid. Because of the lower amount of boric acid in this part of the cycle, a maximum level of 1.0 ppm ammonia should be utilized to maintain feedwater pH values above 8.0. Additionally, since ammonia is volatile, all portions of the feedwater system, including those sections that bypass the normal ammonia injection points, will equilibriate to the same pH level.

The carry-over of the biologically significant radioactive iodine has been shown to be influenced by boiler water chemistry. When coordinated phosphate/sulfite treatment has been used, no vaporization beyond normal entrainment in moisture has been observed.

The benefit derived is a significantly lower release of iodine from the secondary system off-gas. This is because the only form of iodine that is volatile is the elemental (I_2) form. In the presence of reducing sulfites in the steam generator, any iodine introduced via primary-to-secondary leakage will react to form nonvolatile iodides:

$$I_2 + SO_3^{=} + H_2O \rightarrow 2HI + SO_4^{=}$$

The alkaline pH as a result of the phosphates in the steam generator results in hydrolysis of elemental iodine to nonvolatile iodides and iodates:

$$2I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$$

These reactions prevent the escape of iodine activity from the steam generator as volatile iodine vapors in the steam, and limit iodine activity release to that associated with moisture carry-over.

Once-Through Steam Generator

The special considerations of superheat operations have not, at the time of this writing, been observed in plant scale operations. However, extensive testing has been done and is presented here.

In the test boiler, a simulation was made of a reactor coolant to secondary system leak. One accelerated test was equivalent to a 0.0009 m^3/s (15 gal/min) leak on a full-size unit at hot operating conditions. The simulated reactor coolant in that test contained 13 000 ppm H_3BO_3. The test boiler condensate was not polished during the test period. Boric acid was very volatile ($\geq$1800 ppm H_3BO_3) at these pressure-temperature conditions [6378 kPa, 299°C (925 psia, 570°F)] and did not concentrate in the OTSG.

The amount of boric acid that would be present in the secondary system feedwater in a full-size unit depends mainly on the leak rate, the concentration of H_3BO_3 in the reactor coolant, and the H_3BO_3 removel efficiency of the condensate demineralizers. We have made extensive calculations, assuming leak rates from 0.000003 to 0.003 m^3/s (0.05 to 50.0 gal/min), reactor coolant H_3BO_3 concentrations from 0.006 to 0.82 m^3/s (100 to 13 000 gal/min, and 0, 50, and 100 percent removal of H_3BO_3 by the condensate polishing demineralizers. Table 11 lists some of these data.

The feedwater reference pH at 25°C (77°F) decreases with increasing boric acid in the secondary system. However, boric acid at the concentrations studied has little effect on the pH at elevated temperatures. In most cases, the pH [25°C (77°F)] does not decrease below 9.4 [25°C (77°F)] as long as the demineralizer is removing at least 50 percent of the H_3BO_3 leaking into the secondary system. Also, in some cases, the addition of a small amount of ammonia will compensate for a pH [25°C (77°F)] decrease below 9.3.

Earlier research on the behavior of both high-flow-rate deep-bed and Powdex condensate polishers was extended to study their behavior in the event of a boric acid leak. Table 12 shows the ultimate capacities obtained in laboratory tests using 1.0, 10.0, or 100.0 ppm H_3BO_3 and ≈ 1.5 ppm NH_3 [equivalent to a pH (room temperature) of 9.5 at normal conditions] in the influent. The results show that both types of systems can remove low concentrations of boric acid that would be present in the secondary system if a tube leak occurred. The presence of boric acid does not significantly affect the capability of deep-bed demineralizers for removing sodium and chloride. The condensate polishing system will continue to protect the OTSG and turbine from condenser leak contaminants during a simultaneous OTSG tube leak.

Summary

In this brief review, we have attempted to present the salient features of the water chemistry control required for reliable operation of water reactors. The 20 years of development and more than 10 years of operational experience with the control principles described in this paper have led to an accumulation of the technology which supports reliable plant operations.

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TABLE 11—*Reactor coolant to secondary-system boric acid leak calculations.*[a]

Leak Rate, gal/min[g]	Reactor Coolant H_3BO_3, ppm	H_3BO_3[b] ppm	pH@ 25°C (77°F)[c]	pH@ 140°C (285°F)[c]	pH@ 188°C (370°F)[c]	pH@ 237°C (160°F)[c]	pH@ 278°C (532°F)[c]	pH@ 304°C (579°F)[c]	NH_3[d] ppm
0.05	13 000	0.08	9.5	7.1	6.61	6.26	6.09	6.06	0
0.05	100	0.0006	9.5	7.1	6.61	6.26	6.09	6.06	0
0.5	13 000	0.8	9.43	7.1	6.62	6.26	6.09	6.06	0
0.5	100	0.006	9.5	7.1	6.62	6.26	6.09	6.06	0
5.0	13 000	8.1	9.09	7.08	6.61	6.26	6.09	6.06	1.7
5.0	100	0.06	9.5	7.09	6.61	6.26	6.09	6.06	0
50.0	13 000	81.4	8.1	7.00	6.61	6.29	6.14	6.14	24
50.0	100	0.63	9.46	7.12	6.64	6.29	6.15	6.14	0
...	...	...	7.0[e]	5.71	5.36	5.21	5.36	5.43	...
...	...	...	9.5[f]	7.1	6.61	6.26	6.09	6.06	...

[a] Assuming 50 percent removal of H_3BO_3 by condensate polishing demineralizers. Lithium is 2.0 ppm Li in reactor coolant at all times. Ammonia is 1.5 ppm NH_3 in condensate and feedwater. The calculated values are for equilibrium conditions using 100 percent condensate polishing and 50 percent steam flow to the feedwater heaters.

[b] Boric acid concentration at the demineralizer influent, shell side of the feedwater heater, and in the steam generator.

[c] The pH with H_3BO_3 and 1.5 ppm NH_3 present.

[d] The amount of NH_3 necessary to increase the pH to 9.3 @25°C (77°F).

[e] The pH of pure water at various temperatures.

[f] The pH of 1.5 ppm NH_3 at various temperatures.

[g] 1 gal/min = 0.00006 m^3s.

TABLE 12—*Condensate polishing demineralizer tests.*

DEEP-BED TESTS[a]

Influent, ppm		Effluent, ppm		Ultimate Capacity
H_3BO_3	NaCl	Na	Cl	lb H_3BO_3/ft^{3}OH Fora Anion
1.0	..	..	..	0.5
10.0	..	..	..	2.5
100.0	..	..	..	4.5
1.0	<0.1	<0.001	<0.05	0.7
10.0	<0.1	<0.001	<0.05	2.4
100.0	<0.1	<0.001	<0.05	4.1

POWDEX TESTS[b]

Influent, ppm	Ultimate Capacity
H_3BO_3	lb H_3BO_3/lb dry anion (OH)
1.0	0.03
10.0	0.14
100.0	0.24

[a] All tests used NH_4R-ROH resin in a 2:1 ratio. Flowrate was 50 gal/min/ft^2 and temperature 25°C (75°F).

[b] All tests used NH_4R-ROH resin in a 1:1 ratio and dosage of 0.15 lb/ft^2. Flowrate was 163 litres/min/m^2 (4 gal/min/ft^2) and temperature 25°C (75°F).

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STP442A-EB/Jul. 1978

Chapter 18—Practices for Measurement of Radioactivity

This chapter provides a review of the accepted counting practices currently used in radiochemical analyses. It is divided into four sections: General Information, Alpha Counting, Beta Counting, Counting. The General section contains information applicable to all types of radioactive measurements while each of the other sections are specific for a particular type of radiation.

Summary

This chapter is a compilation of the various counting techniques employed in the measurement of radioactivity [*1,2*].[1] The important variables that effect the accuracy or percision of counting data will also be presented. Because a wide variety of instruments and techniques is available for radiochemical laboratories, the types of instruments and techniques to be selected will be determined by the information desired. In a simple tracer application using a single radioactive isotope having favorable properties of high purity, energy, and ample activity, a simple detection will probably be sufficient, and techniques may offer no problems other than those related to reproducibility. The other extreme would be a laboratory requiring quantitative identification of a variety of radionuclides, preparation of standards, or studies of the characteristic radiation from radionuclides. For the latter, a variety of specialized instruments would be required. Most radiochemical laboratories require a level of information between the two extremes.

A basic requirement for accurate measurements is the use of accurate standards for instrument calibration. With the present availability of good standards, only the highly diverse radiochemistry laboratories require instrumentation suitable for producing their own radioactive standards. However, it is advisable to compare each new standard received against the previous standard.

Thus, the typical laboratory may be equipped with proportional or

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[1] The italic numbers in brackets refer to the list of references appended to this chapter.

Geiger-Mueller counters for beta counting, sodium iodide or germanium detectors, or both, in conjunction with multichannel analyzers for gamma spectrometry, and scintillation counters suitable for alpha- or beta-emitting radionuclides.

General

Experimental Design

In order to properly design valid experimental procedures, careful consideration must be given to the following:

(*a*) The radionuclide to be determined.
(*b*) The relative activity levels of interferences.
(*c*) The type and energy of the radiation.
(*d*) The original sample matrix.
(*e*) The required accuracy.

Having considered the foregoing, it is now possible to make the following decisions:

(*a*) In what chemical or physical form must the sample be for radioassay?
(*b*) What chemical purification steps are necessary?
(*c*) What type of detector is required?
(*d*) Is energy spectrometry required?
(*e*) How long must the sample be counted in order to obtain statistically valid data?
(*f*) Must isotopic composition be determined?
(*g*) What size sample is required?

For example, gamma-ray measurements can usually be performed with little or no sample preparation whereas both alpha and beta counting will always require chemical processing. If low levels of radiation are to be determined, very large sample and complex counting equipment may be necessary.

More detailed discussions of the problems and interferences are included in the sections for each particular type of radiation to be measured.

Apparatus

The apparatus required for the measurement of radioactivity consists, in general, of the detector and associated electronic equipment. The latter usually includes a stable power supply, preamplifiers, a device to store or display, or both, the electrical pulses generated by the detector, and one or more devices to record information.

Some detectors and high-gain amplifiers are temperature senstive; therefore, changes in pulse amplitude can occur as the ambient room temperature varies. For this reason, it is necessary to provide temperature-controlled air conditioning in the counting room.

Instrumentation should never be located in a chemical laboratory where corrosive vapors will cause rapid deterioration and failure.

Power Supply—Detector and electronic responses are a function of the applied voltage; therefore, it is essential that only a very stable, low-noise electrical supply be used or that suitable stabilization be included in the system.

Shielding—The purpose of shielding is to reduce the background count rate of a measuremnt system. Shielding reduces background by absorbing some of the components of cosmic radiation and some of the radiations emitted from material in the surroundings. Ideally, the material used for shielding should itself be free of any radioactive material that might contribute to the background. In practice, this is difficult to achieve as most construction materials contain at least some naturally radioactive species (such as potassium-40, on members of the uranium and thorium series). The thickness of the shielding material should be such that it will absorb most of the soft components of cosmic radiation. That will reduce cosmic-ray background by about 25 percent. Shielding of beta- or gamma-ray detectors with anticoincidence systems can further reduce the cosmic-ray or compton scattering background for very low level counting.

Detectors have a certain background counting rate from naturally occurring radionuclides and cosmic radiation from the surroundings, and from the radioactivity in the detector itself. The background counting rate will depend on the amounts of these types of radiation and on the sensitivity of the detector to the radiations.

In alpha counting, low backgrounds are readily achieved since the short range of alpha particles in most materials makes effective shielding easy. Furthermore, alpha detectors are quite insensitive to the electromagnetic components of cosmic and other environmental radiation.

Care of Instruments—The requirements for and advantages of operating all counting equipment under conditions as constant and reproducible as possible have been pointed out earlier in this section. The same philosophy suggests the desirability of leaving all counting equipment constantly powered. This imples leaving the line voltage on the electrical components at all times. The advantage to be gained by this practice is the elimination of the start-up surge voltage which causes rapid aging and the instability which occurs during the time the instrument is coming up to temperature.

A regularly scheduled and implemented program of maintenance is helpful, if not required, to obtain satisfactory results. The maintenance program should include not only checking the necessary operating conditions and characteristics of the components, but also regular cleaning of the equipment.

Sample and Detector Holders—In order to quantify counting data, it is necessary that all samples be presented to the detector in the same "geometry." This means that the samples and standards should be prepared for counting in the same way so that the distance between source and detector remains as constant as possible. In practice, this usually means that the detector and sample are in stationary positions. Another configuration often used is to have the detector in a fixed position. Another configuration often used is to have the detector in a fixed position, within the shield, and beneath it a shelf-like arrangement for the reproducible positioning of the sample at several distances from the detector.

Special Instrumentation

This section describes some radiation detection instruments and auxiliary equipment that may be required for special application in the measurement of radioactivity in water.

4-π Counter—The 4-π counter is a detector designed for the measurement of the absolute disintegration rate of a radioactive source by counting the source under conditions that approach a geometry of 4-π steradians. Its most prevalent use is for the absolute measurement of beta emitters [*3*,*4*], and for this purpose a gas-flow proportional counter similar to that in Fig. 1 is common. It consists of two hemispherical or cylindrical chambers whose walls form the cathode, and with a looped-wire anode in each chamber. The source is mounted on a thin supporting film between the two halves, and the counts recorded in each half are summed. An argon (90 percent)-methane (10 percent) gas mixture can be used; however, pure methane gives flatter and longer plateaus and is preferred for the most accurate work. The disadvantage is that considerably higher voltages, about 3000 V, rather than the 2000 V suitable for argon-methane, are necessary. As with all gas-filled proportional counters, very pure gas is necessary for very high detector efficiency. The absence of electronegative gases that attach electrons is particularly important since the negative pulse due to electrons is counted in

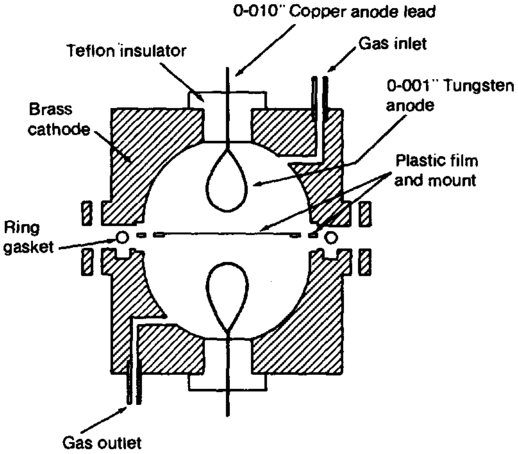


FIG. 1—*The 4π-counting chamber (1 in. = 2.54 cm).*

this detector. Commercial Chemically Pure (CP) gases are ordinarily satisfactory, but they should be dried for best results. A high-voltage power supply for the detector, an amplifier, discriminator, and a scaler complete the system.

To convert counting rate to disintegration rate, the principal corrections required are for self-absorption in the source and for absorption in the support film. The support film should be as thin as practicable to minimize absorption of beta particles emitted in the downward direction. Mylar or other polyester film with a thickness of about 0.9 mg/cm^2 is readily available and easily handled. However, it is too thick for accurate work with the lower-energy beta emitters. For this purpose thin films ($\simeq$ 5 to 10 μg/cm^2) are prepared by spreading on water a solution of a polymer in an organic solvent. VYNS [*3*], Formvar [*4*], and Tygon [*5*] plastics have been used for this purpose.

Since it is a part of the chamber cathode, the film must be made electrically conducting by covering it with a thin layer (2 to 5 μg/cm^2) of gold or palladium by vacuum evaporation. The absorption loss of beta particles in the film must be known. Published values can be used, if necessary, but for accurate work an absorption curve using very thin absorbers should be taken [*3*]. The "sandwich" method, in which the film absorption is calculated from the decrease in counting rate that occurs when the source surface is covered with a film of the same thickness as the backing film, is suitable for the higher beta energies.

The source itself must be very thin and deposited uniformly on the support to obtain negligible self-absorption. Various techniques have been used for spreading the source, for example, the evaporation of ^{63}Ni-dimethylglyoxime onto the support film [*3*]; the addition of a trifluoroethylene resin suspension [*5*], collodial silica, or insulin to the film as spreading agents; and hydrolysis [*4*]. Self-absorption in the source or mount can be measured by 4-π beta-gamma coincidence counting[*6, 7*]. The 4-π beta counter is placed next to a sodium iodide scintillation crystal, or a portion of the chamber wall is replaced by a sodium iodide crystal, and the absolute disintegration rate is evaluated by coincidence counting [*8,9*]. By adding a suitable beta-gamma tracer, the method has been used for pure beta as well as beta-gamma emitters [*10*]. Accurate standardization of pure low-energy beta emitters (for example, ^{63}Ni) is difficult, and the original literature should be consulted by those inexperienced with this technique.

Photon (gamma and strong X-ray) scintillation counters with geometries approaching 4-π steradians can be constructed from sodium iodide (thallium) crystals in either of two ways. A well crystal, that is, a cylinderical crystal with a small axial hole, covered with a second crystal will provide nearly 4-π geometry for small sources, as will two solid crystals placed very close together with a small source between them. The counts from both crystals are summed as in the gas-flow counter. The deviation from 4-π geometry can be calculated from the physical dimensions. For absolute gamma-ray counting, the efficiency of the crystal for the gamma energy being measured and the absorption in the crystal cover must be taken into account.

The liquid scintillation counter is also essentially a 4-π counter for beta particles, since nearly all the radiations are emitted into and interact with the detecting medium.

Low-Geometry Counters—This type of instrument is particularly useful for the absolute counting of alpha particles. The alpha emitter, in the form of a very thin solid source, is placed at a distance from the detector such that only a small fraction ($<$ 1 percent) of the alpha particles are emitted in a direction to enter the counter. This solid angle is obtained from the physical measurements of the instrument. The space between the source and detector is evacuated to eliminate the loss of alpha particles by absorption in air. The detector can be any counter that is 100 percent efficient for all alpha particles that enter the sensitive volume—a gas-flow proportional counter with a window that is thin (about 1 mg/cm^2) covering. The advantages of this instrument for absolute alpha counting are (1) that the effect of absorption of alpha particles in the source itself is kept to a minimum since only particles that travel the minimum distance in the source enter the detector (particles that have longer paths in the source are emitted at the wrong angle), and (2) that back-scattered alpha particles (those emitted into the source backing and reflected back up through the source) lose sufficient energy so they cannot enter the detector. One such instrument is described in Reference *12*.

Internal Gas Counters—The internal gas counter, so named because the radioactive material, in the gaseous state, is placed inside a counting chamber and thus becomes part of the counting gas itself, is useful for high-efficiency counting of weak beta and X-ray emitters. The radiations do not have to penetrate a counter window or solid source before entering the sensitive volume of a detector. The counter may be an ionization chamber, or it may be operated in the Geiger or proportional mode. Most present-day instruments are of the latter type, and they generally take the form of a metal or metal-coated glass cylinder as cathode with a thin anode wire running coaxially through it and insulated from the cylinder ends. A wire through the wall makes electrical contact to the cathode. The counter has a tube opening through which it may be connected to a gas-handling system for filling. The purity of the gas is important for efficient and reproducible counting, particularly in the proportional mode.

In a modification of the internal gas counter, scintillation counting has been used in place of gas-ionization counting. The inner walls of the chamber are coated with a scintillation material and the radioactive gas introduced. An optical window is made a part of the chamber, and the counting done by placing this window on a multiplier phototube to detect the scintillations. This system is particularly useful for counting radon gas with zinc sulfide as the scintillator. Additional details on internal gas counting may be found in Reference [*13*].

Spectrometers and Energy-Dependent Detectors—The availability of energy-dependent detectors (whose output signal is proportional to the energy of the radiation detected) that are easy to operate and maintain and have good resolution makes it possible to measure not only the total activity of a radioactive sample but the energy spectrum of the nuclear radiations emitted. Nuclear spectrometry is most useful for alpha particles, electromagnetic radiation (gamma and X-rays), and conversion electrons, since these radiations are emitted with discrete energies. Beta spectra have more limited use since beta particles are emitted from a nucleus with a continuous energy distribution up to a characteristic maximum (E-max) making a spectrum containing several different beta emitters difficult to resolve into its components. The advantages of spectrometric over total activity measurements of radioactive sources are: increased selectivity, sensitivity, and accuracy, because nuclide identification is more certain; interference from other radioactive nuclides in the sample is diminished or eliminated, and counter backgrounds are reduced since only a small portion of the total energy region is used for each radiation. The detectors for alpha spectra are gridded ion-chambers and silicon semiconductor detectors. These are described in ASTM Recommended Practice for Alpha Spectrometry (D 3084) [*1*]. Gridded ion-chambers are no longer available commercially and must be constructed by the user. A variety of semiconductors can be purchased, and these detectors have essentially replaced ion-chambers for alpha spectrometry, although the chambers have the advantage of high efficiency (nearly 50 percent) for large area sources.

The principal detectors used for gamma-ray spectrometry are thallium-activated sodium iodide scintillation crystals, NaI (Tl), and lithium-drifted germanium semiconductors, Ge(Li). For X-rays very-low-energy gamma rays, lithium-drifted silicon semiconductors, Si(Li), intrinsic germanium, and gas-filled thin-window (about 1 mg/cm^2) proportional counters are used. Sodium iodide is hygroscopic, so the crystal must be hermetically sealed, and the entire crystal-phototube package must be light-tight. The complete spectrometer also requires a high voltage power supply for the phototube (usually operated at 800 to 1000 V), a preamplifier, linear amplifier, pulse-height analyzer, and output recorder. The crystal is packaged in aluminum or stainless steel. The portion of the cover through which gamma-rays enter is normally thinner than the rest of the package in order to reduce low-energy photon attenuation. Sodium iodide crystals are available in a large range of sizes and shapes, from 25- by 25- mm cylinders to hemispheres and cylinders at least 305 mm in diameter. Information on the types of crystal packages and mountings that can be used is available from the manufacturers.

Germanium and silicon detectors are junction-type semiconductor devices (see ASTM Test for Gamma Spectrometry of Water (D 2459) [*1*]) in which a large sensitive region has been produced by drifting metallic lithium into germanium or silicon under the influence of an electric field at an elevated temperature (100 to 400°C). The crystal functions as a "solid ion chamber" when a high voltage is applied. Because of the high mobility of the small lithium atom, the detector must be kept cold to prevent the diffusion of lithium out of the crystal. In addition, in order to obtain high resolution, the detector must be operated at low temperatures to reduce thermal noise. At room temperature, sufficient free electrons will be present in the crystal to obscure the measurement of gamma and X-rays (but not of alpha particles). Consequently, the detectors are operated and kept at liquid nitrogen temperatures by a cryostat consisting of a metallic cold-finger immersed in a Dewar flask containing liquid nitrogen. If the detector is allowed to warm to room temperature for a short time, its resolution will deteriorate and in an hour or so it will lose sufficient lithium so it cannot function as a detector without redrifting. The detector is kept hermetically sealed in a vacuum to prevent impurities from condensing on the surface and lowering its resistance, and to reduce heat transfer from the room to the crystal. Aluminum is the usual covering, and a molecular sieve or vac-ion pump is incorporated into the system to maintain the vacuum. The electronic components required to obtain spectra are similar to that for sodium iodide crystals, except that because smaller pulses must be measured, high-quality electronics are needed. The complete system includes a high-voltage bias supply for the detector (up to 5000 V for large depletion volumes), a preamplifier, amplifier (usually charge-sensitive), biased amplifier (if needed), pulse height analyzer, and recording device.

A gamma-ray entering either a NaI(Tl) crystal or a semiconductor detector may lose all or part of its energy in the detector. In the former case, through multiple Compton interactions or the photoelectric effect, a full energy peak is obtained. Otherwise, only part of the energy will be observed and a Compton continuum spectrum is seen. An alternative process for high-energy gamma-rays ($<$ 1.02 MeV) is pair production, in which an electron-position pair is produced, and gamma-ray peaks are observed at 0.511 MeV intervals below the full energy peak. The two most important operating characteristics of gamma detectors are efficiency and resolution. The "peak-to-Compton" or "peak-to-valley" ratio is frequently given in the literature and is related to both efficiency and resolution. These parameters should be specified by the manufacturer and the conditions under which they were measured should be given.

The resolution of sodium iodide crystals is usually specified in terms of the width of the full-energy gamma-ray peak at half its maximum, the "full width at half maximum" (FWHM). This is shown graphically in the gamma-ray spectrum in Fig. 2. The resolution improves with increasing energy and the standard for comparison is usually the 0.662 MeV gamma ray emitted in the decay of ^{137}Cs. Good sodium iodide crystals have resolutions in the range of 6.5 to 7 percent for ^{137}Cs. Detection efficiency for the same geometry and window thickness is a function of several parameters, and much published information of efficiencies for various energies, detector sizes, source to detector distances, and other variables is available [*14*]. The efficiency for

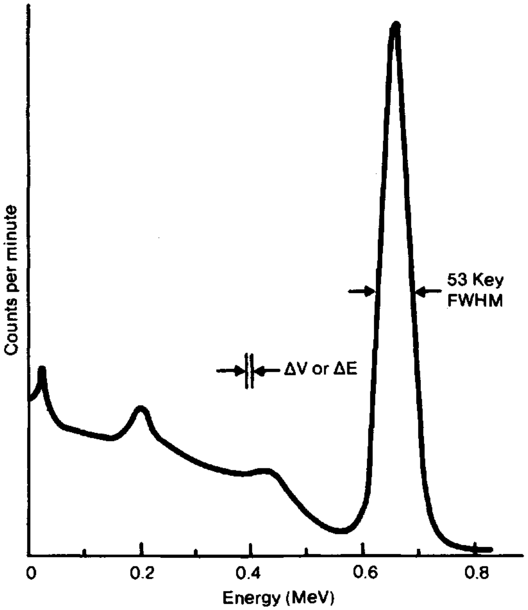


FIG. 2—*Pulse height or energy spectrum of Cs-137.*

gamma-ray detection may be expressed in various ways. Of primary interest in spectrometry is the full peak efficiency—the fraction of incident gamma rays that give full-energy peak for particular source-detector configuration. For a 102-mm-thick NaI(Tl) crystal, with the source on the surface (zero distance), this fraction is about 0.24 for the 0.66-MeV gamma ray of ^{137}Cs and about 0.14 for the 1.33-MeV gamma ray of ^{60}Co. The peak-to-valley or peak-to-Compton ratio is the ratio of counts at the maximum height of the full-energy peak to the counts at minimum of the Compton continum (Fig. 2). A high ratio indicates narrow peaks, that is, good resolution, for that particular efficiency. The Compton spectrum does not give useful information in gamma-ray spectrometry and can be considered as "noise." The ratio varies with energy and is frequently given for the 1.33-MeV peak of ^{60}Co. It increases as the crystal size increases and, after passing through a minimum, increases as the source-to-detector distance increases, since a larger fraction of the gamma-rays passes through the full depth of the crystal. A peak-to-valley ratio of 12:1 for a crystal is very good. This ratio can be increased by anticoincidence shielding to cancel Compton events as described earlier. The efficiency of silicon for gamma rays is considerably less than sodium iodide because of its lower atomic number (the efficiency for photoelectric absorption of gamma-rays is proportional to Z^5) and lower density (the density of sodium iodide is 3.67 g/cm^3 and of silicon 2.4 g/cm^3), so it is more efficient than sodium iodide for the same size detector. For a 1-MeV gamma-ray, the total absorption coefficient is about 2 mm^{-1} for sodium iodide, 1.5 mm^{-1} for silicon, and 3 mm^{-1} for germanium. However, germanium detectors are not yet available in sizes approaching that of sodium iodide. The efficiency of a germanium (lithium) detector is generally expressed by comparison with that of a 76- by 76-mm cylindrical Na(Tl) detector. Comparison is made between the full-energy peak efficiencies for the 1.33-MeV gamma ray of ^{60}Co when the source is 250 mm from the detector. A germanium detector with a volume of 35 cm^3 has an efficiency about 5 percent that of a 76- by 76-mm NaI(Tl) crystal. Larger Ge(Li) detectors are available with relative efficiencies of 25 to 30 percent.

There are limitations in the efficiency of the light production and collection processes in the sodium-iodide-photomultiplier system that make its resolution inferior to that of semiconductor detectors. One important factor is that about 500 eV are required to produce an electron at the photocathode in a sodium iodide detector system, while the average energy to produce the analogous electron-hole pair in silicon is only 3.5 eV and in germanium 2.8 eV. The resolution of semiconductor detectors does not change greatly with energy. Presently available germanium detectors have resolutions of 1.5 to 2.8 keV at 1.33 MeV and are from 3 to 30 percent efficient compared with a 76 by 76 mm NaI(Tl) detector. This greater resolution makes this detector the one of choice for gamma-ray spectrometry and cancels to some extent the higher efficiency available from sodium iodide. Since the pulses from a single photopeak are spread over a much smaller energy range in germanium than in sodium iodide, the background under the peak is much less. This means that for small sources of moderately energetic gamma rays, germanium is more sensitive than sodium iodide. This is indicated in Table 1, where the efficiencies and backgrounds of a 76- by 76-mm sodium iodide crystal and a 35-cm^3 (5.5 percent efficiency) germanium detector are compared.

Spectra of beta particles and conversion electrons can be obtained with sodium iodide and semiconductor detectors sufficiently thick (a few centimetres) to absorb the particles completely. One disadvantage of sodium iodide and cooled lithium-drifted semiconductors is their relatively thick entrance windows. Other semiconductor detectors, particularly the silicon surface barrier type, have thin entrance windows and can be used for beta particles at room temperature or better at 0°C. The 5- to 10-keV resolution for 600-keV electrons is better than the 12- to 30-keV resolution for 5-MeV alpha particles.

Good spectra of low-energy beta particles, conversion electrons, and X-rays can be obtained with a gas-flow proportional counter provided that a linear preamplifer is used. The resolution is intermediate between sodium iodide and germanium. To reduce back-scattering, the chamber should be made of low-Z material. A counter constructed of a cylinder of graphite-impregnated plastic, lucite ends, and a thin coaxial center wire gives good spectra for such radiations [*14*]. A hole is cut into the outer wall and covered with aluminized Mylar film to provide a thin entrance window. Argon (90 percent)-methane (10 percent) is a suitable counting gas.

TABLE 1—*Comparative performance of Sodium iodide (thalium) and germanium (lithium) gamma-ray detectors.*

Photon Energy	Background, cps,	Counting Efficiency, %		Detection Limit, photons/s	
Detector	Under Peak	A	B	A	B
0.14 MeV					
NaI	24	26	18	2.4	3.5
Ge	0.7	12	4	0.92	2.8
0.66 MeV					
NaI	20	14	9	4.1	6.3
Ge	0.11	1.3	0.68	3.6	6.8
1.33 MeV					
NaI	8	5.8	3.8	6.2	9.5
Ge	0.055	0.75	0.38	4.5	8.9

NOTES—

NaI: 76 mm diameter by 76 mm high cylindrical detector.

Ge(Li): 35 cm^3 active volume—5.5 percent efficiency.

A = small source placed on detector.

B = 57 by 57 by 57-mm-thick source place on detector.

Counting efficiency: percent of photons emitted from the source that give a full-energy peak.

Shielding: 152 mm of iron, 3.2 mm lead.

Counting time: One 30 000 s count for both source and background.

Detection limit: The number of photons emitted from the source whose net count equals twice the counting error, or

$$N + N_B = 2(N-N_B)^{1/2}$$

where N is the total number of counts recorded when the source is measured, and N_B is the total number of counts recorded when the background is measured.

Organic scintillators, such as anthracene and polystyrene polymerized with scintillating compounds, are also useful for beta spectrometry. They are packaged with a phototube in a manner similar to sodium iodide crystals. Liquid scintillation mixtures also give beta spectra, and the ouput of a commercial liquid scintillation counter can be fed into a multichannel pulse-height analyzer to obtain a spectrum [*2*]. A spectrum of ^{210}Pb ^{210}Bi-^{210}Po in Fig. 3 shows the resolution obtainable by liquid scintillation counting of aqueous samples in a dioxane-based solution. The ^{210}Bi curve is from a beta particle, and the ^{210}Po peak is from an alpha particle. Organic scintillators are preferable to sodium iodide for beta spectrometry because less backscattering occurs.

The output pulses of any energy-dependent detector, after linear amplification, must be sorted out according to energy to obtain the spectrum of incident radiation. The high-resolution available in detectors requires analyzers with hundreds of channels to realize their full resolving power. The amplified pulse is digitized by an analog-to-digital converter (ADC), and the resulting number for a particular pulse is recorded in a pulse counter whose location is determined by digital circuitry. This makes it possible to use a digital computer to count and store in its memory the number of pulses in each channel. This conversion and storage is relatively slow, and the

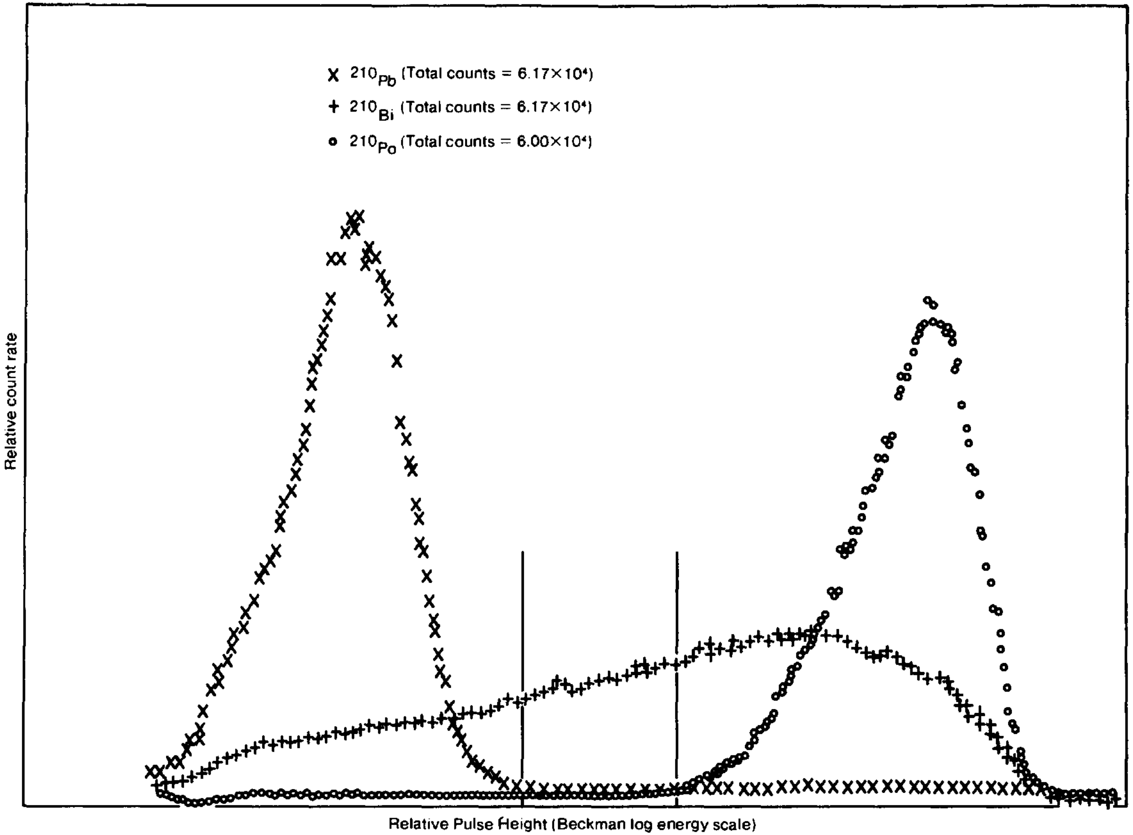


FIG. 3—*Spectrum of* ^{210}Pb ^{210}Bi ^{210}Po.

analyzer is blocked from processing a second pulse until the previous processing is completed. The time required to process a pulse increases with channel number. The instruments now available are sufficiently fast for almost all water measurement purposes. Some loss of pulse information is acceptable, as the analyzers measure and record "live time" fairly accurately. Thus, the counting time recorded by the analyzer will be the actual time it was in a condition to receive detector pulses, and not the elapsed time. To maintain good accuracy, the activity of the sample should be adjusted to give live times of 90 percent or more. A computer may be permanently combined with the ADC to operate only in the pulse-height analyzer mode ("hard wired"), or a separate and larger computer is "soft wired" to the ADC and can also be programmed for operations other than pulse height analysis, such as data reduction and spectrum resolution. In either case, this type of analyzer makes possible automatic digital readout on printers, paper, and magnetic tape, automatic spectrum plotting, cathode-ray tube curve and digital presentation, and internal data reduction.

All multichannel pulse-height analyzers currently available are transistorized, and are fairly reliable instruments and relatively easy to operate. Their maintenance and repair is, however, a specialized skill similar to other computer repair. In comparing analyzers, some of the important specifications to consider are number of channels, count capacity, stability, live-time accuracy, linearity, type of pulse input acceptable, and ADC speed. The minimum number of channels useful for sodium iodide gamma-spectrometry is 128; germanium (lithium) detectors should be used with at least a 1000-channel analyzer, and alpha and beta spectra can profitably use 100 to 400 channels, depending on the energy range to be covered. Analyzers with 4096 channels are fairly common, and larger analyzers are available for special purposes.

Semiconductor detectors require low-noise charge-sensitive amplifiers. Because of their excellent resolution, semiconductor detectors are often used with a biased amplifier following the main amplifier to isolate a portion of the spectrum for analysis. This makes is possible to use smaller analyzers than would otherwise be necessary.

Anticoincidence Counters—Substantial background reduction can be achieved in beta and gamma counters by surrounding or covering the sample detector with another detector also sensitive to beta or gamma radiation, and connecting them electronically so that any pulse appearing in both detectors is cancelled and not recorded as a count. This is usually referred to as anticoincidence shielding, and is recommended for obtaining very low backgrounds. This type of counter was used for many years in directional studies of cosmic rays, and was first applied to reducing the background of beta counters by Libby in his study of natural ^{14}C. The thick metal shielding(lead, iron, or mercury) ordinarily used to reduce cosmic-ray and gamma-ray background must also be present, and is placed outside the anticoincidence shielding. Gas-filled beta detectors are generally shielded by gas-filled detectors, and such anticoincidence shielding is effective primarily against the particulate component of cosmic rays. The anticoincidence shielding for beta counters may consist of a number of long Geiger tubes ("cosmic-ray counters") surrounding the sample detector or a large (about 15.24 cm square) gas-flow detector, with several anode wires so that the entire area of the counter is sensitive, placed just above the sample detector. For counting solid beta sources, the sample detector has a diameter of 2.54 to 5.08 cm. Surrounding these counters on all six sides, there is frequently a layer of high-purity copper to absorb gamma rays emitted from the outermost shielding, and 102 to 152 mm of lead or iron on all six sides. This is the form usually taken by the commercially available anticoincidence shielded beta counters. Plastic or inorganic scintillators could also be used as the anticoincidence shielding.

Anticoincidence shielding of gamma-ray detectors operates in a similar way, and is particularly useful in reducing the Compton continum background of gamma rays [*15*]. Gamma rays that undergo Compton scattering and produce a pulse in both the detector and the anticoincidence shield are cancelled electronically. Ideally, only those gamma rays that are completely absorbed in the sample detector itself produce a count which is recorded with the total energy of the gamma ray (full-energy peak). There are second-order effects that prevent complete elimination of Compton scattering, but the improvement is substantial. The anticoincidence shield can be a large sodium iodide or plastic scintillator suitably attached to phototubes. They usually have a large annular hole into which the sample detector, a smaller sodium iodide detector, or germanium iodide detector is placed [*16,17*].

Coincidence Counters—In coincidence counting, two or more radiation detectors are used together to measure the same sample, and only those nuclear events, or counts, that occur simultaneously in all detectors are recorded. The coincidence counting technique finds considerable application in studying radioactive decay schemes, but, in the measurement of radioactivity, the principal uses are for the standardization of radioactive sources and for counter background reduction.

Coincident counting is a very powerful method for absolute disintegration rate measurement [*8,18*]. Both alpha and beta emitters can be standardized if their decay schemes are such at β-γ, γ-γ, β-β, α-β, or α-X-ray coincidence occur in their decay. Gamma-gamma coincidence counting with two sodium iodide crystals, and the source placed between them, is an excellent method of reducing the background from Compton-scattered events. Its use is limited, of course, to counting nuclides that emit two photons in cascade (which are essentially simultaneous), either directly as in ^{60}Co, or by annihilation of positrons as in ^{65}Zn, or by immediate emission of a gamma ray following electron capture decay. If the crystals are operated with single-channel pulse-height analyzers to limit the events recorded from each crystal to one of the full-energy peaks of the photons being emitted, then essentially only those photons will be counted. Noncoincident pulses of any energy in either one of the crystals will be cancelled, including cosmic-ray photons in the background and degraded or Compton scattered photons from higher-energy gamma rays in the sample. Thus, the method reduces interference from other gamma emitters in the sample. If, instead of single-channel analyzers, two multichannel analyzers are used to record the complete spectrum from each crystal, singly and in coincidence, then the complete coincident gamma-ray spectrum can be obtained with one measurement. The efficiency for coincidence counting is low since it is the product of the individual efficiencies in each crystal, but the sensitivity is generally improved because of the large background reduction [*19*]. This technique is often referred to as two-parameter or multidimensional gamma-ray spectrometry.

Additional background improvement is obtained if the two crystals are surrounded by a large annular sodium iodide or plastic scintillation crystal connected in anticoincidence with the two inner crystals. In this case, a gamma ray that gives a pulse but is not completely absorbed in one of the two inner crystals and also gives a pulse in the surrounding crystal is cancelled electronically. [*16,19*] This provides additional reduction in the Compton scattering background. Lithium-drifted germanium detectors may be used in place of the inner sodium iodide crystals for improved resolution and sensitivities [*17*]. All of the equipment described in this section is available commercially.

Sampling

Collect the sample in accordance with the applicable part of the following:

ASTM Sampling Steam (Method D 1066)

ASTM Sampling Water (Method D 3370) (Particularly Section 14.3)

Sample an appropriate volume depending on the expected concentration of radioactivity in the water. For precise measurements without long counting times, it is advisable to count an aliquot which contains at least 1 nCi of radioactivity.

Chemical treatment of samples to prevent biological or algal growth is not recommended and should be avoided unless essential. When necessary, the reagents used should be selected to avoid chemical interaction with the radioactive species in the sample. Samples should be analyzed promptly.

Chemical treatment of samples to retain radioactive species in solution may be employed, but the specific treatment should be carefully selected. The use of oxidizing acids such as HNO_3 is not recommended when iodide is present, since it may be oxidized to iodine and lost or be absorbed on plastic containers if used. In some cases, extreme chemical treatment may be used to keep a particular chemical species in solution; examples are strongly alkaline conditions to hold molybdenum and ruthenium in solution, or acid conditions with fluoride ion to keep zirconium in solution. The addition of an acid such as hydrogen chloride is generally desirable to reduce hydrolysis and the loss of activity on container walls. Frequently, samples will contain insoluble material. In such cases, the sample should be treated by one of the following methods:

1. Filter the insoluble material and analyze both the filtrate and insoluble matter on the filter. During filtration, some material may be sorbed onto the filter and assumed to be insoluble when in fact it is soluble.
2. Centrifuge the sample and analyze both phases. The insoluble phase should be washed with distilled water to remove all soluble material without dissolving the insoluble fraction.

In either of the foregoing separations, when the total activity is required, the insoluble matter may be dissolved and recombined with the soluble fraction. When radioactivity is left on the walls of the sample container, it should be desorbed and added to the sample.

Composite samples may be made by mixing aliquots of successive samples collected by an automatic sampler. Analysis of such composite samples yields average results only and loses information on short-term effects.

Instrument Operation and Control

These following procedures assure that counting equipment is functioning properly and remains in calibration.

Establishing Counter Characteristics—The first step in instrument control is to establish the operating characteristics of the system. The efficiency for counting the nuclide of interest is carefully measured under the conditions to be employed. Counting conditions are selected; that is, gain, discriminator setting, and voltage are optimized for the radionuclide of interest. The operating voltage should be set so that any change in counting rate is minimized for a given voltage fluctuation. The discriminators should be adjusted to exclude noise and unwanted interferences from the nuclides being counted. Adjustment should be made to optimize the signal-to-noise ratio. When the counting conditions have been selected, known interferences should be monitored to determine such things as the effect of counting betas, in an alpha counter, or alpha pulses in a beta proportional counter.

Daily performance checks should be made and a log maintained for each instrument. This log should include the count for a standard and a background. When the counting rate differs statistically from the expected performance, additional counting should be done to determine if the counter is malfunctioning. High background can indicate either an instrumental problem or counter contamination.

Certified standards are available from several suppliers. Most solution standards have the pH controlled and carrier added to assure that hydrolysis or sorption, or both, do not change the concentration of the solution. When dilutions are made, it is important to maintain the stability of the solution by diluting with proper matrix. The standard should be stored in a container which minimizes evaporation by loss either through the walls or out of the stopper.

If a planchet is prepared as a standard, it should be placed in a suitable container for storage which will prevent the surface containing the activity from being contacted. A recommended practice is the preparation of two standards, using one and storing the second for periodic checks to see that the working standard has not been altered.

Counter Control Charts—The daily standard counts made on any counter must be evaluated on a statistical basis and the best way to do this is to maintain a control chart on each counter. A control chart is a graph showing the number of counts recorded in a fixed counting period against day of the year. The initial entry, $\overline{N}$ is determined from the average of several measurements over a period of days. Then the error bands of $\pm 2\ S_x$ and $\pm 3\ S_x$ are entered ($S_x = \sqrt{\overline{N}}$) and lines are drawn on the chart which allow for decay of the standard over the year. For a long-lived source, such as cesium-137, which has a half life of 30 years, about 2.5 percent of the activity is lost in one year. An example of a control chart is shown in Fig. 4.

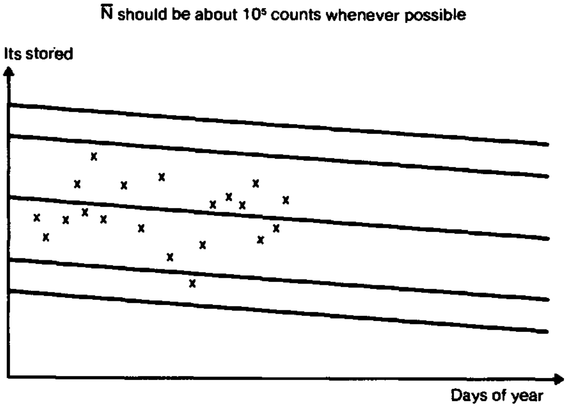


FIG. 4—*Typical counter control chart.*

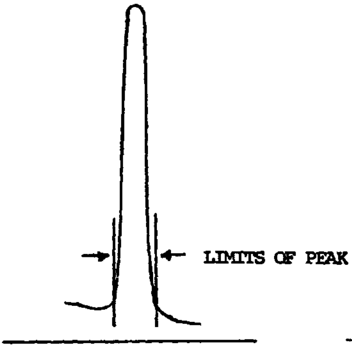
The result of the standard count is entered in the control chart and the following action is taken:

If the result is inside the $\pm\ 2S_x$ band, the counter is considered to be in control.

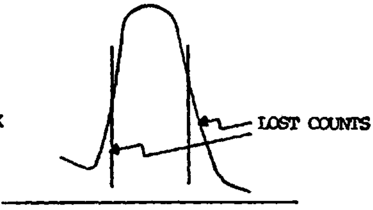
If the result lies outside the $\pm 2S_x$ band but inside the $\pm 3S_x$ band, the counter is considered to be in control, but this result should be flagged.

If the result lies outside the $\pm 3S_x$ band, the counter is considered out of control. Corrective action is needed if repeated counts remain outside the $\pm\ 3S_x$ band.

For alpha and gamma spectrometry it is also important to monitor for system resolution.



NORMAL RESOLUTION



LOSS IN RESOLUTION

In addition to the control charts made on each counter, all pertinent information about the system should be kept in a log book or permanent file:

Counter Logs

α and β Counters	γ Spectrometers
Standard counts	Standard counts
Background counts	Standard resolution
System changes	Background counts
Control charts	Control charts

Counting Statistics

Each nuclear disintegration [*8,20,21*] is a completely random and independent process. Established methods of statistical analysis are available to describe the random phenomenon of nuclear disintegration. The total number of particles counted in a time period can be shown to deviate from the average according to the expression, $N \pm \sqrt{N}$, where N is the number of counts in the counting period t. Similar behavior is found in the background count rate for any counter, and the recorded background will deviate from the average according to the expression $N_B \pm \sqrt{N_B}$, where N_B is the number of counts recorded in the counting period t_B. The net count rate found is then

$$\text{Net count rate} = \left(\frac{N}{t} - \frac{N_B}{t_B}\right) \pm S_x$$

where S_x is the standard deviation of the net count rate and is given by

$$S_x = \sqrt{\frac{N}{t^2} + \frac{N_B}{t_B^2}}$$

or for the net count rate with its standard deviation we have

$$\text{Net count rate} = \left(\frac{N}{t} - \frac{N_B}{t_B}\right) \pm \sqrt{\frac{N}{t^2} + \frac{N_B}{t_B^2}}$$

In practice, many counts will be made which deviate from the average by more or less than the standard deviation since S_x by definition would give those limits $X - S_x$ and $X + S_x$ which would include about 68 percent of all observed values. In terms of the population of observations between limits, we can express the change of probability of a result being between the limits $X - K\ S_x$ and $X + KS_x$ as "confidence levels" where K is simply a multiplier for S_x In evaluating the effect of K, we can tabulate K and the confidence level.

Confidence level, percent	K
68.3	1.0
90	1.645
95	1.96
99	2.575
99.73	3.0

The 95 percent "confidence limit" is frequently used and has been generally accepted, since errors outside this band are considered statistically significant. In practice, K is often rounded off to 2.0 and the term $2S_x$, or 2σ, error is often used. In some cases the $3S_x$, or 3σ, error is used and gives the 99.7 percent confidence limits.

Precision—This is a measure of the reproducibility of a measurement. There are a number of items which affect the precision of radioactivity measurements; the more important of these are the following:

Position: For point sources, the observed radioactivity is proportional to the reciprocal of the square of the distance of the source from the detector. All sources being directly compared must be measured at the same source to detector distance.

Radiation Scattering: Changes in the sample support and backing material can seriously affect the precision of radiation measurements, particularly that of beta radiation. Standards and samples should have the same backing material. The use of a sample support rack constructed of a material with low atomic number will reduce the effect of side-scattering. Scattering from backing material can be minimized by use of a thin, low-atomic-number material.

Background: This radioactivity must be measured with no sample near the detector and subtracted from all measurements of gross sample activity. This requirement becomes more critical as the net sample activity becomes small with respect to the background. Routine periodic measurements of the background must be performed to check for possible detector contamination or malfunction.

Absorption: Alpha and beta radiation is partly absorbed by the sample itself being counted and by all substances separating the sample from the detector. This effect is usually small for gamma radiation, but beta and alpha radiation are seriously affected. If sources of the same atomic number and mass are compared on the same counter in the same geometry, absorption will be constant under these conditions but should not be ignored. Since the sample mass may vary significantly, calibration curves must be constructed to correct for changes in self-absorption.

Quenching: This is any process which reduces the photon output in a scintillation system; this in turn reduces the measured count rate. Quenching can be caused by such things as sample color and chemicals in the sample. The need to correct for this phenomenon can be avoided if samples of the same color and same chemical composition are compared. If this is not possible, most instrument manufacturers and texts describe methods for construction of calibration curves to correct for this phenomenon [*22–24*].

Overall Uncertainty in a Determination—Measurement results should be reported with the estimated overall measurement uncertainties shown. There are two approaches to this. One is a rigid propagation of uncertainties, which is not sound in practice since the individual components are not well characterized, and the second is a combination of known uncertainties. In combining uncertainties, use the relationship

$$S_x = \sqrt{S_1^2 + S_2^2}$$

where

S = overall uncertainty of measurement (RSD),
S_1 = random counting uncertainty (RSD),
S_2 = other random uncertainties (RSD),

and the work can be divided into two main classes.

Gamma Spectrometry: Assuming that the integrity of the sample is known, the sampling and treatment effects are at a minimum and then only two significant terms are present. These are accuracy of calibration and precision of counting, and we have:

$$S\gamma_{\text{spec}} = \sqrt{S_c^2 + S_a^2}$$

where

$S\gamma_{\text{spec}}$ = overall error for the measurement (relative standard deviation or RSD),
S_c = calibration uncertainty (RSD), and
S_a = counting uncertainty (RSD).

In general, S_a is only important at low count rates, that is, environmental and discharge samples.

Separative Work: The sample treatment introduces uncertainty into the measurement. One estimate of great merit is to say that

$$S_x = \sqrt{S_M^2 + S_a^2 + S_c^2}$$

where
S_x = overall uncertainty for measurement (RSD),
S_M = intrinsic precision of method (RSD),
S_a = counting uncertainty (RSD), and
S_c = calibration uncertainty (RSD).

The intrinsic precision may be determined by doing a single operator precision (SOP) test at three or four activity levels.

SOP Test		Error Due to Counting	
Level, dpm	σ % (RSD)	σ % (RSD)	
10	8	C_1	S_{M1}
100	4	C_2	S_{M2}
10 000	2	C_3	S_{M3}

(NOTE: The use of ASTM Methods which have been round-robin tested will give you a method where S_x is known.)

Minimum Detectable Activity—The minimum detectable activity (MDA) is a statistical measure of the sensitivity of a counting determination. In the analysis of environmental samples or discharge samples, the sensitivity obviously becomes an important and often critical item. For gross counting, the minimum detectable activity may be arbitrarily defined as the net count, which is equal to twice the standard deviation for the net count, that is, $2S_x$.

Where complex NaI(Tl) spectra are being analyzed and the components being sought are not completely separable by instrument resolution, the detection limit should be considered as three times the standard deviation. Alpha and Ge(Li) gamma spectrometry generally have well resolved peaks so that a two-standard-deviation uncertainty may be used as a limit of detection.

In computing S_x, the sample and background count rates should be considered, that is

$$S_x = \sqrt{\frac{N}{t^2} + \frac{N_B}{t_B^2}} \text{ cpm}$$

If the sample and background counting times are equal ($t = t_B$), we can use a slightly different form

$$S_x = \sqrt{N + N_b} \text{ counts}$$

The total count form is simpler to use in estimation of MDA's, but care must be taken in converting from total counts back to concentration in the sample. An example of the calculation of MDA's follows for ASTM Test for Radioactive Barium in Water (D 2038), which covers the determination of barium-140 in water:

By beta counting, assuming 80 percent chemical yield and counting at 40 percent efficiency with 1-cpm background. For 100-min count periods we have

$$\text{MDA} = 2\ \sigma = 2\sqrt{n_s + n_b} \text{ counts}$$

and at MDS we know that $n_s \rightarrow n_b$

$\text{MDA} = \ 2n_b = 2 \times 100$
$\text{MDA} = 2\ \ 200 = 28.2$ counts

in disintegrations per minute (dpm) terms

$$\text{MDA} = \frac{28.2}{0.4 \times 100 \times 0.8} = 0.88 \text{ dpm}$$

or for 1 litre sample, MDA = 0.4 pCi/litre.

By gamma counting of the sample as received, we can count the 1.6-MeV peak from lanthanium-140 using either sodium iodide or germanium lithium detectors. These two cases are:

Sodium iodide, 4.9 percent efficiency and a background of 6.4 cpm. Assuming 100-min counts.

$$\text{MDA} = 3\sigma = 3\sqrt{2n_b} = 3\sqrt{2 \times 640}$$
$$\text{MDA} = 107 \text{ counts}$$

in dpm terms

$$\text{MDA} = \frac{107}{100 \times 0.049} = 21.9 \text{ dpm}$$

or for a 1 litre sample, MDA = 9.9 pCi/litre.

Germanium-lithium, 0.85 percent efficiency and a background of 0.12 cpm. Assuming 100-min counts

$$\text{MDA} = 2S_x = 2\sqrt{2n_b} = 2\sqrt{2 \times 12}$$

$$\text{MDA} = 8.8 \text{ counts}$$

in dpm terms

$$\text{MDA} = \frac{14.7}{100 \times 0.0085} = 11.5 \text{ dpm}$$

or for 1 litre sample, MDA = 5.2 pCi/litre.

An independent assessment of this method by the Environmental Protection Agency (EPA) [*25*] suggested sensitivities of 1 pCi/litre for a 1-litre sample by beta counting and 10 pCi/litre for a 3.5-litre sample by gamma counting. The value of the germanium lithium detector is obvious in this case—good resolution is available with a good sensitivity—and in comparing these MDA's to the maximum permissible concentration (MPC) for barium-140 in water, we find

$$\begin{aligned} \text{MPC} = {} & 3 \times 10^4 \text{ pCi/litre soluble} \\ & 2 \times 10^4 \text{ pCi/litre insoluble} \end{aligned}$$

$$\left[\begin{array}{ll} \text{Beta MDA} & = 0.4 \text{ pCi/litre} \\ \text{NaI MDA} & = 9.8 \text{ pCi/litre} \\ \text{Ge(Li) MDA} & = 7.8 \text{ pCi/litre} \end{array}\right] \begin{array}{l} \text{all less than 1 percent of the} \\ \text{most restrictive MPC} \end{array}$$

Calculations and Symbols

To calculate the amount of activity of a substance X, the following general method should be used

$$C = \frac{1}{VY}\left[\frac{N}{t} - \frac{N_B}{t_B}\right]$$

where

N = number of counts accumulated,
t = sample counting period, min,
N_B = number of background counts accumulated,
t_B = background counting period, min,
C = net counts per minute per millilitre, cpm/ml
V = volume of sample, millilitres, and
Y = fractional recovery of species (unity in methods where complete recovery is assumed).

The disintegration rate (D) can be calculated as follows

$$D = \frac{C - R}{E}$$

where

D = disintegrations per minute per millilitre, dpm/ml

E = fractional efficiency of counter, cpm/dpm, and
R = reagent blank correction (cpm) measured on an actual blank sample.

In gamma spectrometry we have

$$E = GP$$

where
G = fractional abundance of gamma ray concerned and
P = photopeak detection efficiency (fraction).

In beta counting

$$E = f_d f_a f_s f_m$$

where
f_d = detector efficiency factor for a source of given beta energy,
f_a = absorber factor for total absorber thickness (detector window + air space + absorber + cover) for a source of given beta energy,
f_s = self-absorption and backscatter factor for a given precipitate thickness and given beta energy, and
f_m = number of charged particles per disintegration.

The concentration of Substance A may be calculated as follows:

$$A = \frac{\mathrm{D}}{2.22 \times 10^8}$$

where
A = concentration in microcuries per millilitre (μCi/ml).

For decay correction, use the expression

$$D = D^\circ \exp\,(-0.693\ t/T)$$

where
D° = disintegration rate at time zero, that is, reference time
t = elapsed time between measurement and reference time, and
T = half-life of nuclide.

Parent-daughter relationships are commonly shown by use of subscripts 1, 2, etc. for count rates, disintegration rates, or values of t and T.

Alpha Counting

This section covers the measurement of the alpha particle radioactivity of water. It is applicable to alpha emitters having energies above 3 MeV at activity levels above 0.5 picocuries per sample.

Summary—Alpha particles are characterized by intense loss of energy in passing through matter. This intense loss of energy is used in differentiating alpha radioactivity from other types through the dense ionization or intense scintillation it produces. This high rate of loss of energy in passing through matter, however, also makes sample preparation conditions for alpha counting more stringent than is necessary for other types of radiation.

Alpha Detectors—Alpha radioactivity is normally measured by one of several types of detectors in combination with suitable electronic components. The detector devices most used are ionization chambers, proportional counters, silicon semiconductor detectors, and scintillation counters. The associated electronic components in all cases would include high-voltage power supplies, preamplifiers, amplifiers, scalers, and recording devices.

Detection Technique—In all of these systems, the initial event is converted to an electrical pulse which is amplified to a voltage sufficient to operate the scaler mechanism where provision is made for recording each pulse. The number of pulses per unit of time is directly related to the disintegration rate of the test sample. The efficiency of the system can be determined by counting standards prepared in the same manner as the samples. An arbitrary efficiency factor can be defined in terms of a different radionuclide such as natural uranium, polonium-210, plutonium-239, or americium-241.

Measurement Variables—The measured alpha counting rate from a sample will depend on a number of variables. The most important of these variables are geometry, source diameter, self-absorption, absorption in air and detector window, coincidence losses, and backscatter. These are discussed in detail in the literature [*4,5*] and in many cases can be measured or corrected for by holding conditions constant during the counting of samples and standards. These effects may be described by the following relationship

$$\text{dpm} = \text{cpm}\ (G_p)\ (f_{bs})\ (f_{aw})\ (f_d)\ (f_{ssa})\ (f_c)$$

where

cpm = recorded counts per minute, corrected for background, and
dpm = alpha disintegrations per minute.
G_p = point source geometry, which is the solid angle subtended by the

sensitive area of the detector. The effect of this variable is eliminated by maintaining a constant geometry for both standard and sample counts.

f_{bs} = backscatter factor, or ratio of cpm with sample backing to cpm without backing. Not important in alpha counting since backscatter is small. In samples mounted on copper or stainless steel planchets for counting 2π geometry, backscatter may be taken as 2 percent (backscatter factor equals 1.02) without any serious error. In samples mounted on platinum, backscatter may be taken as 4 percent.

f_{aw} = factor to correct for losses due to absorption in air or window of external counters.

f_d = factor to correct for dispersion of the source from a point configuration. The effect of this variable is eliminated by preparing the standard in the same configuration as the samples.

f_{ssa} = factor to correct for the absorption and scattering of alpha particles in the sample and its mount. This was covered further in an earlier section.

f_c = factor to correct for losses due to the resolving time of the detector and its associated electronics; $f_c = (1 - nt)$ where n is observed counting rate, cpm, and t is resolving time, min.

Alpha counters have low backgrounds and high efficiencies. However, some counters are easily contaminated internally and care should be taken to avoid contamination. Silicon detectors operated in vacuum may become contaminated due to recoil from sources. Recoil contamination can be eliminated by maintaining an air absorber of 12 $\mu g/cm/^2$ between source and detector [*6*].

Interferences—Some alpha counters are sensitive to beta radiation with a degree of efficiency depending on the detector [*4,5*]. In these cases, electronic discrimination is often used to eliminate the smaller pulses due to beta particles.

Apparatus

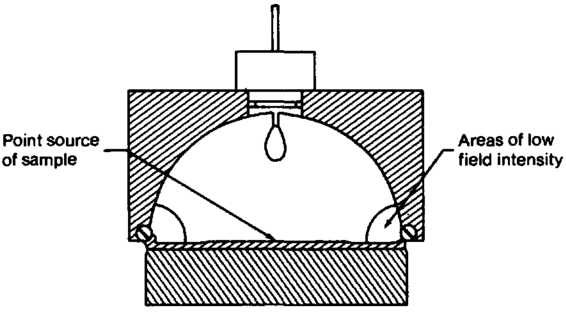
Ionization Chambers—Alpha particles entering the sensitive region of an ionization chamber produce dense ionization of the counting gas. The electrons are collected at the anode, thus developing a voltage pulse. Gridded ion chambers are used for alpha spectrometry, but have been replaced by solid-state detectors. The major advantage of the ion chamber is its ability to measure large area samples with essentially a 2π geometry. The chambers are operated at an overpressure with gas mixtures such as 10 percent methane-90 percent argon or 2 percent ethylene-98 percent argon. The peak resolution of such a detector is about 50-keV FWHM; refer to ASTM Recommended Practice for Alpha Spectrometry (D 3084).

Proportional Counters—Alpha particles entering the sensitive region of a proportional counter produce ionization of the counting gas. In this case, the electrons are accelerated toward the anode, producing secondary ionization and developing a large voltage pulse by gas amplification. Proportional counters are usually operated in the "limited proportional" range, where the total ionization is proportional to the primary ionization produced by the alpha particle.

Proportional detectors are generally constructed of stainless steel or aluminum; see Fig. 5. No additional shielding is required for alpha proportional counting. The counter should be capable of accepting mounts up to 51 mm in diameter. Proportional detectors are available in two types, either with or without a window between the sample and the counting chamber. The manufacturer's specifications for either type should include performance estimates of background count rate, length and slope of the voltage plateau, and efficiency of counting a specified electrodeposited standard source along with the type of gas used in the tests. For a window flow counter, the window thickness in milligrams per square centimetre should also be specified. With windowless low counter, the sample and sample mount should be made of an electrical conductor in order to avoid erratic behavior, due to static charge buildup.

Alpha emitters are counted with proportional instruments in 2π, or 50 percent, configuration. Two-π geometry is obtained by placing the sample on a flat planchet inside the detector. Half the alpha particles are emitted downward into the planchet, of which approximately 2 percent are backscattered in the upward direction. The other half are emitted upward into the gas volume.

Typical parameters for the alpha windowless flow counter are: background count rate—10 counts per hour; length of voltage plateau— 300 V; slope of voltage plateau—1 percent per 100 V for an electrodeposited source. For a window flow counter, typical values are: window thickness—1 mg/cm^2; background count rate—10 counts per hour; length of voltage plateau—300 V; slope of voltage plateau—1 percent per 100 V for an



(Cross section through center of hemisphere)

FIG. 5—*Typical chamber geometry for proportional detector.*

electrodeposited source; and efficiency—35 to 40 percent for an electrodeposited source. Gases commonly used in both types of alpha proportional counters are 10 percent methane-90 percent argon, pure methane, or pure argon.

Scintillation Counters—In scintillation counter, the alpha particle transfers energy to a scintillator, such as zinc sulfide (silver activated). The transfer of energy to the scintillator results in the production of light at a wavelength characteristic to the scintillator, and with an intensity proportional to the energy transmitted from the alpha particle. The scintillator medium is placed in close proximity to the cathode of a multiplier phototube, light photons from the scintillator strike the photocathode, and electrons are emitted. The photoelectrons are amplified by the multiplier phototube and a voltage pulse is produced at the anode.

The counter size is limited by the multiplier phototube size, a diameter of 51 mm being the most common. Two types of systems may be employed. In the first, the phosphor is optically coupled to the multiplier phototube and either covered with a thin (< 1 mg per square centimetre) opaque window or enclosed in a light-proof sample changer. With the sample placed as close as possible to the scintillator, efficiencies approaching 40 percent may be obtained. The second system employs a bare multiplier phototube housed in a light-proof assembly. The sample is mounted in contact with a disposable zinc sulfide disk and placed on the phototube for counting. This system give efficiencies approaching 50 percent, a slightly lower background, and less chance of counter contamination.

A major advantage of alpha scintillation counting is that the sample need not be conducting. For a 51-mm multiplier phototube with the phosphor coupled to the tube, typical values obtained are: background count rate—20 counts per hour, and efficiency for an electrodeposited standard source—35 to 40 percent. With a disposable phosphor mounted on the sample, typical values are: background count rate—10 counts per hour, and efficiency for an electrodeposited standard source—45 to 50 percent. For both systems, voltage plateau length is 150 V with a slope of 5 percent per 100 V.

Liquid scintillation counting of alpha emitters with a commercially available instrument overcomes many of the problems inherent in other techniques [*8,11-13*]. Typical background counting rates range from 440 to 700 counts per hour. Sample preparation involves mixing the sample aliquot with a suitable liquid scintillator solution or gel phosphor before counting. Planchet preparation is eliminated, volatile components are retained, and the completely enclosed sample cannot contaminate the counting chamber. The sample is uniformly distributed in the scintillator so there is no self-absorption, resulting in a counting efficiency of almost 100 percent. Because of the high alpha energies, considerable chemical quenching effects can be tolerated before counting efficiency is reduced. Coincidence losses are small in liquid scintillation counting at count rates up to 10^6 cpm. For samples which contain both alpha and high-energy beta emitters, difficulties do arise in distinguishing between the two. The problem is primarily due to the broad continuum of beta energy distribution up to the maximum energy, and the poor resolution of liquid scintillation spectrometers. This problem is aggravated because the light yield per MeV of alpha particles in most liquid scintillators is approximately tenfold lower than a beta particle of equivalent energy, putting the pulses from alphas and high-energy betas in the same region. Correction for beta activity may be made by certain mathematical or graphical techniques. It is preferable to separate the alpha emitter from the bulk of the beta activity by chemistry.

Semiconductor Detectors—The semiconductor detectors used for alpha counting are essentially solid-state ionization chambers. The ionization of the gas in an ionization chamber by alpha particles produces electron-ion pairs while in a semiconductor detector, electron-hole pairs are produced. The liberated charge is collected by an electric field and amplified by a charge-sensitive amplifier. In general, silicon surface barrier detectors are used for alpha counting. These detectors are *n*-type base material upon which gold is evaporated to make a contact. The semiconductor material must have a high resistivity since the background is a function of the leakage current. This leakage current is present in an electric field since the starting material is a semiconductor, not an insulator. The reversed bias which is applied reduces the leakage current, and a "depletion layer" of free-charge carriers is created. This layer is very thin and the leakage current extremely low; therefore, the interactions of photons with the detector will have a neglible effect. Since the detector shows a linear response with energy, any interactions of beta particles with the detector can be eliminated by electronic discrimination. The semiconductor is of special interest in alpha counting, where spectrometric measurements may be made, since the average energy required to produce an electron-hole pair in silicon is 3.5 ±0.1 eV, compared with the 25 to 30 eV to produce an ion pair in a gridded ionization chamber. Consequently, silicon detectors provide much improved resolution and also normally have lower background count rates.

The detector size is generally less than 25 mm (1 in.) in diameter, since the resolution decreases and cost increases with detector size. For best results, the sample should be electrodeposited to make an essentially massless source. The detector is operated in a vacuum chamber. Typical backgrounds range from 0.3 to 0.6 counts per hour. Additional specifications for detectors may be found in ASTM Method D 3084.

Absorption—The range of alpha particles is a few centimetres in air and a few thousandths of a centimetre in solids. Even fairly short path lengths in air and passage through thin windows will result in the absorption of some fraction of the alpha radiation.

Calibration of alpha counting equipment for specific nuclide measurement should be carried out using a standard of similar alpha energy measured under exactly the same conditions as the sample to be counted.

When the gross alpha activity of a sample is to be measured [ASTM Test for Alpha Particle Radioactivity of Water (D 1943)], the counting equipment should be calibrated using a standard. The standard should contain the same weight and distribution of solids as the sample and be mounted in an identical manner. If the samples contain variable amounts of solids or carrier, a calibration curve should be prepared relating weight of solids present to counting efficiency. The efficiency factor (*E*) is expressed as a fraction of the disintegration rate of the standard.

Calibrated standards of Pu-239, Am-241, Po-210, Th-228, Ra-226, U-233, U-235, and U (Nat.) are readily available either from the National Bureau of Standards or commercial organizations. Calibrated standards of other alpha-emitting radionuclides may be procured from the aforementioned suppliers upon special request.

Source Preparation—The sample whose alpha activity is to be determined must be appropriately mounted for the final measurement. This can be accomplished in a number of ways, some of which are dependent upon the counting method used. In all cases, however, the sample must be mounted in a uniform and reproducible manner.

The most straightforward and commonly used method of preparing a sample for alpha counting is by evaporation onto a suitable planchet. Evaporated sources are usually counted in end-window or windowless proportional counters or in zinc-sulfide scintillation counters. Producing a thin, uniform, and reproducible source by this technique is difficult, and considerable care is necessary. Evaporations must be carried out slowly to avoid spattering, and are usually performed under infrared lamps.

Mounting of solid-free samples resulting from radiochemical separations of specific nuclides is best accomplished by evaporating the sample in the center of a planchet. Define an area in the center of the planchet and keep the sample within this area during evaporation. This can usually be accomplished by carefully evaporating the sample in small portions. Samples which contain solids present the problem that the material does not evaporate uniformly but tends to deposit in crystals and aggregates, producing uneven deposits consisting of rings, ridges, or localized amounts of solids. This will be the case when water samples are prepared for alpha counting without chemical separation of specific nuclides. These samples are best mounted by allowing the sample to evaporate on the entire surface of the planchet. This will produce a more uniform source and minimize the self-absorption effects. Surfactants can be used to spread the sample during evaporation. Dissolution of the solids on the planchet with water and reevaporation may be necessary to obtain a uniformly distributed source.

Samples which contain carriers can be mounted using a precipitation technique. The amounts of carrier used should be kept small (< 10 mg) so as to minimize self-absorption. The carrier is precipitated by suitable chemical procedures and the precipitate is mounted for counting by either filtration through a filter or by evaporation of a slurry of the precipitate onto a planchet. The final surface density of such a deposit should be less than 1

mg/cm^2. These samples should be counted in an end-window proportional counter or in a zinc scintillation counter because they are nonconductors.

Filtration of a precipitate onto a filter produces a more uniform and reproducible source than the evaporation technique. When evaporating a slurry of a precipitate onto a planchet, care must be used to obtain a uniform and reproducible source. However, this is usually more easily obtained with a slurry than when evaporating a solution.

Electrodeposition is the most effective and widely used technique for preparation of a thin, uniform, and reproducible source for alpha counting. Electroplated sources can be counted in any alpha counting equipment except, of course, a liquid scintillation counter. The chemical separation of specific nuclides from the sample is required prior to electrodeposition. The alpha-emitting element is electrodeposited onto a flat metal disk. Platinum, stainless steel, nickel, and tantalum have been used for this purpose. Information on electrodeposition of alpha emitters has been published [*26–28*]. The electrodeposition technique produces the most suitable sources for alpha spectrometry. One disadvantage of this technique is that, for some samples, quantitative deposition is not always obtained and a recovery correction factor must be applied. Electrodeposition followed by alpha spectrometry is particularly useful for alpha analysis in which yield measurements are determined by addition of a known amount of an isotope of the same element to be measured (see ASTM Method D 3084).

The use of liquid scintillation counting avoids some of the difficulties encountered in preparing samples for solid source counting, but has the disadvantage of blindly counting all alphas as does any gross method. Self-absorption problems are eliminated and counting efficiencies are 90 to 100 percent. Samples are prepared for liquid scintillation counting by dissolving the sample in a scintillation mixture [*29, 30*] or extracting the alpha-emitting element into a scintillation mixture containing the extractant [*31*].

Calculations—This method is useful for comparing activities of a group of samples as in a tracer experiment. The following equation may be used to calculate the results.

$$\text{Activity } C = \frac{1}{VY}\left(\frac{N}{t} - \frac{N_B}{t_B}\right)$$

where:

N = number of counts accumulated,
t = sample counting period, min,
N_B = number of background counts accumulated,
t_B = background counting period, min,
C = net counts per minute per millilitre (cpm/ml),
V = volume of sample, millilitres, and
Y = recovery of species (unity in methods where complete recovery is assumed).

The disintegration rate or concentration in microcuries may be calculated as follows:

$$\text{Disintegration rate} \qquad D = \frac{C}{E}$$

D = disintegrations per minute per millilitre (dpm/ml), and
E = efficiency of counter (fraction) (cpm/dpm).

$$\text{Concentration } A = \frac{D}{2.22 \times 10^6}$$

where:

A = concentration in microcuries per millilitre (μCi/ml).

Results may also be reported in terms of equivalent natural uranium activity, employing an efficiency determined by use of a natural uranium reference standard.

$$\text{Alpha activity equivalent to natural uranium, dpm/ml} = \frac{C}{E_u}$$

where

E_u = efficiency of counter for natural uranium (fraction).

To properly evaluate the result, the uncertainty associated with the concentration should be calculated according to the recommended procedure given earlier.

Beta Counting

This section covers the measurement of the beta particle radioactivity of water. It also covers the general techniques used to prepare and measure the activity resulting from radiochemical separation of specific nuclides or groups of nuclides in water samples. It is applicable to beta emitters with activity levels above 10 picocuries per sample for most counting systems. For samples of lower activity, see ASTM Recommended Practice for Low-Level Activity Measurements (D 3085) [*2*]. The method is not applicable to samples containing radionuclides that are volatile under conditions of the analysis. General information on radioactivity and measurement of radiation may be found in the literature [*9,11*].

Summary—Beta radioactivity may be measured by one of several types of instruments which provide a detector and a combined amplifier, power supply, and scaler. The most widely used detectors are proportional or Geiger-Muller counters, but scintillation systems offer certain advantages.

Among the gas ionization-type detectors, the proportional-type counter is preferable because of the shorter resolving time and greater stability of the instrument. For perparing solid sources from water samples for beta activity measurement, the test sample is reduced to the minimum weight of solid material having measurable beta activity by precipitation, ion exchange, or evaporation techniques. For measuring solid sources resulting from individual radiochemical separation procedures, the precipitate is appropriately mounted for counting.

Beta particles entering the sensitive region of the detector produce ionization or scintillation photons which are converted into an electrical pulse suitable for counting. The number of pulses per unit time is directly related to the disintegration rate of the sample by an overall efficiency factor. This factor combines the effects of sample-to-detector geometry, sample self-shielding, backscatter, absorption in air and in the detector window (if any), and detector efficiency. Because most of these individual components in the overall beta-particle detection efficiency factor vary with beta energy, the situation can become complex when a mixture of beta emitters is present in the sample. The overall detection efficiency factor may be empirically determined with prepared standards of composition identical to that of the sample specimen, or an arbitrary efficiency factor can be defined in terms of a single standard such as cesium-137 or other nuclide. Gross counts can provide only a very limited amount of information and therefore should be used only for screening purposes or to indicate trends.

Liquid scintillation counting avoids many sources of error associated with counting solid beta sources, such as (1) self-absorption, (2) backscattering, (3) loss of activity during evaporation due to volatilization or spattering, and (4) variable detection efficiency over a wide beta-energy range. In addition to the greatly improved accuracy offered by liquid scintillation counting, sample preparation time and counting times are significantly shorter. Sample preparation involves only adding a sample aliquot to the scintillator or gel phosphor. Because every radioactive atom is essentially surrounded by detector molecules, the probability of detection is quite high even for low-energy beta particles. Radionuclides having maximum beta energies of 200 keV or more are detected with essentially 100 percent efficiency. Liquid scintillation can, at times, be disadvantageous due to chemiluminescence, phosphorescence, quenching, or the typically higher backgrounds.

Organic scintillators, such as *p*-terphenyl plus a wave shifter, in a plastic monomer are polymerized to form sheet material of any desired thickness. The plastic phosphor counting system [*10*] has its widest use as a beta particle detector for separated, solid samples rather than for beta spectrometry applications.

This plastic beta scintillator phosphor is mounted directly on the sample and is discarded after counting. The phosphor-sample sandwich is placed in direct contact with the photomultiplier tube yielding essentially a 2π configuration. Since the output pulse of the detector system is energy dependent, the counting efficiency for a given phosphor thickness of 0.0254 cm yields the highest counting efficiency with the lowest background.

Solid samples, precipitates from radiochemical separations containing 3 to 5 mg/cm^2 of stable carrier, are measured in such a system. For Y-90, a solid sample of this type would have a counting efficiency of 45 to 50 percent.

A plastic scintillator phosphor system with a 25-cm photomultiplier tube shielded with 12.7 mm of lead has background in the order of 2.5 cpm. For very low backgrounds, about 0.25 cpm, the photomultiplier tube and sample assembly are fitted into a well-type hollow anode Geiger tube operated in anticoincidence. The entire assembly is then place in a heavy shield.

The system has many advantages, but reduction of background is probably most important. The reduction occurs since the scintillation does not see the surrounding mechanical components of the counter. The additional advantage of keeping the counter itself free from contamination by enclosing the phosphor-sample sandwich is also important.

A note of caution is advisable at this point. Any beta particle detection system, whether internal gas counters or scintillation counters, will detect alpha particles. It is not possible to electronically discrimate against all the alpha pulses.

If a sample is suspected of containing alpha activity, a separate alpha measurement must be made to determine the alpha contribution to the beta measurement.

Solid Source Counting—The observed count rate for a solid source is the interaction of many variables. The most important of these are the effects of geometry, backscatter, radiation, source diameter, self-scatter, and self-absorption, absorption in air and the detector window (for external counters), and coincidence counting losses. These effects have been discussed [*11,20*] and in many cases can be reduced or corrected for by counting test standards and samples under identical conditions. For absolute measurements of a single, specific nuclide, appropriate correction factors must be applied.

These effects may be described by the following relation

$$\text{cpm} = \text{dpm}\ (G_p)\ (f_{bs})\ (f_{aw})\ (f_d)\ (f_{ssa})\ (f_c)$$

where

cpm = recorded counts per minute, corrected for background, and

dpm = disintegrations per minute yielding beta particles.

G_p = source-to-detector geometry, which is the solid angle subtended by the sensitive area of the detector. This is corrected for most easily by maintaining constant counting configuration and geometry for standards and sample measurements.

f_{bs} = backscatter factor, or ratio of cpm with backing to cpm without backing. This is the phenomenon in which particles originally emitted away from the detector are scattered back toward it by reflection off the source backing material. Its value ranged from 1 to almost 2, depending on the thickness and atomic number of the backing material. The backscatter error may be minimized by using identical backing material for counting standard and samples.

f_{aw} = factor to correct for losses due to absorption in the air and window of external counters. It is equal to the ratio of the actual counting rate to that which would be obtained if there were no absorption by the air and window between the source and sensitive volume of the detector. It is related to the absorption coefficient and density of the absorber by the approximate equation, $f_{aw} = \exp(-\mu x)$, where μ = absorption coefficient, in square centimetres per milligram, and x = absorber density in milligrams per square centimetre. In practice, it can be accounted for, together with the geometric factor, by maintaining the geometry of the counting configuration constant for standards and samples.

f_b = factor to correct a disk source counting rate to the counting rate of the same activity as a point source on the same axis of the system. This can be corrected for by preparing and counting the standard in the same configuration as the samples.

f_{ssa} = factor to correct for the absorption and scatter of beta particles within the material accompanying the radioactive element.

f_c = factor to correct the counting rate for instrument resolving time losses and defined by the simplified equation, $f_c = (1\text{-}nt)$, where n = observed counts per minute and t = instrument resolving time in minutes. Generally, the sample size or source-to-detector distance is selected to preclude counting losses. Such losses are negligible for count rates of less than 80 000 counts per minute if proportional detectors are used. Information on the effect of instrument resolving time on the sample count rate as well as methods for determining the resolving time of the counting systems may be found in the literature [*11*].

Liquid Scintillation Counting—The observed count rate for a liquid scintillation sample is directly related to the beta (plus conversion electron) and positron emission rate in most cases. The important exceptions are (1) beta emitters whose maximum energy is below 200 keV, and (2) counting systems wherein quenching decreases the expected photon yield, thereby decreasing the overall detection efficiency significantly below 100 percent. Low-energy beta emitters such as tritium or carbon-14 can be measured accurately only when the appropriate detection efficiency factor has been determined with a known amount of the same radionuclide counted under identical conditions. Quenching losses are greatest at low beta energies. Quenching may be evaluated by comparison to known quench standards of the same radionuclide, using the channel ratio technique, or with other techniques as described in the manufacturer's instructions. For absolute measurements of low-energy beta emitters, appropriate correction factors must be applied

$$\text{dpm} = \frac{\text{cpm}}{(fe)\,(fq)}$$

where

dpm = disintegrations per minute, yielding beta particles;

cpm = recorded counts per minute, corrected for background;

*fe** = detection efficiency factor; observed cpm/dpm ratio for known standard of some radionuclide counted under identical conditions with no quenching; and

fq = quench correction factor, observed ratio of cpm-quenched/cpm-unquenched for known standard of same radionuclide with equivalent quenching.

In tracer studies or tests requiring only measurements in which data are expressed relative to a defined standard, the individual correction factors cancel whenever (1) sample composition, (2) sample weight, and (3) counting configuration and geometry remain constant during the standardization and tests.

The limit of sensitivity for both Geiger-Muller and proportional counters is a function of the background counting rate. Massive shielding or anticoincidence detectors and circuitry, or both, are generally used to reduce the background counting rate to increase the sensitivity [*11*]. For a more complete discussion of this, see ASTM Method D 3085 [*1*].

Interferences

Solid Sources—Material interposed between the test sample and the detector, as well as increasing mass in the radioactive sample itself, produces significant losses in sample counting rates. Since the absorption of beta particles in the sample solids increases with increasing mass and varies inversely with the maximum beta energy, sample residue must remain constant between related test samples and should duplicate the residue of the evaporated standard.

Most beta-particle counters are somewhat sensitive to alpha, gamma, and X-ray radiations, with the degree of efficiency dependent upon the type of detector [*11*]. The effect of the interfering radiations on the beta counting rate is more easily evaluated with external-type counters where appropriate absorbers can be placed between the sample and detector to evaluate the effects of interfering radiation.

(NOTE: The detection efficiency may be assumed to be unity for beta emitters having maximum energies of 200 keV or greater.)

Liquid Scintillation—Liquid scintillation samples are subject to interference by substances which quench or enhance the scintillation process. This includes any chemiluminescence which changes the photon yield. Substances such as oxidants, organohalides, ketones, and aldeyhydes are to be particularly avoided. A second type of quenching is color quenching, in which a colored solution impairs the light collection efficiency for the photons produced.

Apparatus

Beta Particle Counter—The end-window Geiger-Muller tube and the internal or external proportional gas-flow chambers are the two most prevalent types of detectors. Other types of detectors include scintillators and solid-state detectors. The material used in the construction of the detector and its surroundings should contain a minimal level of detectable radioactivity. If the detector is of the window-type, the window thickness may be used in calculating beta ray attenuation; however, direct calibration of the entire counting system with standards is recommended. The manufacturer should provide all settings and data required for reliable and accurate operation of the instrument. Detectors requiring external positioning of the test sample shall include a support of low-density material (aluminum or plastic) which assures a reproducible geometry between the sample and the detector. Because different sample-to-detector geometries are convenient for differing sample activity levels, the sample support may provide several fixed positions ranging from 0.5 to 10 cm from the detector.

Liquid Scintillation—Liquid scintillation counting systems use an organic phosphor as the primary detector. This organic phosphor is combined with the sample in an appropriate solvent which achieves a uniform dispersion. A second organic phosphor often is included in the liquid scintillation "cocktail" as a wavelength shifter. The wavelength shifter efficiently absorbs the photons of the primary phosphor and re-emits them at a longer wavelength more compatible with the multiplier phototube. Liquid scintillation counting systems use either a single multiplier phototube or two multiplier phototubes in coincidence. The coincidence counting arrangement is less likely to accept a spurious noise pulse which occurs in a single phototube, and thus provides lower background. The requirement that both multiplier phototubes respond to each has a slight effect on the overall detection efficiency of betas with E-max >200 keV; however, system response to beta E-max <200 keV will be significant. The need to minimize detectable radioactivity in the detector and its surrounding is likewise important in liquid scintillation counting. To achieve this scintillation grade, organic phosphors and solvents are prepared from low carbon-14 materials such as petroleum. The counting vials are of low-potassium glass or plastic to mimimize counts due to potassium-40. Liquid scintillation provides a fixed geometry from a given-size counting vial and liquid volume.

Detector Shield—The detector assembly should be surrounded by an external radiation shield of massive metal equivalent to approximately 51 cm of lead and lined with 3.2-mm-thick aluminium. The material of construction should be of minimal detectable radioactivity. The shield should have a door or port for inserting or removing specimens. Detectors having other than completely opaque windows are light-sensitive. The design of the shield and its openings should eliminate direct light paths to the detector window; beveling of door and opening generally is satisfactory. Liquid scintillation counting systems must provide an interlock which protects the photocathode of the multiplier phototube from light when the sample counting chamber is opened.

Associated Electronic Equipment—The high-voltage power supply amplifier, scaler, and mechanical register normally are contained in a single chassis. The power supply and amplifier sections are matched with the type of detector to produce satisfactory operating characteristics and to provide sufficient range in adjustments to maintain stable conditions. The scaler should have capacity for storing and visually displaying at least 9×10^5 counts. The instrument should have an adjustable input sensitivity matched to that of the detector, and variable high-voltage power supply. (An adjustable power supply and meter are unnecessary for liquid scintillation systems.) Counting chambers of Geiger-Muller and proportional counters contain a suitable counting gas and an electrode. Counting rates which exceed 10 000 cpm must be corrected for dead-time loss when using a Geiger-Muller tube. As the applied voltage to the electrode is increased, the counting chamber exhibits responses which are characteristic of a particular voltage region. At low voltages of the order of 100 V, there is no multiplication of the ionization caused by a charged particle. At voltages approaching 1000 V, there is appreciable amplification of any ionization within the counting chamber; however, the size of the output pulse is proportional to the amount of initial ionization. When operated in this voltage region, the device is known as a proportional counter. Usually there is a region at least 100 V wide, known as a plateau, wherein the count rate of a standard is relatively unaffected. The operating voltage for proportional counters is selected to approximate the middle of this plateau in order to maintain stable responses during small voltage shifts. The plateau region is determined by counting a given source at voltage settings which differ by 25 or 50 V. The number of counts at each setting is recorded, and the resultant counts versus voltage are plotted as shown in Fig. 6. Voltage plateau curves are to be remeasured periodically to ensure continued instrument stability, or whenever an instrument malfunction is indicated. If the voltage is increased beyond the proportional region into the 1500 to 2000 V region, the pulse size increases and the dependence on the initial ionization intensity

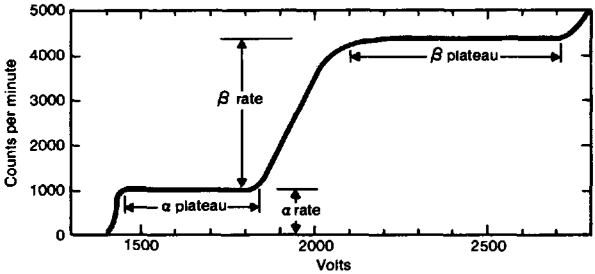


FIG. 6—*Counting rate as a function of applied voltage for a proportional counter exposed to a source emitting both α and β particles.*

disappears. This is the beginning of the Geiger counting region, where a single ion pair produces the same large pulse as an intense initial ionization.

Alpha Interference—Alpha particle interference can be substantial and must be considered with any type of beta counter. One technique involves placing a thin absorber between the solid source and the detector. The absorber diameter should exceed that of the detector window. The absorber should be placed against the window to minimize beta particle scatter. Any absorber which stops alpha particles also will somewhat attenuate low-energy beta particles. For example, an aluminum absorber of 7 mg/cm^2 will absorb 48 percent of beta particles of 0.35-MeV maximum energy. The alpha particle absorber is not recommended for use with internal beta particle detectors, especially when either the composition or activity ratios of the radioelements or radioactivity level might vary significantly between samples. Chemical separation of the alpha and beta particle emitters produces a higher degree of accuracy for internal detector measurements. Published information on beta particle absorption [*11*] should be used as a guide for use of an absorber. In liquid scintillation spectra, the alpha component appears as a peak on the beta continuum and thus provides a basis for resolving the two [*32*].

Self-Absorption and Backscatter—Radioisotopes emit radiation uniformly in all directions. If the radioisotope is intimately mixed with the detector, as in the case with liquid scintillation counting, essentially all beta particles interact with the detector. With solid source counting, however, the source and detector usually are related by a solid angle of 2-π or less. Even so, the number of beta particles reaching the detector can be significantly affected by other factors.

When a radioactive source decays by beta emission, the beta particles (electrons) are emitted with a distribution of energies ranging from zero to definite maximum value. The lower energies are absorbed by the sample itself and this self-absorption is particularly large for certain nuclides, such as carbon-14 and sulfur-35, in which all the beta particles are of low energy. It is therefore, desirable to make solid samples as thin as possible.

Self-absorption corrections can be made, if necessary. A series of counts is made on a number of weighed samples of homogeneous material, with the material spread uniformly over the sample mount. The data are corrected for background, and graphed on a semi-log plot, with the logarithm of the counting rate per milligram of sample plotted against the number of milligrams. The resulting curve can be extrapolated to zero sample weight to give the counting rate per milligram corrected for self-absorption [*5*].

Samples consisting of the final product from radiochemical separations generally are of the same approximate weight from determination to determination because they usually contain the same amount of carrier, and the self-absorption is essentially constant. Corrections can be made by running a standard amount of activity of the nuclide through the procedure, with sample activities expressed in terms of this reference standard.

Beta particles are easily deflected in passing through matter. Some beta particles emitted in a direction away from the detector can be deflected by the source-backing material and scattered toward the detector. This phenomenon leads to an increased number of beta particles reaching the detector over that expressed from geometric considerations alone. Backscatter increases rapidly with increasing thickness and atomic number of the backing material. Backscatter effects may be held constant by maintaining sample size and mounts constant for relative measurements. If backscatter corrections must be made, these corrections can be determined by counting a sample first on thin film mount, and then recounting when backed by the desired backing material. Backscatter does have the effect of increasing the number of particles which reach the detector, thereby increasing the counting efficiency.

Calibration and Standardization

Calibration and Standardization for General Measurements—Solid sources. Place a known amount of cesium-137 or other activity (approximately 5×10^{-4} to 5×10^{-3} microcuries, with the smaller amount more appropriate for Geiger-Muller detectors) in a volume of water containing salts equivalent to those of the test samples and prepare for counting as directed. Throughout the experiment, the evaporation, mounting, counting, and the density of the plate solid of this reference must be identical with those of the test samples. Count for length of time necessary to produce the desired statistical reliability. The combined efficiency factor then is expressed as a percentage of the disintegration rate of the reference standard. (CAUTION: This factor is inaccurate for beta particles whose energies differ appreciably from those of cesium-137; nevertheless, count rates for solid beta sources of undefined energy are often reported relative to cesium-137 standard. The fact that the 662-keV gamma ray of barium-137 is significantly converted accounts for the fact that about 1.10 electrons leave the source for every disintegration. For this reason, cesium-137 standards should be calibrated in terms of combined beta plus electron emission rate.)

Liquid Scintillation—Add a known amount of cesium-137 (approximately 10^{-2} microcuries to the liquid scintillation "cocktail." The volume and composition of the cesium solution and the "cocktail" should simulate those normally used. For samples without serious quenching problems, the counting efficiency should approach 100 percent. (Note that cesium-137 standards must be calibrated in terms of beta plus conversion electron emission rate.)

Calibration and Standardization for Tracer Experiments—Add a known quantity of activity of a reference solution of the tracer (approximately 5×10^{-3} microcuries) to a nonradioactive standard test sample and process.

Source Preparation

Solid Sources—The sample whose activity is being determined must be appropriately mounted for the final measurement. The exact form of the mount is somewhat dependent upon the particular instrument for counting. In general, most counters will accept either flat plate or dish mounts.

Water samples can be evaporated on either flat disks or dishes, with the dishes being preferred for high solids samples. The dishes should have a flat or concentrically ringed bottom whose diameter is no greater than that of the detector window, preferably having 3.1-mm-high sidewalls with the angle between the dish bottom and side equal to or greater than 120 deg to reduce sidewall scattering. Sample dishes with verticle sidewalls may be used, but the exact positioning of these dishes relative to the detector is very important. This factor becomes critical for dishes having the same diameter as the detector. Dishes having sidewalls more than 3.1 mm in height are not recommended. Dishes should be of a material that will not corrode under the plating conditions and should be of uniform surface density, preferably great enough to reach backscatter saturation [*11*].

Samples resulting from radiochemical separations are customarily in the form of a precipitate on a filter. These can be mounted on plates, dishes, or other suitable backing. The filter paper should be fixed to the backing with a double-backed adhesive strip or a liquid adhesive, and should be covered to prevent sample loss and to prevent contamination of the counting equipment. Such covering can be accomplished with a cover of transparent plastic tape or film, or by spraying the precipitate with a collodion. Nonconducting coverings should not be used in internal flow counters.

Liquid Sources—Liquid samples of sufficiently high activity level may be added directly to an appropriate amount of liquid scintillator solution. For aqueous samples the liquid scintillator solution must contain a solvent such as dioxane, which is miscible with water, or a surfactant to maintain a single phase with immiscible solvents. Low-activity liquid samples may be concentrated by evaporation before addition to the liquid scintillator solution.

Liquid samples are sometimes concentrated or separated, or both, by extraction into a suitable organic solvent. This solvent often is suitable for direct addition to the liquid scintillator solution. Caution is advised to avoid solvents which cause substantial quenching.

Radioactive Decay and Decay Curves

Decay curves are useful for identifying radionuclides by their characteristic half-lives and in determining the presence and number of interfering radioactive substances. When two or more beta-emitting isotopes are present in a source, an analysis of the decay curve is required to resolve them since the semi-log plot of the disintegration rate versus time is a curve whose slope changes as the isotopic composition changes. After sufficient time, the longest-lived activity predominates. The half-life of this long-lived component can be determined from extrapolation of the straight-line portion of the curve to t_o, the original count rate for that radionuclide, as shown in Fig. 7. In this graph, the extrapolated line of the 4.6 day half-life component subtracted from the original curve yields a curve that represents all other

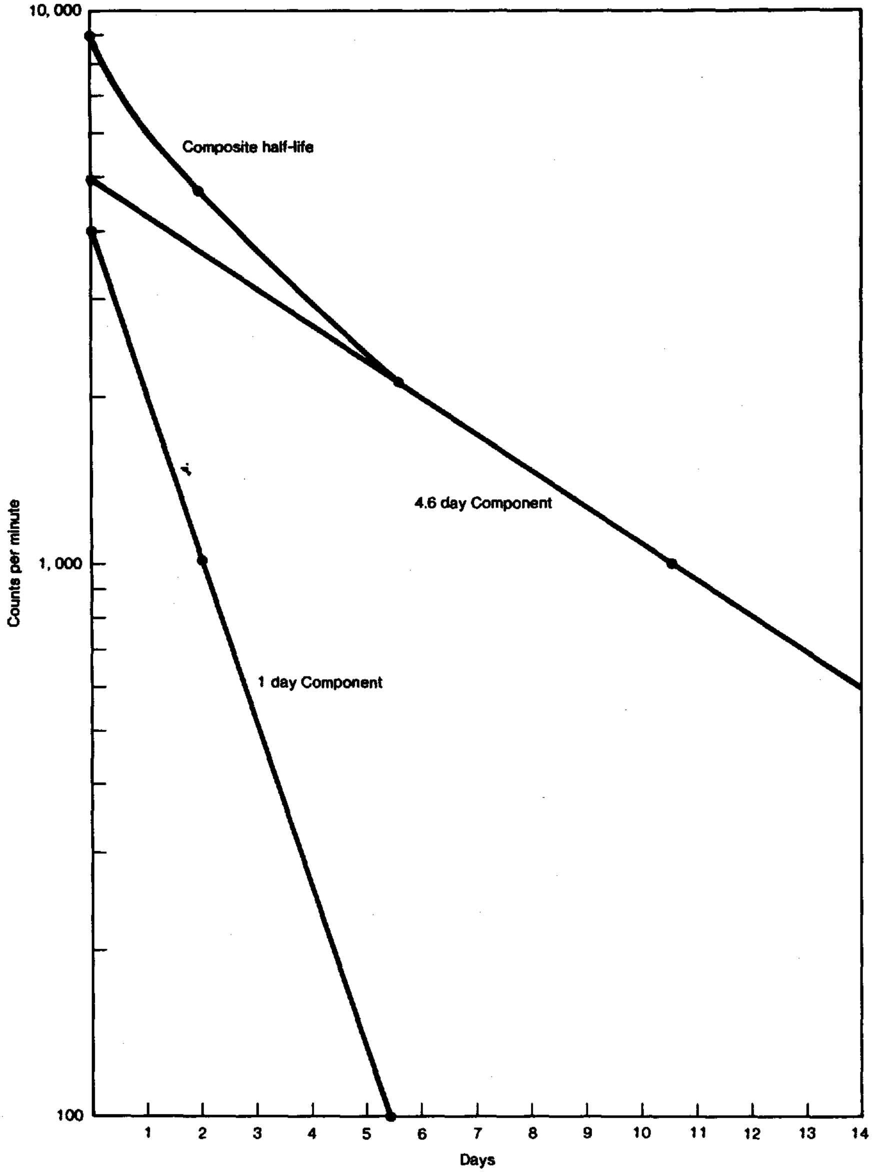


FIG. 7—*Decay curve.*

components; this residual curve may be processed again in the same way to reduce (in principle) any complex decay curve into its component parts. In actual practice, uncertainties in the observed data place a practical limit to a three-component system except in unusual cases, and often a two-component system may not be satisfactorily resolved because of similar decay constants.

Since the residual curve in Fig. 7 (1 day half-life) does not deviate from the straight line, and the original curve is concave except in the final portion, a two-component system on independently-decaying activities is indicated. In accumulating decay data, care must be taken to avoid disturbing the source and to locate the sample in the same geometrical position for each measurement. If the instrument is calibrated for the specific characteristics of the source and for the energies of the radiations measured, the count rate shown at the ordinate intercept of the extrapolated straight lines at t_0 will be equal to the disintegration rate at t_0. However, this technique requires specific beta-energy knowledge for each component of the sample, as well as counting instrument standardization at these same energies under identical conditions. In practice, gamma spectrometry is preferred; see ASTM Test for Gamma Spectrometry of Water (D 2459) [*1*] for resolving mixtures of all radionuclides except pure beta emitters. An additional complication in decay curve interpretation is the growth of radioactive daughters. See standard Refs *11* and *20* for a discussion of this.

Beta Particle Maximum Energy

When a radioactive source decays by beta emission, the beta particles (electrons) are emitted with a distribution of energies ranging from zero to a definite maximum value. The maximum energy of the electrons is characteristics of a particular nuclide and is the "beta energy" shown in nuclear data tables. Determining the approximate maximum energy of the beta particles from a radioactive source thus aids in radionuclide identification.

The combined effects of a continuous beta spectrum and scattering produces an approximately exponential absorption law for a beta particle source of a given maximum energy. In interposing varying thickness of aluminum between the source and the detector and plotting the count rate versus the thickness of aluminum absorber in mg/cm^2 on semi-log paper, an empirical absorption curve is produced. The plotted data can be compared with a standard absorption curve determined for a particular nuclide to check for other radionuclides. If the sample and absorber are as close as possible to the detector and only one radionuclide is present, the absorption curve is nearly a straight line until it tails into the constant background count rate of the instrument, which in most cases includes the gamma rays from the source. Visual inspection of the point at which the beta activity is not detectable above the total background gives an approximate thickness value, although this is usually low. Better results can be obtained by subtracting the background from the total absorption curve, as shown in Fig. 8, to obtain the 220 mg/cm^2 component. The point at which the straight-line extrapolation intersects the count rate error of the background is the absorber thickness value. The maximum beta energy can then be obtained from the range energy relation curve, Fig. 9. If the lower-energy region of the curve deviates from the straight-line extrapolation to zero absorber thickness, a

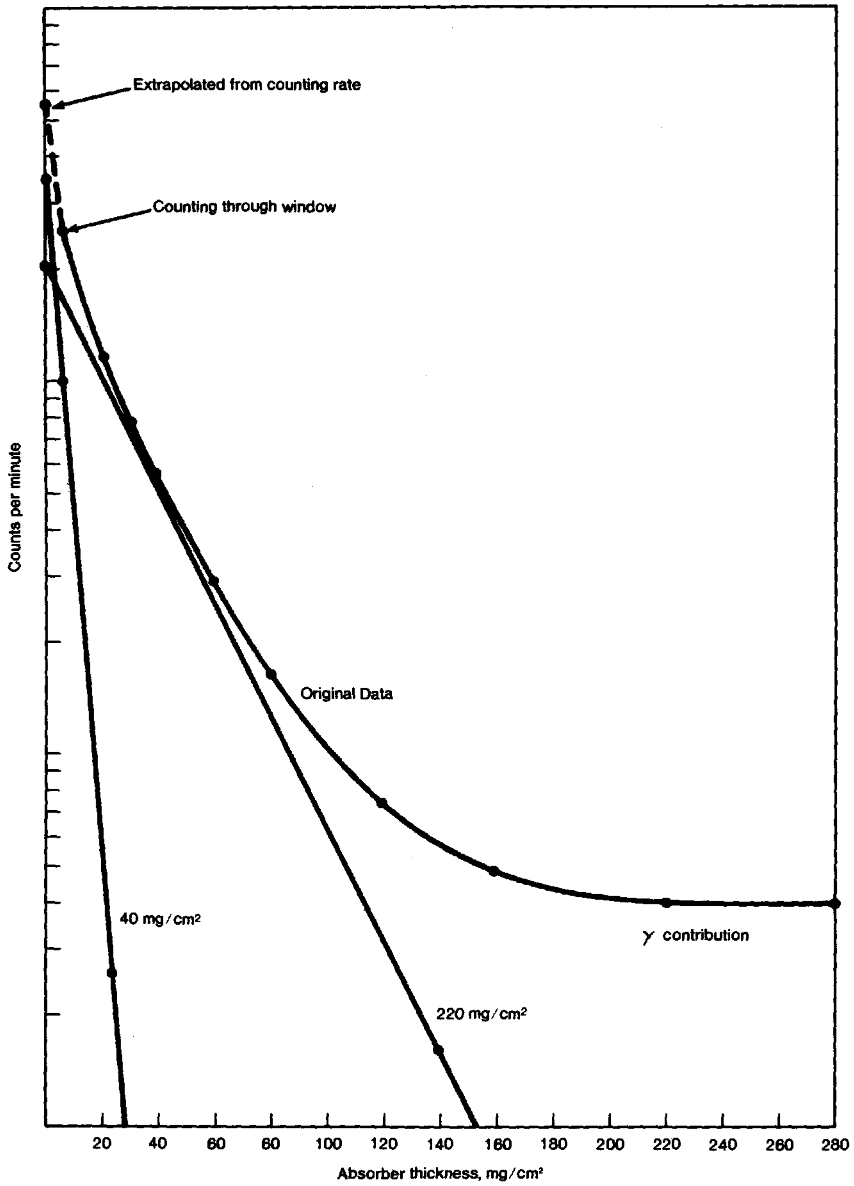


FIG. 8—*Absorption curve.*

second component is indicated. The values on the extrapolated line subtracted from the second curve produced the 40 mg/cm^2 component. The sum of the count rate for both components at zero absorber thickness is the true count rate.

The best absorption curve is obtained with the absorber against the detector and the source positioned for minimum clearance of the thickest

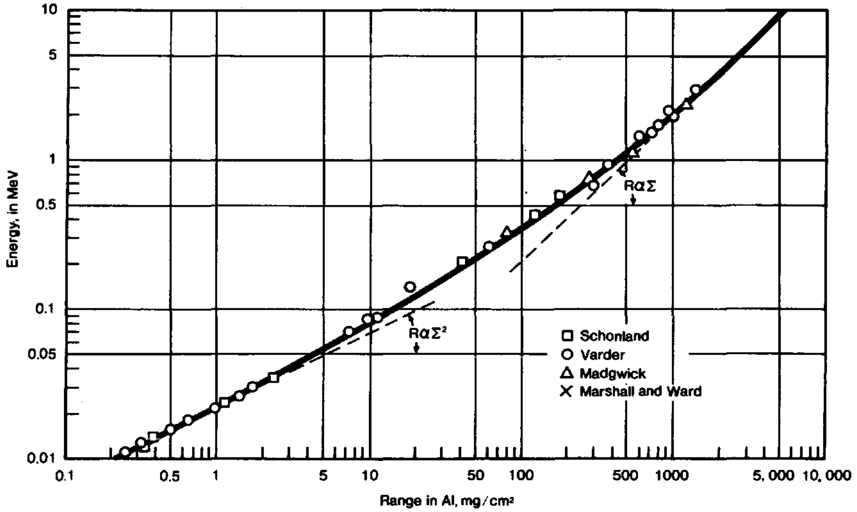


FIG. 9—*Empirical range-energy relationship for electrons absorbed in aluminum. Experimental values by several observers on monoenergetic electrons are shown. For monoenergetic electrons, the range coordinate refers to the extrapolated range. For continuous β-ray spectra, the energy coordinate refers to the end-point energy* E . . . , *and the range coordinate becomes the maximum range. The smooth curve represents the empirical relationship, developed by Katz and Penfeld,* Reviews of Modern Physics. *Vol. 24, 1952, p. 28.*

absorber to be used. The source must not be moved after the first count rate, which is obtained with no absorber between the source and the detector. The activity of the source should be close to the maximum allowed by resolving time of the instrument. Absorption coefficients given in the literature and half-thickness data utilize the initial portions of the absorption curve and are not as accurate as the total absorption determination. More accurate methods for determination of beta particles range, from absorption curves, are the comparison method of Feather [*11*] and Harley et al [*33*]

Many liquid scintillation counting systems provide an output suitable for accumulation and storage of beta spectra of known maximum energy. To obtain the most accurate beta maximum energy measurement, the pulse height-energy relationship of the system must be calibrated [*34*]. With the aid of this relationship, the pulse height distribution of the sample may be converted to a Curie plot [*35*] and extrapolated to obtain maximum beta energy. Excellent agreement with beta-energy spectrometry values has been obtained with this technique [*36*]. A Curie plot is shown in Fig. 10.

Calculations—Results may be expressed in observed counts per minute per millimetre for comparing relative activities of a group of samples as in tracer experiments

$$C = \frac{1}{V}\left[\frac{N}{t} - \frac{N_B}{t_B}\right]$$

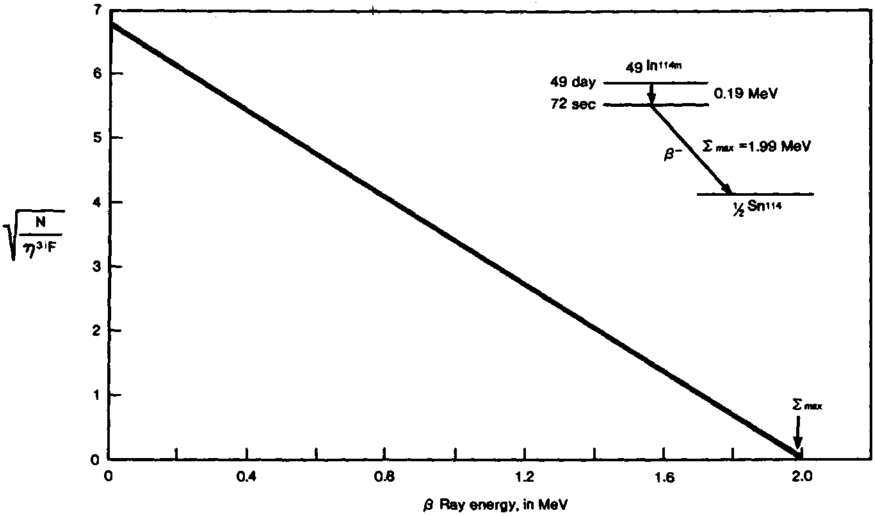


FIG. 10—*Curie plot of the* β- *spectrum of* ^{114} *In. Note especially that* N *means* N*(n), the number of* β *rays in a momentum interval* Δ, *of constant size. The horizontal coordinate is the kinetic energy* E, *which corresponds to the midpoint of the momentum interval* n $+\Delta_n$. *When spectral data give a straight line, such as this one, the* N*(n) is in agreement with the Fermi momentum distribution. The intercept of this straight line, on the energy axis, gives the disintegration energy* E*max* *(*E*s), if the rest mass of the neutrino is zero. (From Lawson and Cork,* Physical Review, *Vol. 57,* 1940 *p. 982.*

where

N = number of counts accumulated,
t = sample counting period, min,
N_B = number of background counts accumulated,
t_B = background counting period, min,
V = volume of initial sample, ml, and
C = net counts per minute per millilitre (cpm/ml).

Results also may be expressed in terms of equivalent cesium-137 activity, using the empirical efficiency determined for the reference standard

$$D_{^{137}\mathrm{Cs}} = \frac{C}{E_{^{137}\mathrm{Cs}}}$$

where

C = net counts per minute per millilitre (cpm/ml), and
$E_{^{137}\mathrm{Cs}}$ = efficiency for counting Cs-137 beta particles plus conversion electrons (count rate + emission rate).

If it is known that only one nuclide is present, its disintegration rate may be determined by use of the efficiency factor measured with a reference standard of the same nuclide. The results may be calculated as follows

$$D = \frac{1}{EVY}\left[\frac{N}{t} - B\right]$$

where

N = number of counts accumulated,
B = background in counts per minute (cpm),
D = disintegration rate per minute per millilitre (dpm/ml),
E = efficiency of counter for specific nuclide (counts ÷ disintegrations),
V = millilitre of test specimen,
Y = recovery of species (unity in cases where complete recovery is assumed), and
t = count period, min.

If it is desired that the activity be expressed in units of microcuries, the following expression is used:

$$A = \frac{D}{2.22 \times 10^6}$$

where

A = concentration, microcuries per millilitre,
D = disintegration rate per minute per millilitre (dpm/ml), and
2.22×10^6 = conversion factor, disintegration per minute per microcurie.

Gamma Counting

This section covers the measurement of gross gamma radioactivity of water. Since gamma radiation is a penetrating form of radiation, it can be used for samples of any form and geometry as long as standards of the same form are available and are counted at the same geometry to calibrate the detector. Because of this penetrating nature, small variations in sample density or sample thickness are usually not significant and gamma counting is the preferred method in general radiochemical work. When a standard cannot be obtained in the matrix being counted, a correction for the different absorption in the matrices must be made.

Since different nuclides emit distinct and constant spectra of gamma radiation, the use of an energy-discriminating system provides identification and measurement of all the components present in a mixture of radioactivity, and this technique is covered in ASTM Recommended Practice for Gamma-Ray Spectrometry (D 2459) [*1*]. Gamma counting and gamma spectrometry are applicable to levels of about 10 picocuries or above. General information on gamma ray detectors and gamma counting is covered in the literature [*11,16*].

Summary

Gamma counting is generally carried out using solid detectors since a gas-filled detector will not provide adequate stopping power for energetic gammas. In solids such as sodium iodide (thallium) or cesium iodine, the gammas interact by excitation of atoms, and energy is transferred to orbital electrons and then released as light photons when the orbits are refilled. The scintillations are easily detected and amplified into useable electrical pulses by a multiplier phototube. The NaI (Tl) detector is the recommended detector for gross gamma counting.

In semiconductor detectors such as Si (Li) and Ge (Li) the gamma photons produce electron-hole pairs and the electrons are collected by an applied electrical field. A charge-sensitive preamplifier is used to detect the change transferred and produce a useable electrical pulse. The semiconductor detectors are widely used in gamma spectrometry (see ASTM Method D 2459-72) and are not reviewed in this practice.

The output pulses from the multiplier phototube or preamplifier are directly proportional to the amount of energy deposited, which could either be total and be included in the photopeak or fractional and be included in the continuum or escape peaks, in the detector, by the incident photon. The pulses may be counted using a scaler or analyzed by pulse height to produce a gamma ray spectrum.

Gamma photons interact with the detector by three distinct processes. The photoelectric effect results in complete absorption of the photon energy and produces the full energy or photopeak shown in Fig. 11 results. The third interaction is pair production, which occurs at energies above 1.02 MeV and results in disappearance of the photon when an electron positron pair is produced. The electron and positron give up their kinetic energy to the detector and the resulting electron joins the electron population of the detector; the positron, however, is annihilated in combining with an electron and produces two gamma photons of 0.511 MeV each. One or both of the 0.511 MeV photons may escape from the detector without interacting and the "single escape" and "double escape" peaks shown in Fig. 12 result. The Comptons from a higher energy photon always present an interference problem in the counting of gamma photons, and appropriate corrections must be made for this effect. Pair production can also be considered as an interference since the excape peaks may have an energy equal to the lower-energy gamma of interest.

The change of absorption coefficient with gamma energy results in a wide variation of detection efficiency. The detection efficiency falls rapidly as gamma energy increases, for a fixed size of detector. Two other important effects are seen as a result of variation of absorption coefficient; firstly, low-energy photons may be absorbed in massive samples, such as large bottles of water, and erroneous results obtained. A similar absorption effect is seen in germanium (lithium) systems where the can around the detector acts as an absorber for very-low-energy gammas and the efficiency passes through a

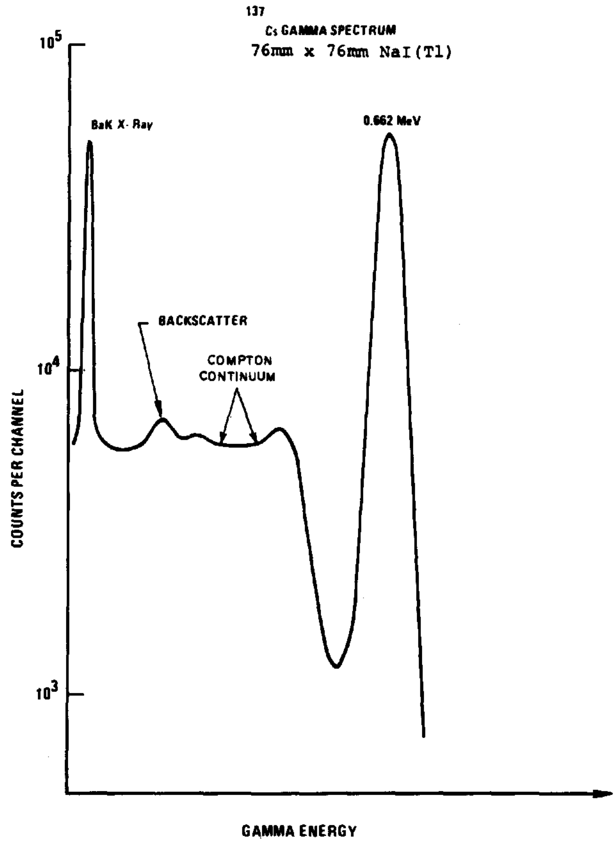


FIG. 11—*Compton contenuum.*

maximum usually around 100 keV. The second results is that for low-energy gammas a thin detector may be as efficient as a much thicker one since the low-energy gammas are easily stopped in the thin detector.

Because of this variation in efficiency and the possible interferences from other activities, gross gamma counting is only reliable when used to compare standards and samples of the same nuclide. The use of gross gamma monitoring systems should be avoided when possible, and, in all cases, proper allowance must be made for the lack of accuracy.

Interferences

The natural background persent at all locations is detected very efficiently by gamma detectors and presents a significant interference which must be reduced by the use of shielding. Low-radioactivity-level lead or steel should be used and, for a 76- by 76-mm sodium iodide detector, about 102 mm of

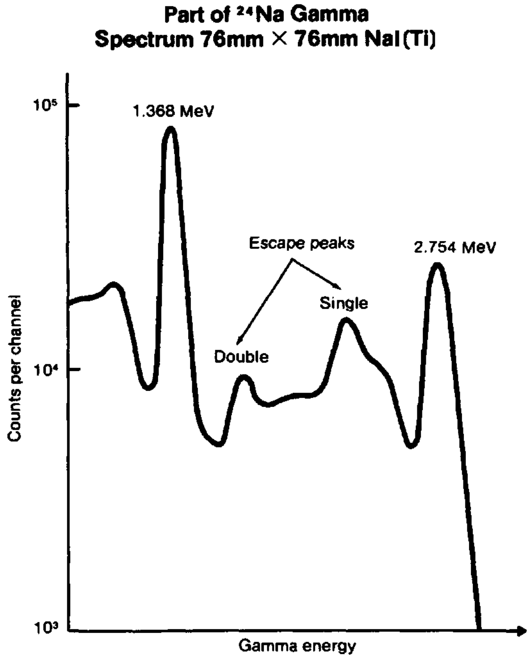


FIG. 12—*Single and double escape peaks.*

lead or 15.24 cm of steel shielding produces an acceptable background for most work. Details of shield designs are given by Heath [*37*]. Lead shields are a source of X-rays when high activity samples are counted, and this X-ray emission can be reduced in amount and energy by using a graded liner such as 1.6 mm of cadmium and 0.4 mm of copper—the copper being nearer the detector. The cadmium strongly absorbs the lead X-rays and in turn emits its own X-rays at a much lower energy, and these are strongly absorbed by the copper. Any residual copper X-rays are usually below the energy level of interest.

The "Compton" and "pair production" effects can be very significant interferences and must be corrected for.

At high count rates, "random sum peaking" may occur. Two absorptions may occur within the resolving time of the detector and are summed and seen as one pulse. For a detector of resolving time t and a count rate of A counts per unit time, the time window available for summing is $2At$ (since the count summed could occur as early as t before or as late as t after the other count) and the probability of another count at any time is simply A. Therefore, the sum count rate will be $2A^2t$ in unit time. Random summing is strongly dependent on the count rate A, and if summing occurs it can be reduced by increasing the sample to detector distance.

Well counters which have very high efficiencies are prone to summing since for a given source strength the count rate is higher than for a detector of lower efficiency. For moderate and high source strengths, the tradeoff is a poor one and the well counter is best suited for low level work where its high efficiency is an important advantage.

Cascade summing may occur when nuclides which decay by a gamma cascade are counted. Cobalt-60 is an example; 1.17 MeV and 1.33 MeV from the same decay may enter the detector and be absorbed, giving a 2.50 MeV sum peak. Cascade summing may be reduced by increasing the source to detector distance.

The resolution of a gamma detector is the effective limit to its utility even when complex data reduction methods are used. A typical 76- by 76-cm sodium iodide (thallium) detector will give full widths at half maximum (FWHM) of about 60 keV at 662 keV gamma energy and about 90 keV at 1.33 MeV gamma energy.

Apparatus

Sodium Iodide Detector Assembly—A 76- by 76-mm sodium iodide detector is activated with about 0.1 percent thallium iodide, cylindrical, with or without an inner sample well, optically coupled to a multiplier phototube and hermetically sealed in a light tight container. The sodium iodide (thallium) crystal should contain less than 5 ppm of potassium and be free of other radioactive materials. In order to establish freedom from radioactive materials, the manufacturer shall supply a gamma spectrum of the background of the detector between 0.08 and 3.0 MeV. The resolution of the detector for the cesium-137 gamma at 0.662 MeV should be less than 60 keV FWHM or less than 9 percent.

Shielding for the detector shall be constructed as needed from low-radioactivity-level lead or steel. A thickness equivalent to 10.16 cm of lead usually provides adequate shielding. If the shield is made of lead; a graded liner should be used unless the shield-to-detector distance is more than 254 mm.

High-voltage Power Supply—500 to 2000 V dc regulated to 0.1 percent with a ripple of not more than 0.01 percent.

Preamplifier: Linear Amplifier System—to amplify the output from the multiplier phototube to a maximum output of 10 V.

Analyzer with Scaler and Timer—A single-channel discrimination system will accept all or any part of the output from the amplifier and pass it to the scaler. Any pulses lying outside the preset limits are rejected. The lower limit is usually referred to as the "threshold" and the difference between the two limits is the "window."

Sample mounts and containers may consist of any reproducible geometry container which is commerically available. Other considerations are cost, ease of use, disposal, and effective containment of radioactivity for protection of the workplace and personnel from contamination.

Geometry Control System—A system of shelves or supports for the various sample containers which allows the user to place a sample in any of several preset and reproducible geometries.

Beta Absorber—A beta absorber of 3 mm (⅛ in.) to 6 mm (¼ in.) of aluminum, beryllium, or lucite should completely cover the upper face of the detector to prevent betas from reaching the detector.

Energy Efficiency Relationship

Because of the rapid fall-off in gamma absorption as gamma energy rises, the detection efficiency shows a similar effect and Fig. 13 shows the efficiency versus gamma energy plot for a 76- by 76-mm sodium iodide (thallium) detector. The portion of the curve at low energy shows that, as the absorption coefficient increases, geometry becomes the limiting factor. The maximum efficiency seen is well below 50 percent due to the presence of the beta absorber and the containment of the detector. The 76- by 76-mm sodium iodide (thallium) detector is the most widely used size, and a large amount of data are available in the open literature on the use of this size and results obtained. Heath [2] has written a comprehensive review and supplied many gamma-ray spectra in both graphical and digital form.

Other sizes of detector may be used. However, the following should be noted.

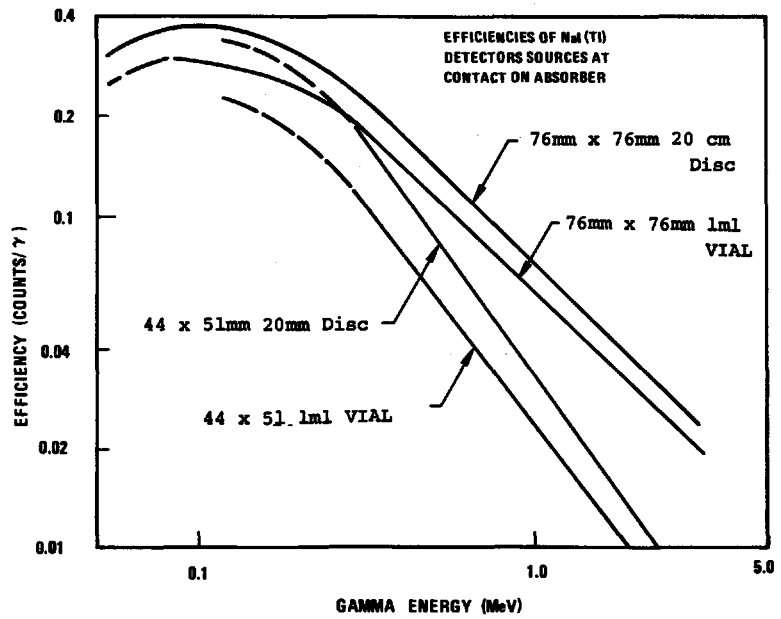


FIG. 13—*Efficiency versus gamma energy.*

Smaller detectors such as 38 by 38 mm will give efficiencies which are low and fall off more rapidly as gamma energy increases. Small or thin detectors are useful for the measurement of low-energy gammas since they are less responsive to high-energy ones, and the interference from Compton effects is reduced.

Larger detectors will give higher efficiencies and less fall-off as gamma energy increases. Larger detectors are useful for situations where the highest attainable efficiency is desired and for the assembly of complete absorption detectors. The increase in efficiency is accompanied by an increased background count rate and an increase in the probability of summing in the detector.

Well detectors will give very high efficiencies, up to about 80 percent for low- and moderate-energy gammas. The well detector is useful for low levels of activity, and the background of a well detector is essentially the same as that of a plain cylindrical detector of the same overall dimensions. Summing becomes a definite problem at high activities since both random and cascade summing result from the high efficiencies and the high geometry of the detector.

Calibration and Standardization

The system should be calibrated for energy or gain by using at least two sources of different gamma energies. Cesium-137 at 662 keV and cobalt-60 at 1.17 and 1.33 keV are generally adequate. These sources are used to establish two parameters: first, the required MeV or keV per volt of amplifier output, and second, the condition that zero MeV is equal to zero volts output. Subsequent efficiency calibrations are carried out with the same gain settings.

Efficiency calibrations are obtained by counting known amounts of single nuclides in the geometry and matrix which will be used for the unknown samples. Standards are available from the National Bureau of Standards and other sources. Extreme care should be taken in the preparation of subsamples of standards and whenever possible gravimetric dilution and division techniques should be used. The threshold and window levels used in volts are obtained using the energy calibration data obtained previously.

In comparing a standard and samples of the same nuclide, accurate results are possible. When an arbitrary standard is used to estimate the activity of a mixture of nuclides, the data are not accurate since the real detection efficiency varies with energy. Because of this gross gamma count, data obtained on mixtures of nuclides are only useful as an indication of approximate activity. Such data can be used for sample screening to select aliquot sizes for gamma spectrometry, comparison of process or waste samples with each other, and as a general screening for liquid wastes.

Data obtained using an arbitrary standard for a mixture of nuclides should be reported as being based on a "calibration using nuclide-X" or as being "relative to nuclide-X." Data obtained by using this technique *should not be reported as dpm or Ci units without qualification.*

Source Preparation

Samples must be prepared in an identical manner to the standards and counted in the same geometry under identical conditions. For gamma counting, samples may be liquid, solid, or gaseous form in suitable containers.

The evaporation of liquid samples to dryness before counting is not necessary. However, samples which have been evaporated to dryness for gross beta counting can also be gamma counted. Evaporation may also be used as a sample concentration technique, especially with pure water such as evaporator condensates where large samples may be evaporated to small volume and counted with a higher efficiency.

Gaseous samples can be collected in any type of gas container, but care must be taken to ensure that all the gas containers of a particular type have a constant wall thickness. Wall thickness variation can be a significant problem in counting radioactive xenons which have gammas of 80 keV and 250 keV energy.

Calculations

Results may be expressed in observed counts per minute per millilitre for comparing relative activities of a group of samples as in tracer experiments

$$C = \frac{1}{V}\left[\frac{N}{t} - \frac{N_B}{t_B}\right]$$

where

N = number of counts accumulated,

t = sample counting period, min,

N_B = number of background counts accumulated,

t_B = background counting period, min,

V = volume of initial sample, ml, and

C = net counts per minute per millilitre (cpm/ml).

Results also may be expressed in terms of equivalent cesium-137 activity, using the empirical efficiency determined for the reference standard

$$D_{^{137}\mathrm{Cs}} = \frac{C}{E_{^{137}\mathrm{Cs}}}$$

where

C = net counter per minute per millilitre (cpm/ml), and

$E_{^{137}Cs}$ = efficiency for counting Cs-137 beta particles plus conversion electrons (cpm/dpm).

If it is known that only one nuclide is present, its disintegration rate may be determined by use of the efficiency factor measured with a reference standard of the same nuclide. The results may be calculated as follows

$$D = \frac{1}{EVY}\left[\frac{N}{t} - B\right]$$

where

N = number of counts accumulated,
B = background in counts per minute, (cpm),
D = disintegrations per minute per millilitre (dpm/ml),
E = efficiency of counter for specific nuclide (cpm/dpm),
V = millilitres of test specimen,
Y = recovery of species (unity in cases where complete recovery is assumed), and
t = count period, min.

If it is desired that the activity be expressed in units of microcuries, the following expression is used

$$A = \frac{D}{2.22 \times 10^6}$$

where

A = concentration, microcuries per millilitre,
D = disintegration rate per minute per millilitre (dpm/ml), and
2.22×10^6 = conversion factor, disintegrations per minute per microcurie.

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STP442A-EB/Jul. 1978

Appendix—Reference Tables and Curves

Table of Atomic Weights

The following values apply to elements as they exist in materials of terrestrial origin and to certain artificial elements. They are based on the assigned relative atomic mass of carbon-12 and when used with regard to the footnotes they are considered reliable to ±1 in the last digit, or ±3 if that digit is a subscript. These values are accepted by the International Union of Pure and Applied Chemistry, Division of Inorganic Chemistry Commission on Atomic Weights, and are the 1971 data revised in 1973.

Name	Symbol	Atomic No.	Atomic Weight
Actinium	Ac	89	. . .
Aluminum	Al	13	26.98154
Americium	Am	95	. . .
Antimony	Sb	51	121.75
Argon	Ar	18	39.94_8[b,c,d,g]
Arsenic	As	33	74.9216[a]
Astatine	At	85	. . .
Barium	Ba	56	137.3_4
Berkelium	Bk	97	. . .
Beryllium	Be	4	9.01218[a]
Bismuth	Bi	83	208.9804[a]
Boron	B	5	10.81[c,d,e]
Bromine	Br	35	79.904[c]
Cadmium	Cd	48	112.40
Cesium	Cs	55	132.9054[a]
Calcium	Ca	20	40.08[g]
Californium	Cf	98	. . .
Carbon	C	6	12.011[b,d]
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.453[c]
Chromium	Cr	24	51.996[c]
Cobalt	Co	27	58.9332[a]
Copper	Cu	29	63.54_6[c,d]
Curium	Cm	96	. . .
Dysprosium	Dy	66	162.5_0

(*Continued*)

Name	Symbol	Atomic No.	Atomic Weight
Einsteinium	Es	99	. . .
Erbium	Er	68	167.2_6
Europium	Eu	63	151.96
Fermium	Fm	100	. . .
Fluorine	F	9	18.99840[a]
Francium	Fr	87	. . .
Gadolinium	Gd	64	157.2_5
Gallium	Ga	31	69.72
Germanium	Ge	32	72.5_9
Gold	Au	79	196.9665[a]
Hafnium	Hf	72	178.4_9
Helium	He	2	4.00260[b,c]
Holmium	Ho	67	164.9304[a]
Hydrogen	H	1	1.0079[b,d]
Indium	In	49	114.82
Iodine	I	53	126.9045[a]
Iridium	Ir	77	192.2_2
Iron	Fe	26	55.84_7
Krypton	Kr	36	83.80
Lanthanum	La	57	138.905_5[b]
Lawrencium	Lr	103	. . .
Lead	Pb	82	207.2[d,g]
Lithium	Li	3	6.94_1[c,d,e,g]
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.305[c,g]
Manganese	Mn	25	54.9380[a]
Mendelevium	Md	101	. . .
Mercury	Hg	80	200.5_9
Molybdenum	Mo	42	95.9_4
Neodymium	Nd	60	144.2_4
Neon	Ne	10	20.17_9[c]
Neptunium	Np	93	237.0482[f]
Nickel	Ni	28	58.70
Niobium	Nb	41	92.9064[a]
Nitrogen	N	7	14.0067[b,c]
Nobelium	No	102	. . .
Osmium	Os	76	190.2
Oxygen	O	8	15.999_4[b,c,d]
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97376[a]
Platinum	Pt	78	195.0_9
Plutonium	Pu	94	. . .
Polonium	Po	84	. . .
Potassium	K	19	39.09_8
Praseodymium	Pr	59	140.9077[a]
Promethium	Pm	61	. . .
Protactinium	Pa	91	231.0359[f]
Radium	Ra	88	226.0254[f,g]
Radon	Rn	86	. . .
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.9055[a]
Rubidium	Rb	37	85.467_3[c]
Ruthenium	Ru	44	101.0-
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559[a]
Selenium	Se	34	78.9_6
Silicon	Si	14	28.08_6[d]

(Continued)

Name	Symbol	Atomic No.	Atomic Weight
Silver	Ag	47	107.868[c]
Sodium	Na	11	22.98977[a]
Strontium	Sr	38	87.62[g]
Sulfur	S	16	32.06[a]
Tantalum	Ta	73	180.947_{9}[b]
Technetium	Tc	43	. . .
Tellurium	Te	52	127.6_{0}
Terbium	Tb	65	158.9254[a]
Thallium	Tl	81	204.3_{7}
Thorium	Th	90	232.0381[f]
Thulium	Tm	69	168.9342[a]
Tin	Sn	50	118.6_{9}
Titanium	Ti	22	47.9_{0}
Tungsten	W	74	183.8_{3}
Uranium	U	92	238.029[b,c,e]
Vanadium	V	23	50.941_{4}[b,e]
Wolfram	W	74	183.8_{5}
Xenon	Xc	54	131.30
Yitterbium	Yb	70	173.0_{4}
Yttrium	Y	39	88.9059[a]
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

[a] Mononuclide element.

[b] Element with one predominant isotope (about 99 to 100 percent abundance).

[c] Element for which the atomic weight is based on measurements calibrated by comparing with synthetic mixtures of known isotopic composition.

[d] Element for which variation in isotopic abundance in terrestrial samples limits precision of atomic weight given.

[e] Element for which there is the possibility of large variations in atomic weight due to inadvertent or undisclosed artificial isotopic separation in commercially available materials.

[f] Most commonly available long-lived isotope.

[g] In some geological specimens this element has a highly anomalous isotopic composition, corresponding to an atomic weight significantly different from that given.

Viscosity of water.

Temperature, °C	Viscosity, Pascal-second
10	0.0013077
15	0.0011404
20	0.0010050
25	0.0008937
30	0.0008007
35	0.0007225

Density of water.[a]

Temperature Deg°C		Density of Water, kg/m³ at T deg C									
		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	999	8396	8463	8528	8591	8653	8713	8771	8827	8882	8934
1		8985	9034	9082	9127	9171	9213	9254	9293	9330	9365
2		9398	9430	9460	9489	9516	9541	9564	9586	9606	9625
3		9642	9657	9670	9682	9692	9701	9708	9713	9717	9719
4		9720	9719	9716	9712	9706	9699	9690	9680	9668	9654
5		9639	9622	9604	9584	9563	9540	9516	9490	9462	9433
6		9403	9371	9338	9303	9266	9229	9189	9148	9106	9062
7		9017	8970	8922	8873	8822	8769	8715	8660	8603	8545
8		8485	8424	8362	8298	8233	8166	8098	8029	7958	7886
9		7812	7737	7661	7583	7504	7424	7342	7259	7174	7088
10		7001	6913	6823	6732	6639	6545	6450	6354	6256	6157
11		6056	5955	5852	5747	5642	5535	5427	5317	5206	5094
12		4981	4866	4751	4634	4515	4396	4275	4153	4029	3905
13		3779	3652	3523	3394	3263	3131	2998	2863	2728	2591
14		2453	2313	2173	2031	1888	1744	1599	1452	1305	1156
15		1006	0855	0702	0549	0394	0238	0081	9923*	9763*	9603*
16	998.	9441	9278	9114	8949	8783	8615	8447	8277	8106	7934
17		7761	7587	7412	7235	7058	6879	6699	6518	6336	6153
18		5969	5784	5597	5410	5221	5031	4841	4649	4456	4262
19		4067	3870	3673	3475	3275	3075	2874	2671	2467	2263
20		2057	1850	1642	1433	1223	1012	0800	0587	0373	0158
21	997.	9942	9725	9506	9287	9067	8846	8623	8400	8176	7950
22		9724	9496	7268	7039	6808	6577	6344	6111	5877	5641
23		5405	5167	4929	4690	4449	4208	3966	3723	3478	3233
24		2987	2740	2492	2243	1993	1741	1490	1237	0983	0728
25		0472	0215	9958*	9699*	9439*	9179*	8917*	8655*	8391*	8127*
26	996.	7862	7596	7329	7061	6792	6522	6251	5979	5706	5433
27		5158	4883	4607	4329	4051	3772	3492	3211	2929	2647
28		2363	2079	1793	1507	1220	0932	0643	0353	0062	9770*
29	995.	9478	9184	8890	8595	8299	8002	7704	7405	7106	6805
30		6504	6202	5899	5595	5290	4984	4678	4370	4062	3753
31		3443	3132	2820	2508	2195	1880	1565	1249	0932	0615
32		0296	9977	9657	9336	9014	8691	8368	8044	7718	7392
33	994.	7066	6738	6409	6080	5750	5419	5087	4755	4421	4087
34		3752	3416	3079	2742	2403	2064	1724	1383	1042	0700
35		0356	0012	9668*	9322*	8976*	8628*	8280*	7932*	7582*	7232*
36	993.	6880	6529	6176	5822	5468	5113	4757	4400	4043	3684
37		3325	2966	2605	2244	1881	1518	1155	0790	0425	0059
38	992.	9692	9324	8956	8587	8217	7846	7475	7103	6730	6356
39		5982	5606	5230	4854	4476	4098	3719	3339	2959	2577
40		2195	1813	1429	1045	0660	0274	9888*	9500*	9112*	8724*
41	991.	8334	7944	7553	7161	6769	6376	5982	5587	5192	4796
42		4399									

[a] ASTM Designation E-500.

Chemical conversion factors: residue to pertinent element or radical.

Weighed	Sought	Factor
Al_2O_3	Al	0.529
$BaSO_4$	Ba	0.588
$BaSO_4$	SO_4	0.412
CaO	Ca	0.715
CdS	S	0.778
CO_2	CO_3	1.364
CuO	Cu	0.799
Fe_2O_3	Fe	0.699
$KMnO_4$	Mn	0.348
$Mg_2P_2O_7$	Mg	0.219
$Mg_2P_2O_7$	PO_4	0.853
$Mn_2P_2O_7$	Mn	0.387
$(NH_4)_3PO_4 \cdot 12MoO_3$	P	0.0022
Ni-glyoxime	Ni	0.203
PbO_2	Pb	0.866
SnO_2	Sn	0.788
TiO_2	Ti	0.60
ZnO	Zn	0.803

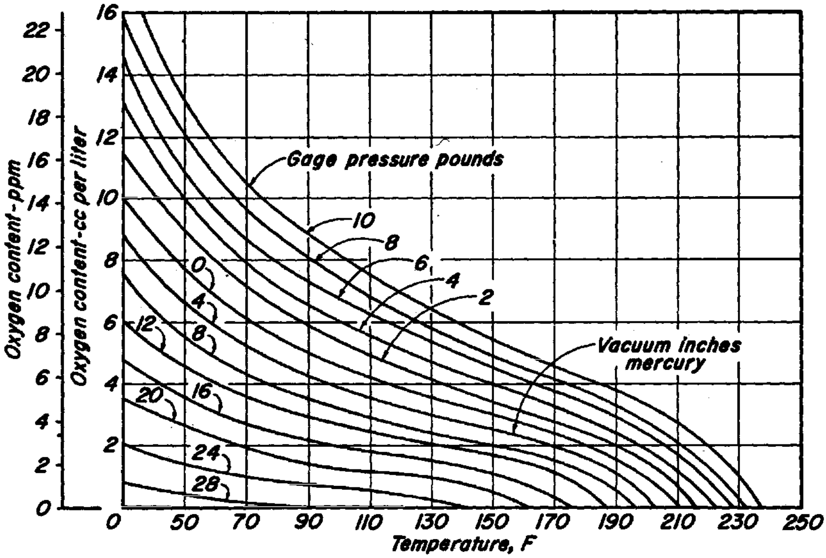
Dissolved oxygen (saturation values).

Temperature, °C	mg/litre
10	11.33
15	10.15
20	9.17
25	8.38
30	7.63
35	7.1
40	6.6
45	6.1
50	5.6

Ionic equivalent conductance at 25°C.

Ion	λ_o[a]
K^+	73.52
Na^+	50.11
H^+	349.82
NH_4^+	73.4
½ Ca^{++}	59.5
½ Mg^{++}	53.06
Cl^-	76.34
NO_3^-	71.44
½ SO_4^-	79.8
OH^-	198
HCO_3^-	44.48
½ CO_3^-	83
HS^-	72
HSO_3^-	71
½ SO_3^-	80
$H_2PO_4^-$	29
½ HPO_4^-	60
⅓ PO_4^-	78

[a] λ_o = Ionic equivalent conductance at infinite dilution.



Dissolved oxygen from air in contact with water—solubility of oxygen as a function of temperature and pressure.

Temperature conversion formulas.

Deg C = 5/9 deg F - 32
Deg F = 9/5 deg C + 32

Bicarbonate, carbonate, and hydroxide relationships.

	Bicarbonate	Carbonate	Hydroxide
$P = 0$	M	0	0
$P < \frac{1}{2} M$	$M - 2P$	$2P$	0
$P = \frac{1}{2} M$	0	$2P$	0
$P > \frac{1}{2} M$	0	$2(M - P)$	$2P - M$
$P = M$	0	0	M

M = Methyl orange alkalinity.
P = Phenolphthalein alkalinity.

Common conversion factors.

Multiply	By	To Obtain
Acres	43,560	square feet
Acre-feet	325,851	gallons
Centimetres	0.394	inches
Centimetres	0.01	metres
Centimetres	10	millimetres
Cubic feet	1728	cubic inches
Cubic feet	7.48	gallons
Cubic feet	28.32	litres

(*Continued*)

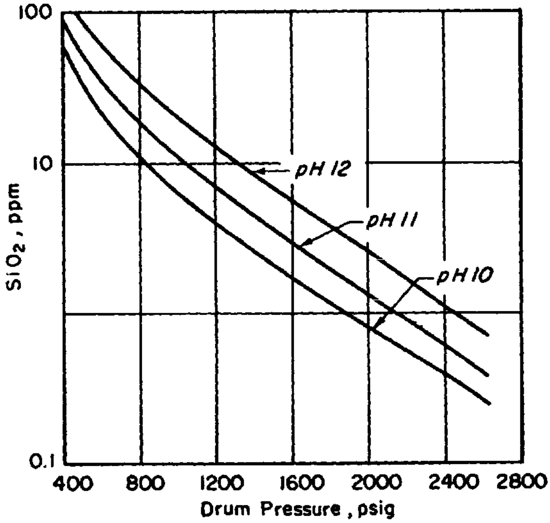
Common conversion factors—Continued.

Multiply	By	To Obtain
Cubic feet per minute	62.43	pounds of water per minute
Cubic feet per second	0.646	million gallons per day
Cubic feet per second	448.83	gallons per minute
Cubic inches	16.39	cubic centimetres
Cubic metres per day	0.000264	millon gallons per day
Cubic metres per day	0.1834	gallons per minute
Feet	30.48	centimetres
Feet of water	0.8826	inches of mercury
Feet of water	62.43	pounds per square foot
Feet of water	0.4335	pounds per square inch
Gallons	3785	cubic centimetres
Gallons	0.1337	cubic feet
Gallons	231	cubic inches
Gallons	3.785	litres
Gallons, Imperial	1.2	gallons, U. S.
Gallons of water	8.345	pounds of water
Grains	0.0648	grams
Grains per gallon	17.12	parts per million
Grains per gallon	142.86	pounds per million gallons
Grams	15.43	grains
Grams	0.001	kilograms
Grams	1000	milligrams
Grams	0.0021	pounds
Grams per litre	58.42	grains per gallon
Grams per litre	8.345	pounds per 1000 gallons
Grams per litre	1000	parts per million
Inches	2.54	centimetres
Inches of mercury	1.133	feet of water
Inches of mercury	0.4912	pounds per square inch
Inches of water	0.0736	inches of mercury
Inches of water	0.036	pounds per square inch
Kilograms	2.205	pounds
Kilograms	1000	grams
Kilometers	3281	feet
Kilometers	0.6214	miles
Litres	1000	cubic centimetres
Litres	0.0353	cubic feet
Litres	61.02	cubic inches
Litres	0.2642	gallons
Metres	100	centimetres
Metres	3.281	feet
Metres	39.37	inches
Milligrams	0.001	grams
Millilitres	0.001	litres
Milligrams per litre	1	parts per million
Million gallons per day	1.547	cubic feet per second
Ounces	437.5	grains
Ounces	28.35	grams
Parts per million	0.0584	grains per gallon
Parts per million	8.345	pounds per million gallons
Pounds	7000	grains
Pounds	453.6	grams
Pounds per cubic foot	0.016	grams per cubic centimetre
Pounds per square inch	2.31	feet of water
Pounds per square inch	2.036	inches of mercury
Square miles	640	acres

(*Continued*)

Common conversion factors—Continued.

Multiply	By	To Obtain
Tons, long	2240	pounds
Tons, metric	2205	pounds
Tons, short	2000	pounds



Percentage of silica in steam versus boiler drum pressure at selected boiler water pH.

Interconversion factors from milligrams per litre to equivalents per million of the common ions.

Ion	Multiplier mg/litre to epm	epm to mg/litre	Ion	Multiplier mg/litre to epm	epm to mg/litre
Al^{+++}	0.1112	8.99	Cn^-	0.03843	26.02
Ba^{++}	0.01456	68.68	$CO_3^=$	0.03333	30.00
Ca^{++}	0.04990	20.04	F^-	0.05263	19.00
Cu^{++}	0.03148	31.77	HCO_3^-	0.01639	61.02
Fe^{++}	0.03581	27.92	$H_2PO_4^-$	0.01031	96.99
Fe^{+++}	0.05372	18.62	HS^-	0.03024	33.07
H^+	0.9921	1.008	$HPO_4^=$	0.02084	47.99
K^+	0.02558	39.10	HSO_4^-	0.01030	97.07
Mg^{++}	0.08224	12.16	HSO_3^-	0.01233	81.07
Mn^{++}	0.03640	27.47	I^-	0.00788	126.91
Mn^{+++}	0.07281	13.735	NO_3^-	0.01613	62.01
Na^+	0.04350	22.99	NO_2^-	0.02174	46.01
NH^+	0.05543	18.04	OH^-	0.05880	17.01
Pb^{++}	0.00965	103.60	$PO_4^=$	0.03159	31.66
Sr^{++}	0.02282	43.81	$S^=$	0.06237	16.03
Zn^{++}	0.03059	32.69	$SiO_4^=$	0.02172	46.04
Br	0.01251	79.92	$SO_4^=$	0.02082	48.03
Cl^-	0.02820	35.46	$SO_2^=$	0.02498	40.03

Analyses of typical public water supplies in the United States.
(From U. S. Geological Survey Water Supply Paper 1812)
(milligrams per litre)

Water supply[a]	1	2	3	4	5	6	7	8
Date of collection	4/17/62	8/24/61	7/21/61	5/16/61	3/16/61	1/8/62	7/11/61	8/25/61
Silica (SiO_2), mg/litre	3.1	1.3	4.5	2.0	5.7	7.1	2.7	4.8
Iron (Fe), mg/litre	0.04	0.05	0.02	0.06	0.06	0.12	0.03	0.00
Manganese (Mn), mg/litre	0.00	0.09	. . .	0.00	0.00	. . .	0.00	0.00
Calcium (Ca), mg/litre	4.5	32	20	6.9	27	1.0	3.2	40
Magnesium (Mg), mg/litre	0.4	11	7.8	1.0	3.9	0.6	0.6	8.8
Sodium (Na), mg/litre	2.4	4.0	18	1.8	4.7	1.1	2.9	8.2
Potassium (K), mg/litre	0.8	0.8	2.8	0.5	2.8	0.4	0.4	1.9
Bicarbonate (HCO_3), mg/litre	8	128	36	13	32	8	11	106
Carbonate (CO_3), mg/litre	0	0	0	0	0	0	0.3	0
Sulfate (SO_4), mg/litre	7.0	20	46	9.0	43	0.8	1.5	45
Chloride (Cl), mg/litre	3.5	8.0	32	3.8	16	2.2	3.6	15
Fluoride (F), mg/litre	0.0	1.0	0.2	0.0	0.8	0.0	0.1	0.9
Nitrate (NO_3), mg/litre	0.0	0.4	1.4	0.9	3.6	0.2	0.0	1.2
Dissolved solids, mg/litre	31	149	187	41	130	22	27	198
Hardness as $CaCO_3$, mg/litre	13	125	82	21	84	5	10	137
Noncarbonate hardness as $CaCo_3$, mg/litre	6	20	52	11	58	0	1	50
Specific conductance (micromhos at 25°C)	47	261	284	62	211	18	34	313
pH	6.4	7.5	7.9	6.5	7.2	6.4	9.1	7.9
Color	4	2	10	3	2	5	1	2
Turbidity	1	. . .	. . .	1	. . .	. . .	1	. . .

[a] Water supplies are identified as follows:

1. Boston, Mass. Norumbega Reservoir (finished).
2. Chicago, Ill. Lake Michigan (finished).
3. New Orleans, La. Mississippi River (finished).
4. New York, N. Y. Catskill and Delaware River supplies (finished).
5. Philadelphia, Pa. Delaware River (finished).
6. Portland, Ore. Gull Run River (finished).
7. San Francisco, Calif. Hetch-Hetchy supply (finished).
8. Washington, D. C. Potomac River (finished).

Analyses by U. S. Geological Survey of typical surface waters of the United States.
(milligrams per litre)

	1			2			3			4		
Surface waters[a]	max	min	avg	max	min	avg	max	min	avg	max	min	avg
Date of Collection	Jan. 1 to 10, 1962	May 1 to 10, 1962	Oct. 1961 to Sept. 1962	Oct. 1 to 31, 1961	Apr. 1 to 30, 1962	Oct. 1961 to Sept. 1962	Dec. 1 to 9, 1961	Mar. 1 to 31, 1962	Oct. 1961 to Sept 1962	Dec. 13 to 28, 1961	Mar. 29 to Apr. 5, 1962	Oct. 1961 to Sept. 1962
Silica (SiO_2), mg/litre	8.7	2.1	4.4	9.0	7.6	9.5	6.4	5.6	6.2	16	15	15
Iron (Fe), mg/litre	0.20	0.00	0.01	0.03	0.10	0.07	. . .	. . .	. . .	. . .	. . .	. . .
Manganese (Mn), mg/litre	0.14	0.00	0.03	. . .	. . .	. . .	. . .	. . .	. . .	. . .		. . .
Calcium (Ca), mg/litre	20	8.2	16	8.7	7.5	7.5	46	29	33	83	35	61
Magnesium (Mg), mg/litre	8.0	2.6	6.0	2.5	1.8	2.4	14	7.1	8.3	24	14	17
Sodium (Na), mg/litre	10	2.2	7.3	9.0	5.9	7.4	26	7.6	10	64	13	40
Potassium (K), mg/litre	2.5	1.2	1.9	2.9	1.6	2.1	3.0	2.0	2.0	9.2	4.0	7.6
Bicarbonate (HCO_3), mg/litre	66	18	51	41	31	36	86	73	80	301	146	195
Carbonate (CO_3), mg/litre	0	0	. . .	0	0	. . .	0	0	. .	0	0	. . .
Sulfate (SO_3), mg/litre	30	17	26	7.8	6.4	6.9	103	42	49	178	45	124
Chloride (Cl), mg/litre	9.0	3.2	7.5	7.6	4.1	5.4	36	10	14	21	8.2	14
Fluoride (F), mg/litre	0.6	0.0	0.2	0.1	0.1	0.1	0.4	0.1	0.2	0.5	0.3	0.4
Nitrate (NO_3), mg/litre	5.7	2.6	4.1	4.0	1.7	2.3	5.8	4.2	4.4	4.6	3.0	4.0
Dissolved solids, mg/litre	125	46	104	81	59	69	296	154	175	554	220	394
Hardness as $CaCO_3$, mg/litre	83	32	65	32	26	28	173	102	116	307	145	223
Noncarbonate hardness as $CaCO_3$, mg/litre	31	17	24	0	1	0	102	42	50	61	26	66
Specific conductance (micromhos at 25°C)	198	86	168	113	84	96	475	249	288	867	346	607
pH	7.8	6.5	. . .	6.9	7.7	. . .	8.2	6.9	. . .	7.6	7.3	. . .
Color	8	2	4	15	32	25	20	5	11			

Surface waters[a]	5			6			7			8		
	max	min	avg	max	min	avg	max	min	avg	max	min	avg
Date of Collection	Sept. 1 to 30, 1962	Apr. 1 to 30, 1962	Oct. 1961 to Sept. 1962	Mar. 1 to 31, 1962	Nov. 1 to 30, 1961	Oct. 1961 to Sept. 1962	Sept. 27 to 30, 1962	May 8 to 23, 1962	Oct. 1961 to Sept. 1962	Mar. 9 to 28, 1962	June 1 to 30, 1962	Oct. 1961 to Sept. 1962
Silica (SiO_2), mg/litre	8.7	7.4	9.5	11	9.5	11	19	18	18	18	6.5	13
Iron (Fe), mg/litre	0.16	0.00	0.03	. . .	. . .	. . .	0.01	0.00	0.00	. . .	. . .	. . .
Manganese (Mn), mg/litre												
Calcium (Ca), mg/litre	46	32	40	48	39	43	230	55	77	22	18	20
Magnesium (Mg), mg/litre	14	8.0	10	18	18	19	51	12	20	6.4	3.9	4.1
Sodium (Na), mg/litre	26	11	18	37	34	34	212	28	68	10	3.6	6.2
Potassium (K), mg/litre	3.1	2.1	2.7	3.9	3.8	3.7	4.3	3.2	4.1	1.8	0.8	1.7
Bicarbonate (HCO_3), mg/litre	160	101	128	193	172	177	239	170	195	101	61	76
Carbonate (CO_3), mg/litre	0	0	. . .	0	0	. . .	0	0	. . .	0	0	. . .
Sulfate (SO_4), mg/litre	47	34	41	37	29	33	730	77	156	20	11	15
Chloride (Cl), mg/litre	36	11	19	54	51	57	200	20	58	5.0	1.0	3.0
Fluoride (F), mg/litre	0.2	0.0	0.2	0.3	0.2	0.3	0.5	0.3	0.4	0.3	0.1	0.2
Nitrate (NO_3), mg/litre	1.8	1.7	2.2	1.8	0.5	1.6	8.9	2.3	3.6	1.5	0.4	1.0
Dissolved solids, mg/litre	279	157	218	330	268	293	1,629	314	531	140	69	99
Hardness as $CaCO_3$, mg/litre	171	113	140	194	172	186	785	185	271	88	54	67
Noncarbonate hardness as $CaCO_3$, mg/litre	40	30	35	36	30	40	585	46	111	5	4	4
Specific conductance (micromhos at 25°C)	434	275	352	540	464	516	2,180	477	803	221	125	161
pH	7.6	7.2	. . .	7.5	7.2	7.3	7.9	7.5	7.7	7.8	7.7	. . .
Color	10	5	18									

[a] Surface waters are identified as follows:

1. Delaware River at Trenton, N. J. (Water-Supply Paer-1941).
2. Roanoke River at Jamesville, N. C. (WSP-1941).
3. Ohio River at Lock and Dam 53, near Grand Chain, Ill. (WSP-1942).
4. Missouri River at Nebraska City, Nebr. (WSP-1943).
5. Mississippi River at St. Francisville, La. (WSP-1944).
6. Colorado River at Austin, Tex. (WSP-1944).
7. Colorado River near Grand Canyon, Ariz. (WSP-1945).
8. Columbia River near The Dalles, Ore. (WSP-1945).

Temperature conversion tables (-100 TO 1000 deg).

Interpolation Factors

C		F
0.56	1	1.8
1.11	2	3.6
1.67	3	5.4
2.22	4	7.2
2.78	5	9.0
3.33	6	10.8

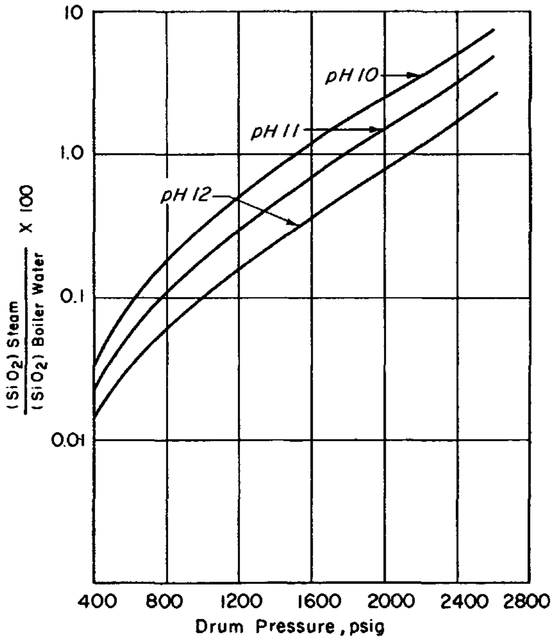
C		F	C		F	C		F	C		F
-73.3	**-100**	-148	5.0	**41**	105.8	33.3	**92**	197.6	277	**530**	986
-67.8	**-90**	-130	5.6	**42**	107.6	33.9	**93**	199.4	282	**540**	1004
-62.2	**-80**	-112	6.1	**43**	109.4	34.4	**94**	201.2	288	**550**	1022
-56.7	**-70**	-94	6.7	**44**	111.2	35.0	**95**	203.0	293	**560**	1040
-51.1	**-60**	-76	7.2	**45**	113.0	35.6	**96**	204.8	299	**570**	1058
-45.6	**-50**	-58	7.8	**46**	114.8	36.1	**97**	206.6	304	**580**	1076
-40	**-40**	-40	8.3	**47**	116.6	36.7	**98**	208.4	310	**590**	1094
-34.4	**-30**	-22	8.9	**48**	118.4	37.2	**99**	210.2	316	**600**	1112
-28.9	**-20**	-4	9.4	**49**	120.2	37.8	**100**	212	321	**610**	1130
-23.3	**-10**	14	10.0	**50**	122.0	43.0	**110**	230	327	**620**	1148
-17.8	**0**	32	10.6	**51**	123.8	49.0	**120**	248	332	**630**	1166
-17.2	**1**	33.8	11.1	**52**	125.6	54.0	**130**	266	338	**640**	1184
-16.7	**2**	35.6	11.7	**53**	127.4	60.0	**140**	284	343	**650**	1202
-16.1	**3**	37.4	12.2	**54**	129.2	66.0	**150**	302	349	**660**	1220
-15.6	**4**	39.2	12.8	**55**	131.0	71.0	**160**	320	354	**670**	1238
-15.0	**5**	41.0	13.3	**56**	132.8	77.0	**170**	338	360	**680**	1256
-14.4	**6**	42.8	13.9	**57**	134.6	82.0	**180**	356	366	**690**	1274
-13.9	**7**	44.6	14.4	**58**	136.4	88.0	**190**	374	371	**700**	1292
-13.3	**8**	46.4	15.0	**59**	138.2	93.0	**200**	392	377	**710**	1310
-12.8	**9**	48.2	15.6	**60**	140.0	99.0	**210**	410	382	**720**	1328
						100.0	**212**	413			
-12.2	**10**	50.0	16.1	**61**	141.8	104.0	**220**	428	388	**730**	1346
-11.7	**11**	51.8	16.7	**62**	143.6	110.0	**230**	446	393	**740**	1364
-11.1	**12**	53.6	17.2	**63**	145.4	116.0	**240**	464	399	**750**	1382
-10.6	**13**	55.4	17.8	**64**	147.2	121	**250**	482	404	**760**	1400

3.89	7	12.6	-10.0	**14**	57.2	18.3	**65**	149.0	127	**260**	500	410	**770**	1418
			-9.4	**15**	59.0	18.9	**66**	150.8	132	**270**	518	416	**780**	1436
			-8.9	**16**	60.8	19.4	**67**	152.6	138	**280**	536	421	**790**	1454
4.44	8	14.4	-8.3	**17**	62.6	20.0	**68**	154.4	143	**290**	554	427	**800**	1472
			-7.8	**18**	64.4	20.6	**69**	156.2	149	**300**	572	432	**810**	1490
			-7.2	**19**	66.2	21.1	**70**	158.0	154	**310**	590	438	**820**	1508
5.00	9	16.2	-6.7	**20**	68.0	21.7	**71**	159.8	160	**320**	608	443	**830**	1526
			-6.1	**21**	69.8	22.2	**72**	161.6	166	**330**	626	449	**840**	1544
			-5.6	**22**	71.6	22.8	**73**	163.4	171	**340**	644	454	**850**	1562
5.56	10	18.0	-5.0	**23**	73.4	23.3	**74**	165.2	177	**350**	662	460	**860**	1580
			-4.4	**24**	75.2	23.9	**75**	167.0	182	**360**	680	466	**870**	1598
			-3.9	**25**	77.0	24.4	**76**	168.8	188	**370**	698	471	**880**	1616
			-3.3	**26**	78.8	25.0	**77**	170.6	193	**380**	716	477	**890**	1634
			-2.8	**27**	80.6	25.6	**78**	172.4	199	**390**	734	482	**900**	1652
			-2.2	**28**	82.4	26.1	**79**	174.2	204	**400**	752	488	**910**	1670
			-1.7	**29**	84.2	26.7	**80**	176.0	210	**410**	770	493	**920**	1688
			-1.1	**30**	86.0	27.2	**81**	177.8	216	**420**	788	499	**930**	1706
			-0.6	**31**	87.8	27.8	**82**	179.6	221	**430**	806	504	**940**	1724
			0	**32**	89.6	28.3	**83**	181.4	227	**440**	824	510	**950**	1742
			0.6	**33**	91.4	28.9	**84**	183.2	232	**450**	842	516	**960**	1760
			1.1	**34**	93.2	29.4	**85**	185.0	238	**460**	860	521	**970**	1778
			1.7	**35**	95.0	30.0	**86**	186.8	243	**470**	878	527	**980**	1796
			2.2	**36**	96.8	30.6	**87**	188.6	249	**480**	896	532	**990**	1814
			2.8	**37**	98.6	31.1	**88**	190.4	254	**490**	914	538	**1000**	1832
			3.3	**38**	100.4	31.7	**89**	192.2	260	**500**	932			
			3.9	**39**	102.2	32.2	**90**	194.0	266	**510**	950			
			4.4	**40**	104.0	32.8	**91**	195.8	271	**520**	968			

To convert from any Celsius temperature to the Fahrenheit equivalent, select the temperature C from the center (boldface) columns, then read temperature F to the right. To convert from F to C, select the temperature F from the center (boldface) columns, and read equivalent temperature C to the *left*. Use factors above for interpolations.

Volume conversion factors.

to→ from	cm^3	litres	m^3	$in.^3$	ft^3	yd^3	Fluid oz	Fluid pt	Fluid qt	gal (U.S.)	gal (U.K.)
cm^3	1	0.001	1×10^{-6}	0.06102	353×10^{-5}	1.3×10^{-6}	0.03381	0.00211	0.00106	2.64×10^{-4}	2.2×10^{-4}
litre	1000	1	0.001	61.02	0.03532	0.00131	33.81	2.113	1.057	0.2642	0.220
m^3	1×10^{6}	1000	1	6.1×10^{4}	35.31	1.308	3.38×10^{4}	2113	1057	264.2	220
in^3	16.39	0.01639	1.64×10^{5}	1	5.79×10^{4}	2.14×10^{-5}	0.5541	0.03463	0.01732	0.00433	0.00360
ft^3	283×10^{4}	28.32	0.02832	1728	1	0.03704	957.5	59.84	29.92	7.481	6.229
yd^3	7.65×10^{5}	764.5	0.7646	4.67×10^{4}	27	1	259×10^{4}	1616	809.7	202.0	108.2
fluid oz	29.57	0.02957	2.96×10^{-5}	1.805	0.00104	3.87×10^{-5}	1	0.0625	0.03125	0.00781	0.00651
fluid pt	473.2	0.4732	4.73×10^{-4}	28.88	0.01671	6.19×10^{-4}	16	1	0.50	0.1250	0.1041
fluid qt	946.4	0.9463	9.46×10^{-4}	57.75	0.03342	0.00124	32	2	1	0.25	0.2082
gal (U.S.)	3785	3.785	0.00379	231.0	0.1337	0.00495	128	8	4	1	0.8327
gal (U.K.)	4546	4.546	0.00455	277.4	0.1605	0.00595	153.7	9.608	4.804	1.201	1



Maximum boiler water silica concentration versus drum pressure at selected boiler water pH. (Based on maintaining 0.02 mg/litre SiO$_2$ maximum in steam.)

Flow rate conversion factors.

from / to →	litre/s	gal/min	ft^3/s	ft^{3}min	m^3/s	m^3/min
litre/s	1	15.85	0.03532	2.119	0.001	0.06
gal/min	0.06309	1	0.00223	0.1337	0.000063	0.00379
ft^3/s	28.32	448.8	1	60	0.02832	1.699
ft^3/min	0.4719	7.481	0.01667	1	0.000472	0.02832
m^3/s	1000	15852	35.31	2118.6	1	60
m^3/min	16.667	264.2	0.5885	35.31	0.01667	1

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