POWER PLANT INSTRUMENTATION FOR MEASUREMENT OF HIGH-PURITY WATER QUALITY

Lane/Otten, *editors*

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POWER PLANT INSTRUMENTATION FOR MEASUREMENT OF HIGH-PURITY WATER QUALITY

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Foreword

The symposium on Power Plant Instrumentation for Measurement of High-Purity Water Quality was held on 9–10 June 1980 in Milwaukee, Wis. The event was sponsored by the American Society for Testing and Materials, through its Committee D-19 on Water, and was also cosponsored by the American Society of Mechanical Engineers. Gerard Otten of Puricons, Inc., and R. W. Lane of the Illinois State Water Survey presided as chairmen of the symposium and also served as editors of this publication.

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A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers—this body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

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SUMMARY

Introduction

This symposium was organized to present the need for power plant instrumentation in the measurement of high-purity water quality and to disclose the latest developments in this instrumentation. Present water treatment techniques in high-pressure electric utility plants are complex, and monitoring the water quality assumes a very important role in ensuring continuous and efficient operation of these power plants. Proper and efficient monitoring of water quality is necessary to avoid expensive plant outages (at reported costs of $1 000 000 per day) that can occur if the plant chemistry is allowed to vary from specified limits, possibly because of inadequate instrumentation.

The papers in this volume disclose the problems involved in monitoring the water quality of high-purity water and provide information on new instrumentation and the refinements that have been developed. The information contained here should be helpful to engineers designing the instrumentation for new plants, for those charged with the responsibility of updating instrumentation for plants that do not have adequate monitoring equipment, and for plant chemists who must continually monitor the water quality to ensure uninterrupted and economical maintenance-free operation.

Since as many as seven or more different general methods of measurement are described here, a full picture of the available instrumentation has been provided. Techniques employing various methods of measurement, such as ion chromatography, atomic absorption spectrometry, specific-ion electrodes, ion-exchange columns, electrical conductivity, a gravimetric method, and differential pulse polarography, are covered in this volume. Discussions on methods of sampling, desired points of sampling, and other details are included. This publication should bring the reader up to date on the present methods available for monitoring the quality of high-purity water for utility power plant usage.

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Panel Discussion

J. K. Rice[1]

Introduction to the Panel Discussion

REFERENCE: Rice, J. K., "**Introduction to the Panel Discussion,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 5–7.

ABSTRACT: This introduction presents the motivating forces behind the gradual evolution of power plant instrumentation for the measurement of substances in high-purity water. Recent results underscore the need for precision and bias studies for each of the many different methods that are being employed.

KEY WORDS: continuous measurements, high-purity water, precision, bias, water quality, power plants, instrumentation

There was a time when water containing 1 ppm total dissolved solids (TDS) was considered high-purity water in a power plant. The measurement of TDS was either by evaporated residue or by specific conductance instrumentation. When the latter was employed, corrections were made for the contribution by the carbon dioxide (CO_2) and ammonia (NH_3) present to the conductance of the water. An early refinement of this technique was continuous mechanical degassing of the sample so that only relatively small corrections for the residual CO_2 and NH_3 were necessary. Examples are the Straub degasser and its successor, the Calgon degasser, the latter still contained in ASTM Tests for Deposit-Forming Impurities in Steam (D 2186-79).

Even before the concern with 1 ppm TDS in the steam, measurements of dissolved oxygen at the 5 to 30 ppb level in feedwater had become necessary. Deposits of silica (SiO_2) in steam turbines brought on the development of methods for dissolved SiO_2 at the 2 to 50 ppb level. Boiler tube corrosion failures spawned the continuous measurement of hydrogen in steam at the parts-per-billion level. Deposits of iron oxides and copper in boiler tubes hastened development of sensitive methods for iron and copper in boiler feedwater. In the early 1950s, a large jump in steam pressure and temperature accompanied by increased turbine size created new needs for measurement of impurities in steam at parts-per-billion levels. Flame photometers for sodium, cation conductivity for anionic species (chlorides, sulfates, phosphates, and so on) furnished some of the new measurement tools at the

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time. Continuous colorimetric analyzers, particularly for silica, began to be used at various points in the power plant cycle, such as makeup, feedwater, and steam condensate.

Today the power industry finds itself again in a period of new demands on instrumentation for the measurement of impurities in high-purity water. As expected, one of the demands is for lower limits of detection, now to the nearest 0.1 ppb. Another insistent demand is for *continuous* measurement. This demand is brought on not only by the desire to automate as much as is practical, but also by a growing realization that transient conditions, not readily detected by periodic grab sampling, can be of critical importance in determining system reliability.

When making measurements at the 1.0-ppb level, the strongest driving force for continuous measurements is the potential contamination that results from grab sampling and the associated manipulation of the sample between the sample point and the instrument used for analysis. As has become painfully evident, however, eliminating the manual operations associated with grab sampling does not eliminate all of the problems. One problem that still remains whether continuous or manual grab sampling is employed is the representativeness of the sample. This problem is especially significant when sampling steam, or any of the two or three-phase systems common to the steam power plant.

Not surprisingly, the methods of analysis, whether for continuous or grab samples, require an instrumental precision at least five times smaller than the lowest quantifiable number desired for operating the particular power plant system. For example, measurements for sodium must have a precision of 0.2 ppb if there is to be any confidence placed in operating levels of 1.0 ppb. Without this requirement for instrumental precision, it is not possible to discern, let alone solve, the problems of contamination and, later, of the representativeness of the sample itself.

One of the most difficult tasks for those working in the area of impurities in high-purity water is that of obtaining and maintaining absolute standards at the parts-per-billion level. The next most difficult task is to accept that the existence of highly reproducible results by a single operator does not make those results accurate. Bias, unknown to the single operator, may introduce serious error both in the results and in the conclusions drawn from them. The absence of standards and the potential bias of each given method as well as the random errors introduced at every step between the sample tap and the final reported result were the factors that strongly supported the employment of parallel techniques during the recently completed Electric Power Research Institute RP 1124 project at Arkansas Nuclear One, Unit 1.

Preliminary analysis of the results of this study have fully justified the concern expressed here. Although the concentrations of sodium obtained by the study at various points in the feedwater–steam cycle by widely different techniques were in reasonably good agreement, the results for chloride and sulfate were not. Not only that, but the differences for sulfate between the different techniques were not the same for different points in the cycle, which has raised still unanswered questions about what forms of sulfur were actually present at each of the sample points.

Although RP 1124 made only limited measurements for organic matter around the cycle, enough evidence of substantial organic carbon (50 to 800 ppb) was found to confirm that additional studies on a much broader scale using total organic carbon, gas chromatography-mass spectrometry, and liquid ion chromatography for organic compounds are warranted.

F. J. Pocock[1]

Monitoring Power Plant Water Chemistry

REFERENCE: F. J. Pocock, "**Monitoring Power Plant Water Chemistry,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 8–10.

ABSTRACT: The objectives and requirements for water quality monitoring in utility power plants is discussed in an overview fashion. This includes the available instrumentation and some discussion of further development work that is needed.

KEY WORDS: water quality monitoring, instrumentation, modern utility plants, power plants, water quality

Modern, efficient utility power plants require very large quantities of high-purity makeup water and nearly perfectly conditioned recycle water to ensure long-term reliable operation. This need requires continuous precise measurement of trace impurities at the parts-per-billion level and the careful monitoring and control of injected conditioning chemicals.

The principal objective of cycle water conditioning in power plants is the maintenance and repair of the protective oxide film on the water-side material surfaces of cycle components, water piping, and steam piping. An equally important objective is the prevention of damaging or efficiency-reducing accumulation of deposits on the energy conversion surfaces.

To accomplish this job of corrosion and deposition prevention, it is increasingly necessary to have full-time and real-time monitoring of trace cations, anions, and dissolved gases that may contaminate the high-purity water along with the monitoring and control of protective oxide film–preserving chemical additives.

Power plant water chemistry monitoring instruments to do this are reaching a high state of development, but much still needs to be done to improve their measurement precision and reliability.

The present developmental aim has been toward instruments which depend on direct physical measurements without the use of injected chemical reagents (the so-called chemist-in-a-box concept). The latter method is, how-

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ever, still widely applied (and necessary) for some measurements, such as soluble silica content, but it requires much more attention from chemical technicians and incorporates added uncertainties with the addition of possibly contaminated chemical reagent supplies.

The current water treatment philosophy and requirements for system component reliability have tended toward high-purity water systems which are treated with volatile chemicals (such as ammonium hydroxide and hydrazine) to control system pH and dissolved oxygen content. Deaeration is, of course, used to remove dissolved gases from the water. This simple high-purity water conditioning system has somewhat simplified measurement requirements.

Currently and commonly applied monitoring instruments include dissolved oxygen, hydrazine, dissolved hydrogen, pH, specific and cation conductivity, selective-ion electrodes (usually sodium), automatic flame photometers, turbidimeters, ion chromatographs, continuous membrane tape analyzers, continuous evaporators, and colorimetric analyzers (principally for silica).

The purpose of the measurement of dissolved oxygen and hydrogen is to evaluate deaeration efficiency and monitor metal surface corrosion, respectively. Specific conductance and pH are used for controlling and monitoring volatile alkaline additives while cation conductivity is a useful measure of contaminant ingress where an anion such as sulfate or chloride is involved. The other measurements are specific for certain cycle contaminants that are commonly encountered.

Specific continuous measurement of anions such as sulfate and chloride has been a significant problem over the years, but the development of the ion chromatograph appears to be overcoming this problem also and has been extensively tested in some power plants. There is a need for ensuring the interlaboratory and interplant accuracy of this instrument for these anions.

With the exception of sampling and monitoring parts-per-billion levels of transported corrosion products, the power station chemist now has at his disposal a set of well-developed instruments that allow him to measure and monitor the effectiveness of his water treatment program during power operation. The equally important off-line control must, of necessity, be mostly manual.

There have been many attempts at effective, continuous monitoring of corrosion product transport. The instruments used have included membrane filter tape analyzers and parts-per-billion turbidimeters. Some experimentation is being conducted on high-temperature laser turbidimeters for this purpose. However, the only way proven to be effective has been the use of specially designed in-line sampling systems that incorporate membrane filters and either cation and anion papers or ion-exchange columns or continuous sample evaporators. These corrosion-product and cation-anion accumulation systems are usually maintained at a fixed flow rate for a long enough period to allow reproducible and correlatable data to be developed. The continuous sample evaporators, although used in the field, have been more useful in evaporating large samples of high-purity water in the laboratory. An additional laboratory device to quantitatively measure organic material contaminations of high-purity water is the total organic carbon (TOC) analyzer.

The proven in-line monitoring instruments, when coupled with minicomputers and alarmed cathode ray tube (CRT) readouts in control centers, now allow good control of cycle water purification, contaminant ingress, and evaluation of total corrosion product transport.

These systems are, of course, not without problems. One of the most difficult problems to overcome has been the design of reliable sampling systems for corrosion products. Most commonly applied, at present, is the ASTM Specifications for Equipment for Sampling Water and Steam [D 1192 = 70 (1977)]. There are many ongoing discussions regarding proper sampling nozzles. There are also many debates regarding proper sampling of corrosion products from feedwater. Generally accepted is the need for a pitot-type sampling nozzle in the sample stream and a continuously flowing sample in a sample line whose length is as short as possible while still able to obtain the proper sample cooling. Even under these conditions, when sampling from high pressures and temperatures, deposition of both soluble and suspended materials in sampling lines is a problem. If flows are carefully controlled and valve movement minimized (to prevent dislodging of corrosion products), it is believed that good relative values are obtained. Experiments have shown, however, that corrosion product transport at the economizer outlet sample point (boiler inlet) may be low by more than a factor of 2.

O. Jonas[1]

Critical Overview of Power Station Sampling and Analysis of Water and Steam

REFERENCE: Jonas, O., "**Critical Overview of Power Station Sampling and Analysis of Water and Steam,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 11-23.

ABSTRACT: Because of the potential deleterious effects of impurities in water and steam, the current sampling and analytical practices are being critically evaluated, and methods and utilization of analytical data are being improved. To control the corrosion and efficiency loss, particularly in turbines, once-through boilers, reactors, and nuclear steam generators, low parts-per-billion levels of impurities are being sampled and analyzed.

The critical areas reviewed in this presentation are sampling, grab sample, continuous, and *in situ* analysis; analysis of organics; and utilization of the data for system control and corrosion prediction. Certain improvements and refinements in all these areas are discussed.

KEY WORDS: steam, water, power system, boiler, turbine, sampling, analysis, chemical control, instrumentation, nozzles, power plants, water quality

The cost of corrosion and additional fuel due to concentration of impurities in critical regions of steam power systems is estimated to be several billion dollars annually. As an example, the number of corrosion outages in a sample of about 500 utility turbines is given in Fig. 1. Over 160 units (30 percent) have experienced corrosion failures since 1964 with the annual rate up to 5 percent [*1*].[2] Corrosion in nuclear steam generators, boiling water reactor (BWR) piping, condensers, heaters, and boilers is also caused by water impurities. In most problem areas, the impurities concentrate locally from an average parts-per-billion concentration to concentrations of several percent. Typical concentration mechanisms include concentration in crevices, precipitation from superheated steam and deposition, evaporation and drying, and concentration due to a temperature gradient. The most frequent

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

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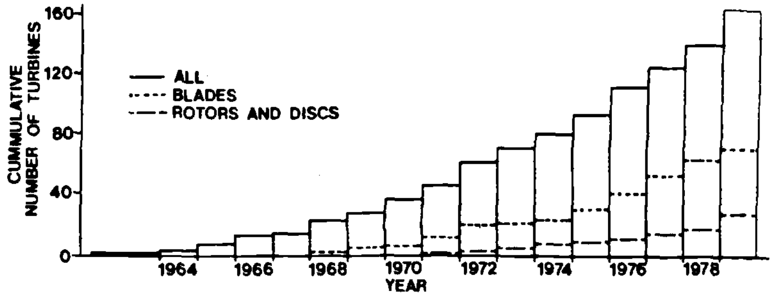

FIG. 1—*Turbine corrosion failures.*

sources of impurities are condenser leaks, air inleakage, improperly operated condensate polishers, and makeup water [*1,2*].

To reduce concentration of impurities in steam power systems, impurity levels have to be controlled to a few parts per billion. This introduces stringent requirements on sampling and analytical techniques. The important chemical parameters which need to be analyzed in different types of power systems include pH, conductivity, cation conductivity, free hydroxide (OH), dissolved oxygen, carbon dioxide (CO_2), ammonium (NH_4), hydrazine (N_2H_4), sodium, potassium, chloride, phosphate (PO_4), sulfate (SO_4), other sulfur compounds (S_xO_y), or at least total sulfur, carbonate (CO_3), silica (SiO_2), copper, iron, total organic carbon (TOC), organic acids, and resin fines. These are usually measured in samples cooled to room temperature. In addition, *in situ* pH and redox potential could be used to give valuable information on corrosiveness and concentration of impurities on metal surfaces in critical areas of a power system. Analysis of fluoride may be needed in systems utilizing titanium alloys.

This chemical information, even if available, would still not provide complete information on chemical species, which is needed for corrosion testing. More than 160 chemical species in water, steam, and turbine and boiler deposits (Table 1) have been identified.

Compilation of 28 chemical specifications, standards, and recommendations for steam, feedwater, and boiler water, all converted to equivalent steam chemistry (Table 2, from Ref *1*), gives an indication of the most commonly controlled chemical parameters. Some, such as pH, conductivity, oxygen, and sodium, are sampled and analyzed at several points of a power system.

Combination of Continuous Analysis and Grab Sampling

In analyzing problems of corrosion and deposition in turbines, we have found that a combination of on-line continuous analysis (pH, oxygen, conductivity, cation conductivity, sodium, and chloride) with liquid ion chromatography [sodium, NH_4, potassium, chloride, PO_4, SO_4] gives the best results. Continuous analysis of steam, just upstream of a corrosion area

TABLE 1—*Chemicals found in steam power systems.*

Oxides

Fe_3O_4—iron oxide
Fe_2O_3—iron oxide (α, γ, ϵ)
FeO—iron (II) oxide
$FeO(OH)$—iron oxide hydrate (α, β, γ)
$FeCuO_2$—copper iron (II) oxide
$FeCr_2O_4$—iron chromium oxide
$(Cr,Fe)_2O_3$—chromium, iron oxide
CuO—cupric oxide
Cu_2O—cuprous oxide
$Cu_6Fe_3O_7$—copper iron oxide
$CuAlO_2$—copper aluminum oxide
αAl_2O_3—alpha aluminum oxide
Cr_2O_3—chromium oxide
$CoFe_2O_4$—cobalt iron oxide
$NaFeO_2$—alpha sodium iron oxide
$Na_2Fe_2O_4$—sodium iron oxide
$Ca(AlO_2)_2$—calcium aluminum oxide
$MgFe_2O_4$—magnesium iron oxide
PbO—lead oxide
$PbFe_4O_7$—lead iron oxide
TiO_2—titanium oxide
$CaTiO_3$—calcium titanium oxide
Na_2O—sodium oxide
SiO_2—silica (hexagonal, rhombohedral, rhombic, tetrahedral, amorphous)

Silicates

Na_2SiO_3—sodium metasilicate
$Na_2SiO_3 \cdot 5H_2O$—sodium metasilicate pentahydrate
$Na_2SiO_3 \cdot 9H_2O$—sodium metasilicate nanohydrate
$\beta Na_2Si_2O_5$—sodium disilicate
$Na_4Si_3Al_3O_{12}Cl$—sodalite
$NaAlSiO_4$—sodium aluminum silicate
$Na[AlSi_2O_6] \cdot H_2O$—sodium aluminum silicate hydrate
$Na_4Al_2Si_6O_{17} \cdot 2H_2O$—sodium aluminum silicate hydrate
$Na_4Al_3Si_3O_{12}(OH)$—sodium aluminum silicate hydroxide
$Na_8Al_6SO_4(SiO_4)_6$—sodium aluminum sulfate silicate
$NaFeSi_2O_6$—sodium iron silicate
$Na_8[Cl(AlSiO_4)_6]$—sodium chloro hexa-aluminum silicate
$NaAlSi_3O_8$—sodium aluminum silicate
$Na_6Ca_2[(CO_3)_2(AlSiO_4)_6]$—sodium calcium carbonate aluminum silicate
Al_2SiO_5—aluminum silicate
$KAlSi_3O_8$—potassium aluminum silicate
$KNa_3(AlSiO_4)_4$—potassium sodium aluminum silicate
$KNa_3(AlSiO_4)_6$—potassium trisodium aluminum silicate
$K_{0.33}Na_{0.67}AlSiO_4$—nepheline
$Mg_4[(OH)_2Si_6O_{15}] \cdot 2H_2O + 4H_2O$—sepiolite
$Mg_6[(OH)_8Si_4O_{10}]$—magnesium octahydride silicate
$Mg_3Si_4(OH)_2$—magnesium silicate hydrate
$Ca_2Si_2O_4$—calcium silicate
$Ca_2Al_2Si_3O_{10}(OH)_2$—calcium aluminum silicate hydroxide
$Ca_2SiO_4 \cdot H_2O$—calcium silicate hydrate
$Ca_6[(OH)_2Si_6O_{17}]$—calcium silicate hydroxide (xonotlite)
$Ca(Al_2Si_4O_{12}) \cdot 6H_2O$—calcium aluminum silicate hydrate
$Ca_2NaH[Si_3O_9]$—sodium calcium silicate hydroxide (pectolite)

TABLE 1—*Continued.*

$CaMg(Si_2O_6)$—calcium magnesium silicate
$Ca_2Mg_5(OHSi_4O_{11})_2$—calcium magnesium hydroxide silicate
$3Al_2O_34Na_2O \cdot 6SiO_2 \cdot SO_3$—noselite
$(Fe,Mg)_7Si_8O_{22}(OH)_2$—iron magnesium hydroxide silicate
$Na_8Al_6Si_6O_{24}MoO_4$—sodium aluminum molybdenum oxide silicate
$Mg_3[(OH)\ Si_4O_{10}]$—magnesium hydroxide silicate
Zn_2SiO_4—zinc silicate
Amorphous silicon compounds

Sulfates

Na_2SO_4—sodium sulfate
$FeSO_4$—iron (II) sulfate
$FeSO_4 \cdot H_2O$—iron (II) sulfate hydrate
$NaFe(SO_4)_2 \cdot 12H_2O$—sodium iron sulfate dodecihydrate
$CaNa_2(SO_4)_2$—calcium sodium sulfate
$Cu_4SO_4(OH)_6$—copper sulfate hydrate
$Na_2Cu(SO_4)_2$—sodium copper sulfate
$CuFe(OH)_2SO_4$—copper iron sulfate hydrate
Al_2SO_4—aluminum sulfate
$Al_4SO_4(OH)_{10} \cdot 5H_2O$—aluminum sulfate hydroxide, pentahydrate
$CaSO_4 \cdot 2H_2O$—calcium sulfate dihydrate
$CaSO_4$—calcium sulfate
$Na_6CO_3(SO_4)_2$—sodium carbonate sulfate
$Na_8Al_6(SiO_4)_6SO_4$—sodium aluminum silicate sulfate
$(NH_4)_2SO_4$—ammonium sulfate

Phosphates

Na_3PO_4—trisodium phosphate
$Na_3PO_4 \cdot 12H_2O$—trisodium phosphate-12 water
Na_2HPO_4—disodium hydrogen phosphate
NaH_2PO_4—sodium dihydrogen phosphate
$NaPO_3$—sodium metaphosphate
$(NaPO_3)_3 \cdot 6H_2O$—trisodium metaphosphate hexahydrate
$FePO_4$—iron (III) orthophosphate
$Fe(PO_3)_3$—iron phosphate
$NaFe_3(PO_4)_2(OH)_4 \cdot 2H_2O$—sodium iron phosphate hydroxide dihydrate
$(Fe,Mn)_2[(OH)\ (PO_4)]$—iron manganese phosphate hydroxide (wolfeite)
$(Fe,Me)_2[(OH)\ (PO)_4]$—wolfeite
$Na_2(Fe,Mn)_5[PO_4]_4$—sodium iron manganese phosphate
$Ca_4P_2O_9$—calcium phosphate
$Ca_5[(OH)\ (PO_4)_3]$—calcium phosphate hydroxide
$Mg_x(OH)_y(PO_4)_z$—magnesium hydroxide phosphate
Sodium, calcium, iron, copper, nickel—mixed phosphate

Carbonates

Na_2CO_3—sodium carbonate
$Na_2CO_3 \cdot H_2O$—sodium carbonate monohydrate
$Na_2CO_3 \cdot 10H_2O$—sodium carbonate decahydrate
$NaHCO_3$—sodium bicarbonate
$Na_3H(CO_3)_2 \cdot H_2O$—sodium hydrogen carbonate monohydrate
$Na_3H(CO_3)_2 \cdot 2H_2O$—sodium hydrogen carbonate dihydrate
$5Na_2O \cdot 8CO_3 \cdot 3H_2O$—sodium carbonate trihydrate
$3NaAlSiO_4 \cdot Na_2CO_3$—sodium aluminun silicate sodium carbonate
$CaCO_3$—Calcium carbonate
$CaNa_2(CO_3)_2 \cdot 2H_2O$—calcium sodium carbonate dihydrate
$CuCO_3Cu(OH)_2$—copper carbonate, basic
$(NH_4)_2CO_3$—ammonium carbonate

TABLE 1—*Continued.*

Chlorides

$NaCl$—sodium chloride
KCl—potassium chloride
$FeCl_2$—iron (II) chloride
$FeCl_3$—iron (III) chloride
$CrCl_2$—chromium (II) chloride (possible)
$CrCl_3$—chromium (III) chloride (possible)
NH_4Cl—ammonium chloride
$Cu_2(OH)_3Cl$—copper (II) oxychloride

Acids

H_2SO_4—sulfuric
HCl—hydrochloric
CH_3COOH—acetic
$CH_3CH_2CO_2H$—propionic (propanoic)
$CH_3CH_2CH_2CO_2H$—butyric (butanoic)
$HCOOH$—formic
H_2SiO_3—silicic
H_3BO_3—boric
$H_2S_xO_6$; $x = 3$, 4, or 5—polythionic

Gases

CO_2,N_2, O_2, H_2, Cl, H_2S

Uncompounded elements

Silicon
αFe—alpha iron
Graphite (carbon)
Copper
Chromium
Sulfur

Other

$NaOH$—sodium hydroxide
$LiOH$—lithium hydroxide
$AlOOH \cdot nH_2O$—aluminum oxide hydroxide
NaF—sodium fluoride
NO_3—nitrate
Oils and oil decomposition products

Other additives

NH_4OH—ammonium hydroxide
C_4H_9NO—morpholine
$C_6H_{11}NH_2$—cyclohexylamine
N_2H_4—hydrazine
H_2O_2—hydrogen peroxide
Na_2SO_3—sodium sulfite

EPA organics

Methoxychlor
Toxaphene
2,4,5-TP (silvex)
Traces of endrin, lindane, 2-4-D

TABLE 2—*Steam chemistry limits for normal operation.*

		Conductivity, μS/cm		Maximum, ppb										
	pH	Specfic	Cation,	O_2	Na	K	Cl^-	SiO_2	Cu	Fe	SO_4	PO_4	Free OH	Other
Westinghouse, steam^b			0.3	10	5		5	10	2	20				
Westinghouse, PWR-AVT	8.5 to 9.6 Cu		(2.0)	5	0.25		0	4					0.4	SS (1.0)
General Electric, steam^b			0.2		3									
U.S. NRC and G.E., BWR	5.6 to 8.6	(1.0)	0.1				0.5							$O_2 \sim 30$ ppm
Allis Chalmers Limit^b			0.3D		Na + K < 10			20	3	20				
			0.20T		Na + K < 10			20	3	20				
A-C recommended^b			0.1		Na + K < 10			10	1	10				
VGB, steam^b			0.2		Na + K < 10			20	3	20				
VGB, recycle, FW	>9.0			20					10	50				FW CO_2 < 1 ppm, oil < 0.5 ppm
VGB, supercritical	9.0 to 9.5		0.2	20				20	3	20				FW CO_2 < 1 ppm, oil < 0.3 ppm
VGB, BWR	5.6 to 8.6	(1.0)					0.5	16						
VGB, PWR-AVT	>9.0		FW0.2	FW 20			2.5	16	3	20				
VGB, PWR-PO4	8.8 to 9.5	(50.)	FW0.2	FW 20			2.5	16	3	20		15		Na/PO4 < 2.6
KWU, steam^b			0.2		Na + K < 5			20	FW 3	FW 20				
CEGB, steam D^b					10			20						
CEGB, drum	9.1 to 9.3						1.0	20						
CEGB, supercritical	9.0 to 9.3		0.1	15	5			20	10	Fe + Ni < 3				
CEGB, Magnox FW	9.0 to 9.3		0.1	15	10			20	Cu + Fe + Ni < 20					
CEGB, AGR, FW	9.0 to 9.3		0.1	15	5			20	Cu + Fe + Ni < 10					
JIS, recycle	8.5 to 9.5		0.3	7				20		FW 5		3		
JIS, supercritical	9.0 to 9.5		0.3	7				20	2	10				
USSR, Martynova^b	8.9 to 9.1							15	5	20				
Mitsubishi, PWR	8.8 to 9.2	(5.0)	(0.3)	5			0.25	2	5	15			0	Ni 5, Na/Cl < 0.7
Hitachi, supercritical			0.3		0.15			20	2	10				
B&W, PWR-OT	8.8 to 9.2 Cu		0.5	7	2			20	2	20				TS 50, Pb 1
	9.3 to 9.5													
Combustion, D-AVT	8.5 to 9.0													TS (2)
Combustion, D-PO4	9.4 to 9.7							20				20		TS (50)
Combustion, supercritical	9.2 to 9.4			5	10									TS 50
Calgon, drum steam^b	8.0 to 9.0	(2.0)						10				0	0	
Averages	8.55 to 9.26		0.22	11.6	6.5		1.5	17.4	5.0	17.4		7.0	0.1	

[a] Key to abbreviations:

D = drum or recycle boiler
AVT = all volatile treatment
Cu = systems with copper
TS = total solids
OT = *once-through boiler*
PO_4 = phosphate treatment
FW = feedwater limits
SS = suspended solids

Numbers in parentheses are parts-per-million concentrations or conductivity of boiler water.

[b] Direct steam limits.

(usually the low-pressure turbine) gives time and load-related information which allows a correlation of chemical upsets with a particular mode of system operation. The around-the-cycle grab sampling allows identification of impurity sources, such as condensers, condensate polishers, makeup, attemperating sprays, or the boiler. All these methods provide information from 1 ppb up. Forty-four fossil and nuclear units have been monitored so far by Westinghouse; six of them involved intensive total plant surveys lasting more than a week. Improvements in chemical operation have been suggested and a correlation of chemistry, deposits, and corrosion found.

In addition to this continuous and grab sample analysis, grab samples for analysis of TOC, and sometimes for U.S. Environment Protection Agency (EPA) *organics* analysis, and for analysis of *organic acids* by ion exclusion chromatography are collected. Surprisingly high concentrations of organics have been found, with TOC up to 8 ppm (in several units using all volatile water treatments). Frequently, concentrations of TOC are orders of magnitude higher than concentrations of all other impurities. During recent chemistry monitoring in a once-through pressurized water reactor (PWR) unit, 32 ppb of methoxychlor was found in feedwater. Organic acids that are frequently present are listed in Table 1.

Analysis of gases in low-pressure steam by mass spectroscopy has been attempted on steam sampled at pressure and temperature into stainless steel bombs [*3,4*]. The results were erroneous because of the chemical reactions and adsorption in the containers. They improved with a use of gold-plated containers, but the work had not been brought to a successful conclusion. Except for analysis of oxygen and hydrogen in condensate, we don't have a direct, qualified method for analyzing parts-per-billion levels of gases in steam. Cation conductivity and air inleakage measurements indicate high concentration of *carbon dioxide* in many units. Analysis and control of carbon dioxide and carbonates are needed because of the corrosion effects on carbon and low-alloy steels.

Analytical Round Robin

Numerous investigators, water consultants, and utilities are starting to use analytical techniques to analyze parts-per-billion levels of impurities. These techniques include ion chromatography, concentration by evaporation and on ion-exchange columns followed by wet chemistry, ion-sensitive electrodes, atomic absorption, emission, and inductively coupled plasma. Although the analytical accuracy within one laboratory seems to be adequate, comparison of results from different laboratories is needed to provide information on the practical reproducibility and usefulness of the parts-per-billion data. Recent comparison of sodium, chloride, and sulfate results by three investigators, and problems with ammonium hydroxide interference in ion chromatographic analysis of chlorides, indicate that up to order-of-magnitude differences may exist. This was particularly significant for *sulfates,* where the differences were up to 1 order of magnitude. There are unanswered questions about efficiency of collection on ion-exchange columns, efficiency of elution, diffusion of ions in and out of the resin beads and grab sample containers, adsorption, interferences, temperature effects, contamination, and so on.

It has been suggested that an analytical round robin program be initiated as soon as possible, in which several single compound and mixed standards will be made available for sampling and analysis by different laboratories using their sampling hardware and analytical procedures. Sampling and analysis of sodium, chloride, sulfate, ammonia, TOC, and several organic acids should be included. The American Society for Testing and Materials, (ASTM), Electric Power Research Institute (EPRI), or the National Bureau of Standards (NBS) should assume the responsibility. The American Society of Mechanical Engineers' Steam Purity Control Task group is presently formulating such a round-robin program.

Sampling

Improper sampling can be a source of greater errors than the analysis. Sampling problems are initiated during system design and installation when considerations on clean sample cooling water, short stainless steel downsloping lines, and flow Reynolds numbers (recommended higher than 4000) are not included. There is little selection of qualified samping nozzles, particularly for superheated and wet steam. The ASTM Sampling Steam [D 1066-69 (1975)] nozzles are rarely used in the large steam pipes of modern utility systems. With attemperation, their performance on sodium was reported to be good [*5*].

For sampling of superheated steam in large-diameter pipes, such as in the low-pressure turbine inlet pipes, we have designed and qualified an isokinetic pitot-type nozzle which removes the sampling location several inches from the pipe wall. The nozzle should be immediately followed by a large flow section cooler to avoid flow choking and deposition.

We have also tried to sample low-pressure extraction steam (the highest pressure one) after it condenses in the feedwater heater, by tapping the heater drain with a surface tap. During a steady load, this gives good agreement with the low-pressure turbine inlet steam samples.

In a *multiple-phase flow,* such as when sampling wet steam with suspended solids (three phases), it is difficult to draw a representative sample of all phases.

Sample flow disturbances, particularly in low Reynolds number lines where the sample impurities can plate out, can produce up to several orders-of-magnitude concentration changes. During a recent chemical monitoring program, a short interruption of moisture separator drain sample flow resulted in an apparent increase of sodium concentration from 40 to more than 1000 ppb. An increase of the sample flow from 600 ml/min to approximately 900 ml/min resulted in a sodium spike from 25 to 300 ppb. The 6 mm (0.25 in.) stainless steel sample line was over 275 m (900 ft) long and had 71 right-angle bends. Similar observations are described in Ref *6*.

The plated-out impurities contain metal oxides which can retain soluble impurities by ion exchange. Chemical reactions in sampling lines include thermal decomposition of hydrazine and reaction of hydrazine with oxygen and oxides. These chemical reactions are minimized by cooling of the sample immediately after the sample probe and by short sample lines.

Most continuous analyzers are sensitive to the sample flow rate, and proper sample pressure reduction and flow control are necessary.

Dissociation of water and increase of oxygen concentration in the sample stream had been observed when a pressure-reducing valve was used on high-pressure, high-temperature samples. Use of the rod-in-tube pressure-reducing device corrected the situation.

What to Sample and How Frequently

The first objective in sampling and analysis should be to *prevent ingress of impurities* into a power system as soon as possible. For this, fast-response, preferentially continuous, reliable instrumentation is needed. For example, triplicate cation conductivity cells are installed in condenser hot wells in many West German power stations, so that the operator can trust the signal and respond to a condenser leak within minutes. Alarms from these cells are in the main control room.

Similarly, for the other potential sources of impurities, sample connections should be immediately downstream of the source. For the modern units which utilize large volumes of water and can be sensitive to small increases of impurity concentration, *continuous sampling and analysis* is imperative.

For a system chemistry control, response to changes does not have to be so fast, particularly in drum boiler units, which have greater chemical inertia. However, there may be some system chemical characteristics that can result in fast feedwater or steam chemistry changes with load, pressure, and temperature changes. These include hideout, drying and washing in superheaters and moisture separator–reheaters (MSRs), and attemperation.

Since *turbine steam chemistry* cannot always be adequately predicted from feedwater, boiler blowdown, or condensate chemistry, and since all major turbine vendors now have steam chemistry limits (see Table 2), sampling and analysis of steam is recommended. Because of the corrosion in low-pressure turbines, and the possible chemical effects of MSRs in nuclear units and reheaters in fossil units, low-pressure turbine steam is now sampled and analyzed in some stations.

We have recently recommended that *air inleakage* into a utility power system should not exceed 0.03 m^3 (1 SCFM) per 100-MWe rating. The air inleakage is usually measured as a volume of noncondensable gases exhausted from the system by air ejectors and vacuum pumps in condensers. Rotometers or orifices with differential manometers are used. To find locations where the air is leaking into the system (such as valve seals, sight glasses, and pump seals), a tracer gas with an appropriate detector is used. With Freon and a halogen leak detector, about 10^{-6} cm^3/s of the tracer gas can be detected. With helium and a mass spectrometer, 10^{-12} cm^3/s can be detected.

Several countries have guidelines, specifications, or standards prescribing what streams should be sampled, what should be analyzed, and how often [*7,8*]. In view of these specifications and the experience in the United States, some utility and boiler vendor guidelines for system chemical sampling may not be adequate. As an example, an adequately sampled drum boiler unit is shown in Fig. 2 and a once-through unit in Fig. 3 [*7*].

Use and Treatment of Analytical Data

Both the absolute value of a chemical reading and its trend are important for a system chemical control. These can be compared with specified limits and previous experiences. Signals from the control instrumentation should be wired to the control room and used by the main operators. In addition, for prediction or explanation of deposition, oxidation, and corrosion damage, integrated chemistry (for example, parts-per-million days of chloride in a boiler or a turbine) and time above a limit are useful.

For an assessment of corrosiveness of the environment, cation to anion molar ratios need to be calculated.

For evaluation of condensate polisher performance, ratio of impurities (sodium, chloride, SO_4, cation conductivity) in influent to the effluent, together with their absolute values, are useful measures.

The most important chemical instrumentation used for unit control may be duplicated or triplicated to increase its reliability (such as the triplicate cation conductivity meters on condenser hot-well water), and their signals need to be compared.

Currently, station analytical data are usually underutilized, in both system control and corrosion prediction. To improve data utilization through better presentation, storage, and analysis, computer treatment, storage, and plotting are being introduced.

Conclusions and Recommendations

1. The initial years of a power system operation, transient operation, and improper lay-up account for many of the chemical and corrosion problems. Intensive chemical monitoring and establishment of system chemical characteristics during commissioning, continuous instrumentation following transients, and lay-up chemistry monitoring would improve the situation.

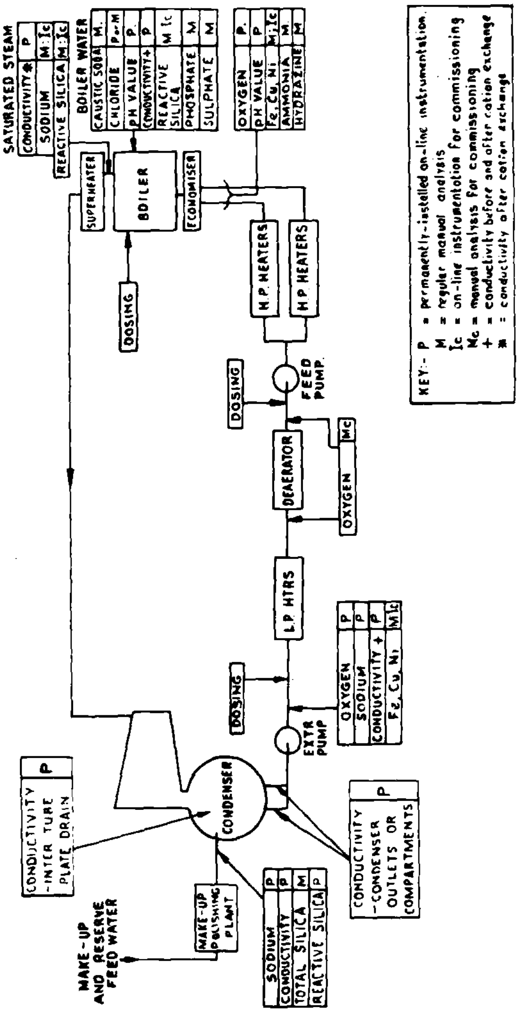

FIG. 2—*Sampling and analytical requirements for drum boiler systems [7].*

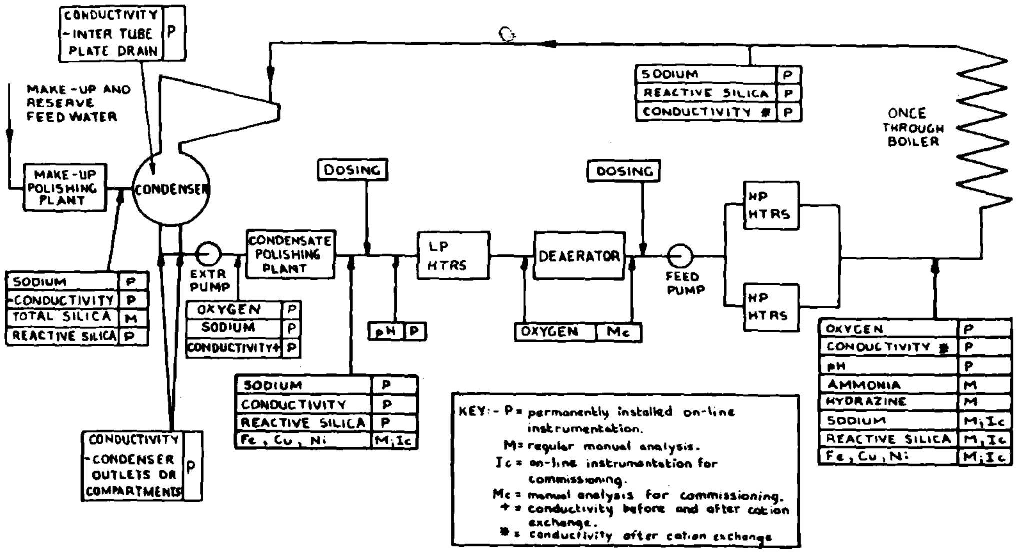

FIG. 3—*Sampling and analytical requirements for once-through systems [7].*

2. Both continuous monitoring and grab sample analysis are needed to control major chemical parameters and to provide fast, reliable information to operators. Better analytical techniques for organics, CO_2, and sulfur compounds should be applied in power systems.

3. Practical interlaboratory accuracy and sensitivity of techniques for sampling and analysis of parts-per-billion levels of impurities should be established. An interlaboratory round robin program to sample and analyze typical single and mixed impurities should be initiated as soon as possible.

4. Sampling can influence sample composition by several orders of magnitude. Sampling nozzles need to be developed and qualified and design and installation of sampling systems should improve. Short sample lines with coolers next to the sampling point, chilled condensate quality cooling water, and a flow Reynolds number above 4000 are recommended.

5. Analytical techniques for *in situ* analysis of steam, water, and deposits, including high-temperature pH, conductivity, and redox potential, are needed.

6. More attention should be paid to the measurement, monitoring, and control of air inleakage.

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T. C. Hoppe[1]

A Consulting Engineer's Role in Power Plant Instrumentation for Measurement of High-Purity Water Quality

REFERENCE: Hoppe, T. C., "**A Consulting Engineer's Role in Power Plant Instrumentation for Measurement of High-Purity Water Quality,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 24–29.

ABSTRACT: The reassessment of high-purity water is a never-ending process. Although the best available instrumentation is used, it is not always good enough when component failures are attributed to infinitesimal impurities in the water. This paper describes the necessary technology and personnel requirements for implementing a successful water quality control program.

KEY WORDS: power plants, low-level impurities, supercritical unit, instrumentation, water quality, consulting engineers

Over the past 30 years, operating pressures of steam generators for power production have increased from low to high subcritical and to supercritical. Makeup water quality had to meet the stringent demands imposed by the higher pressure operation, with condensate polishing becoming a mandatory requirement for once-through or supercritical as well as subcritical drum pressure operation in excess of 2200 psi.

The transition was accomplished most successfully only because of the continual efforts of professional societies such as the American Society for Testing and Materials (ASTM) and the American Society of Mechanical Engineers (ASME) to improve and maintain high-purity cycle water quality. Meanwhile, a continuous evolution of instrumentation developed to measure impurities routinely in not only parts per million but parts per billion and trillion. The reassessment of what is meant by high-purity water is a never-ending process.

However, as one author has stated, all of these measuring devices have a

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single common problem, which is the preparation of zero impurity water to be used in their calibration or standardization. This problem, however, is relatively minor compared with the possibility that maintaining "ultrahigh-purity cycle water" to meet the criteria of turbine and steam generator manufacturers will be an economic challenge. Not too many years ago, steam purity to the turbine was satisfactory as long as silica did not exceed 0.02 ppm. That criterion was subsequently changed to 0.01 ppm, with sodium at 3 ppb as one of the other parameters. Presently, there are theoretical indications that chloride and sulfate in the steam at less than parts-per-billion levels can contribute to stress-corrosion cracking of low-pressure turbine blades.

Notwithstanding the availability of instrumentation to measure such low-level impurities, though with varying degrees of reliability, what can the design engineering consultants specify that will ensure power plant operation uninterrupted by water-related problems? Although the best available design technology is used, it is ironic to find that the best is not good enough when, in some cases, component failures are attributed to infinitesimal impurities in the water.

The basic water technology design by Black & Veatch for a supercritical unit would include pretreatment of the service water supply, including the reduction of colloidal silica followed by filtration. The water to be used as makeup would be routed through an activated carbon filter for the removal of residual chlorine and organics, then through a six-bed demineralization system comprised of, in sequence, primary cation, weak-base anion, vacuum degasifier, secondary cation, and strong-base anion, followed by a polishing pair of cation–strong-base exchangers. Typical effluent quality will show specific conductance at about 0.1 μS and silica at about 5 ppb and less. The makeup is routed to a high-purity water storage tank; a second storage tank is maintained for condensate surge or dump during any period of condenser tube leakage. Full-flow, deep-bed condensate polishing is included in the basic design for normal filtration in the start-up modes of operation and for ion exchange at all times.

Instrumentation in this sampling system design for a supercritical unit would include the capability of recording the following:

1. Cation conductivity:
   makeup to the condenser
   influent and effluent condensate polisher
   economizer inlet
   convection pass outlet
   primary superheater outlet
2. Specific conductance:
   influent and effluent condensate polisher
   after chemical feed
   economizer inlet

3. pH:
   influent condensate polisher
   economizer inlet
4. Dissolved oxygen:
   influent condensate polisher
   deaerator outlet with alternate use to inlet
5. Sodium:
   influent condensate polisher
   effluent condensate polisher
   deaerator inlet, alternate use with polisher effluent
   deaerator outlet, alternate use with polisher effluent
   heater drips, alternate use with polisher effluent
   economizer inlet, alternate use with polisher influent
   convection pass outlet, alternate use with polisher influent
   primary superheater outlet, alternate use with polisher influent
6. Hydrazine:
   condensate after chemical feed, alternate use with economizer inlet
   economizer inlet

For a high-pressure subcritical drum unit without condensate polishing, cation conductivity measurements for condenser tube leak detection would be provided from internally located cells in both the high-pressure and low-pressure condensers. Boiler water would be monitored continuously for pH, specific conductance, and silica; saturated and main steam would be monitored for specific conductance and cation conductivity, in addition to the usual routine recorders for sodium, dissolved oxygen, pH, and hydrazine at other sampling points. All automatic sampling systems are designed for temperature control at 25°C.

Grab samples are analyzed for each pertinent system related to the cycle regardless of the instrumentation.

It might be noted that hydrogen analyzers are not specified in either subcritical or supercritical design or, at least for the present, in the more exotic sampling systems for continuous monitoring of chlorides, sulfates, nitrates in the main or crossover steam, or total carbon in the makeup and condensate.

From a realistic standpoint, it is immaterial what automatic analyzing instrumentation has been provided to monitor the cycle water quality if the operating personnel have a detached interest in the results. Lack of training to interpret data, lack of incentive, poor pay, jurisdictional disputes, and inadequate maintenance are a few items that can nullify a well-designed program of instrumentation. Even though a water quality control program at an electric generating station is a primary function in preventive maintenance to ensure on-line operation, there have been too many instances where managers of utilities have either disregarded or were uninformed of its importance.

Conversely, there are other utilities that know a well-trained and well-paid water technology group can pay for itself many times over by eliminating, or at least minimizing, just one major outage from a water-related incident.

But, first, the primary professional group should be composed of experienced graduate chemists, preferably with electronic, mechanical, and corrosion engineering background and instilled with a conscientious incentive for performance, with adequate compensation as a perpetual inducement.

Second, a workable and practical liaison with all other station groups and management without jurisdictional edicts can contribute to the success of a water quality control program.

Third, all station chemistry data should be reviewed periodically by an outside consultant with expertise in water treatment to assess if any corrective action is needed before deviations become significant.

Unfortunately, a major disruption of a well-intentioned quality control and preventive maintenance program can be caused by condenser tube leakage in varying amounts, especially if there is no condensate polishing system. Further complications develop in the cycle if the dispatcher cannot arrange an immediate reduction in the unit load to correct the leakage until after peak operation. Notwithstanding the extensiveness of instrumentation provided, uncorrected contamination of the condensate is one of the two primary contributors to problems at electric generating stations; the other contributor is dissolved oxygen.

Condenser tube leakage is a highly variable condition and can stem from various causes, one of which is quality control from a tube manufacturing standpoint, tube contamination during shipment, shoddy installation of tubes, and quality of the circulating water. The operating water technology group can do little about the first three items but can be most important in maintaining circulating water quality to minimize deposition that can lead to repetitive tube leaks. Tube cleanliness is too frequently disregarded, and failures are wrongly attributed to an improper choice of alloy when leaks develop. In some stations it is not known what the cleanliness factor is supposed to be at initial operation or what it should be afterwards.

The philosophy of quality control is applicable whatever the source of cooling water. The recirculating system, whether with freshwater or seawater makeup, can be chemically controlled economically to prevent scaling or biological fouling to reduce condenser tube failures. Once-through systems using seawater only need the judicious shock application of a biocide. In either case, an on-line mechanical tube cleaning system can be a valuable asset to minimize deposition or blockage to maintain cleanliness and prevent tube failures.

Black & Veatch has long realized the importance of maintaining water quality parameters in *all* systems pertinent to electricity generation in the initial design. The overall design incorporates the best available technology not only in the water treatment equipment but also in the choice of instrumentation and sampling to provide complete data. This is followed by preparing control guidelines for all systems, the analysis to be made at what frequency for grab samples, and a log sheet for reporting analytical data in all modes of operation with added emphasis on both shutdown and start-up.

Realizing that many of the subsequent operational problems in water treatment can develop before operation, this company provides consulting services pertaining to all water treatment processes and initial acid cleaning, including preoperational training, through the initial operation and 6 months to a year thereafter to ensure adherence to basic quality control.

Based on past experience, the inherent high quality of personnel in a station water technology group is much more essential than the amount of instrumentation; the alternative of specifying more and more automatic analyzers with ever-increasing complexity should not be, nor can it ever be, a substitute.

The majority of water-related outages in a central generating station can be narrowed down to either uncorrected condenser tube leakage or inadequate air removal in the preboiler cycle, or both, whether in normal or cycling operation, assuming that high-purity makeup water is constant. And, along this line, when makeup is kept at a minimum of 0.1 percent or less, the potential for water-related outages is reduced proportionately, particularly when the preboiler cycle is copper-free.

With a technology group having the background discussed previously, the basic automatic analyzers-recorders needed for supercritical steam generation could be reduced to one or two for sodium, two or three for cation conductivity, one or two for specific conductance, and perhaps the same for pH. Neither dissolved oxygen nor hydrazine automatic analyzers should be needed; the system demand for hydrazine is a more reliable guideline for air inleakage. A well-equipped laboratory for analyses of all types of samples is an economical supplement to decrease the amount of automatic recordings.

Design engineers are facing a dilemma in specifying power plant instrumentation for measurement of high-purity water, granting that part-per-billion or part-per-trillion levels of supposed contaminants can be measured. The design engineer has to provide such instrumentation as a concession to measuring the criteria imposed by the turbine supplier. But, what is the approach to water conditioning to be if it is conjectured that part-per-trillion levels of contamination in the cycle are responsible for stress-corrosion cracking of low-pressure turbine blades? What is the next step in improving condensate polishing when the effluent sodium quality is only 0.1 ppb? Is high-pressure steam to be polished to protect the turbine, and how can it be done economically? Variable pressure operation may reduce some of the station's generating capability but at the same time minimize potential water-related outages. If supercritical operation produces more outages, then another dilemma arises concerning the comparative economics of operating subcritically. Much more needs to be learned about the cycle materials of construction in relation to the effect of parts-per-trillion contamination levels instead of depending on better instrumentation to measure those levels.

Still another question that needs to be answered is why, under identical conditions of operation, certain turbines are prone to showing stress-corrosion cracking and others are not. And the same question applies to boiler tube failures. Progress will be made; investigations are already underway, largely stimulated by the appropriate committees of ASTM and ASME, to find the answers.

James Brown[1]

Power Plant Instrumentation for Measurement of High-Purity Water Quality

REFERENCE: Brown, James, "**Power Plant Instrumentation for Measurement of High-Purity Water Quality,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 30–33.

ABSTRACT: Work undertaken by Ontario Hydro, Toronto, to determine levels of feedwater impurities, including corrosion products and condenser cooling water inleakage contaminants, is reviewed. Corrosion product measurement using a grab method gave some useful data but was found to be too labor-intensive. Continuous analysis of corrosion products, in conjunction with a valveless capillary sampler, is now being evaluated as a method. Ion chromatography appears to be a promising technique to determine anions in feedwater. Tests to adapt such an instrument for continuous analysis are planned.

KEY WORDS: power plants, instrumentation, water quality, corrosion products

A program to determine the concentrations of corrosion products entering the steam generators of fossil fuel fired and nuclear units of Ontario Hydro, Toronto, Canada, during each phase of operation was reviewed. The overall objective of the program was to provide practical recommendations for the institution and maintenance of corrosion control methods for present and future units.

Each sample was collected by passing a known volume of water through a Millipore filter and cation resin–impregnated paper to remove particulate and soluble materials, respectively. The filter and resin paper combinations were contained in high-pressure filter holders attached to the ends of the normal sampling lines at the generating stations. Each sampling system was fitted with a bypass line to allow bleeding of the sample line between the taking of samples and also to allow occasional grab samples to be obtained. The material collected by the filters and resin papers was analyzed simultaneously for iron, copper, nickel, and zinc (most Ontario Hydro units have ad-

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miralty brass condensers and low-pressure heaters and Monel or carbon steel high-pressure heaters) by energy-dispersive X-ray fluorescence spectrometry.

During normal unit operation the concentration of iron was usually below 10 μg/litre, and the concentrations of copper, nickel, and zinc were generally less than 5 μg/litre. The concentration of iron often decreased between the condensate extraction pump and the economizer inlet, particularly across the high-pressure heaters. The decrease is probably due to deposition on the walls of the feed system. Occasionally the element concentrations increased to values above 10 μg/litre, often accompanying load changes greater than 50 MW. During unit start-up large increases in element concentration, often to the milligrams-per-litre range, occurred shortly after synchronization; this was probably the result of sloughing and exfoliation of scale initiated by expansion, temperature differentials, and the inflow of steam to the shell sides of the feed preheaters. During boiler shutdown relatively small increases in the levels of metallic impurities in the feedwater and condensate were observed.

By sampling at both the inlet and outlet of condensate polisher systems, quantitative estimates of the ability of the polisher to remove soluble and insoluble material were obtained. The polishers are only used during unit start-up, and it was found that the system design profoundly affected the performance. A system in which the effluent from the polisher is recycled to the hot well was much less efficient for corrosion product removal than one in which the effluent was piped to the condensate line downstream of the polisher intake. The degree of exhaustion of the resin had no measurable effect on the polisher performance.

Further work showed that a tenfold increase in the dissolved oxygen level in the low-pressure heater system from 14 to 140 μg/litre produced an increase in copper concentration only after 270 h of steady load operation. This result appeared anomalous in terms of current corrosion theory but could be explained by assuming that the higher dissolved oxygen concentration creates a much thicker oxidized layer on the heater tube internals. The scale may only be dislodged during periods of aggravated thermal and mechanical cyclic stresses, such as those applied to the unit during start-up or large changes of load.

As expected, a change of less than 0.5 pH units from the normal operating range of pH 8.8 to 9.0 was followed by a change in the relative amounts of corrosion products; copper levels increased with an increase in pH, and iron levels decreased, whereas the reverse occurred with a drop in pH. The effect was most severe in the high-pressure heater drip samples (Monel tubes with carbon steel shells).

A change in the point of dosage of hydrazine (used for oxygen control) from the deaerater outlet to the condensate pump discharge produced no change in corrosion product levels during normal operation. However, following the change in treatment, higher copper levels were noted in the low-pressure heaters effluent. This result is difficult to interpret, and more data are required before a firm conclusion can be made. Corrosion studies designed to compliment the field work are planned for a laboratory model boiler corrosion test loop.

Sampling and analysis of feedwater by the technique described here is time-consuming and extremely labor-intensive. Techniques and instrumentation available for continuously monitoring total iron and copper in boiler feedwater are being investigated by the Research Division of this company. Such a continuous analyzer consists of four separate units, namely, the capillary sampler, the sample splitter, the dissolution module, and the analyzer.

The valveless capillary sampler provides an unbiased sample of feedwater particulates, with the capillary tubing acting as both sampling probe and pressure reducer. The stainless steel capillary is inserted into the feedwater line with the entry nozzle pointing upstream. The capillary is mounted in a high-pressure carbon steel probe which is welded into the process pipe. A cooler is also provided. Blockage is cleared by forcing deionized water in a reverse direction through the capillary by means of a suitable pump.

The sample splitter reduced the flow of sample from the capillary sampler to the dissolution module and the analyzer. The capillary sample flows into the splitter at the top and the majority of the sample exits at the bottom to waste. The sample for analysis is drawn isokinetically through a glass probe which is pointed in the direction of flow (assumed to be laminar through the main body of the splitter).

The sample from the splitter is dosed with acid prior to its entry into a length of coiled glass tubing approximately 12 m long. The coil is immersed in a heating bath regulated at 95°C. After the sample exits the bath, it passes through a cooler before entering the analyzer. The dissolution of particulates has been found to be complete with 10 g/litre thioglycolic acid and hydrochloric acid for iron and 0.25 mol/litre nitric acid for copper.

The function of the analyzer is to take the prepared sample and automatically analyze for the element of interest, usually by a colorimetric technique. The sensitivity, precision, drift in response, lag time, and time constant of a continuous flow analyzer are dependent not only on the chemistry of the colorimetric reaction but also on the design of the hydraulic system. Lag time is the time elapsed from the entry of the sample into the monitor until a steady-state response is measured in the detector. The time constant or washout time is the time elapsed from the entry of a portion of sample into the detector of the analyzer until a steady response is recorded. Monitors with long time constants cannot respond to rapid changes in feedwater corrosion product levels during start-up or load changes.

Work has also begun to determine concentration levels of anions in the condensate, feedwater, boiler, and steam system using ion chromatography. Initially, the object of the study is to evaluate materials for storage of aqueous solutions for trace and ion analysis. Two concentration ranges, 0 to 5 mg/litre and 0 to 50 μg/litre, were examined. Fluoride, chloride, nitrate, and sulfate can be easily measured in the higher range by direct ion chromatography analysis. Soft glass as a storage material gave large chloride blanks, whereas polyethylene gave large fluoride blanks. Pyrex glass and polystyrene appeared suitable for storage. However, chloride blanks were of the order of 30 μg/litre even with these materials. This was attributed to manual manipulation, and modifications were made to the ion chromatograph to allow for automatic injection. Direct measurements to 2 μg/litre fluoride, 4 μg/litre chloride, and 20 μg/litre nitrate and sulfate are now possible.

Little data are available for storage materials over the low-concentration range. A preconcentration technique must be used at this level, but fluoride cannot be measured using such a method. A continuous dilution system for preparing standards has been developed for good reproducibility. A chloride detection limit as low as 0.5 μg/litre has been obtained.

In summary, extensive data were obtained on feedwater line corrosion product concentrations using an intermittent sampling technique. However, some of the field work will be repeated and extended using a model boiler and corrosion test loop to check seemingly anomalous results. Continuous analysis for metallic contaminants in feedwater is preferred. Work has begun to determine anion concentrations in the water–steam cycle over various operating modes.

General Guidelines and Requirements for Monitoring

D. E. Noll[1]

Status of Continuous Monitoring in Central Stations

REFERENCE: Noll, D. E., "**Status of Continuous Monitoring in Central Stations,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 37-48.

ABSTRACT: The high level of sophistication required for the continuous monitoring of water quality in central stations follows from the need to produce ultrapure steam. Although there may not be agreement on the precise levels of contamination that are tolerable in steam, there is concensus that the levels are extremely low—so low, in fact, that it is questionable whether commercially available instrumentation has been adequate for the job.

During the past 5 years or so, the disastrous consequences of caustic and sodium chloride in steam have been emphasized over and over, yet many central stations do not take advantage of the instrumentation that is available for monitoring these contaminants.

Once the steam requirements are established, the specifications for boiler water and feedwater follow in order. This paper outlines several monitoring schemes for the complete utility plant cycle which employ the best monitoring equipment currently available and discusses some of the reasons that improved instrumentation is required.

The author points out that there are frequently alternative methods for detecting contamination in condensate and describes how the most sensitive monitoring device is selected in each case.

KEY WORDS: monitoring, steam electric power generating, power plants, condensers, contaminants, continuous sampling, corrosion fatigue, desuperheating, feedwater, steam boilers, steam turbine blades, stress-corrosion cracking, instrumentation, water quality

When the water treatment chemist sits down to assign limitations on chemical concentrations in the steam–water cycle of an electric generating unit, the first thing he has to look at is the turbine. The very first question that has to be resolved is how good must the steam be that is driving the machine. Once that hurdle is surmounted, the specifications for boiler water, feedwater, condensate, and makeup fall into line in logical sequence. This paper reviews the factors that influence our judgment on what acceptable steam is, develops the bases for water specifications throughout the cycle, and describes monitoring systems available for making sure that the requirements are met.

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Steam Purity

Steam for driving turbines must be sufficiently pure that deposits will not form in steam passages and potential corrodents will not cause cracking of turbine alloys. In recent years a consensus seems to have developed that concern for cracking imposes the more stringent conditions on steam purity.

Agreement on precisely what these stringent conditions should be is not universal, however. For instance, Table 1 [*1,2*][2] shows some divergence of thinking by the two major utility turbine manufacturers in the United States. A poll of water consultants experienced in utility operation would unquestionably produce further divergence of opinion. We might ask at this point if these differences mean that the manufacturers' machines really differ in their susceptibility to corrodents in the steam. The answer to this question is not known. The values that appear in Table 1 were not established through carefully monitored pilot plant tests in which real turbines were run to failure in steam environments of known purity; they simply represent judgments of people skilled in the trade on the lowest levels of contamination likely to be achieved in commercially operating equipment.

Let's look at what happens when impurities enter the turbine. Chlorides and hydroxides at high concentrations are known to promote stress-corrosion cracking of turbine alloys [*3*], and chloride has been shown to contribute to corrosion fatigue [*4*]. While quantities of these contaminants, measured in micrograms per litre, may exist in the superheated steam, very high concentrations, measured in percent, may be produced in the initial condensate [*5*]. This condensation occurs in the last or next-to-last stages, which in modern large machines have long and massive blades that are subjected to very high tensile stresses. The presence of impurities in regions of high stress and under conditions of resonance is alleged to be responsible for many of the turbine cracking incidents that have occurred in the past decade [*2,6,7*].

TABLE 1—*Turbine manufacturer's steam purity limits.*

	General Electric [*1*][a]			Westinghouse [*2*]		
	Normal	100-h Excursion	24-h Emergency	Normal	2-Week Excursion	24-h Emergency
Cation conductivity, μmho	0.2	0.5	1.0	0.3	0.5	1.0
Dissolved oxygen, μg/litre	...	...	...	10	30	100
Sodium, μg/litre	3	6	10	5	10	20
Chloride, μg/litre	...	...	...	5	10	20

[a] General Electric limits are not applied to systems in which boilers operate below the coordinated phosphate-pH control curve.

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

Critical Contaminants

Obviously each utility plant should monitor steam for those contaminants that are deleterious to turbine performance. With the high degree of sophistication of laboratory equipment that is available today, we can determine just about all we need to know on grab samples conveyed to the laboratory for analysis. However, the analysis of grab samples collected with sufficient frequency to maintain surveillance of the cycle is very costly and frequently involves a long response time that precludes rapid corrective action. Only continuous, automatic analyzers can fill this need adequately. Although pH and conductivity analyzers have seen many years of service in utility plants and sodium analyzers have gained acceptance in a fairly large percentage of plants during the past 5 years, there remains a need for the development of reliable analyzers that will measure directly the contaminants that are considered detrimental.

The most pressing need is for a continuous chloride analyzer that is reliable in the microgram-per-litre range. Chloride analyzers using a chloride-sensitive electrode have been marketed for several years, and contact with plants that have purchased them suggest that most of the bugs have been worked out and that we may be on the threshold of a new era in which continuous chloride analysis becomes the major technique for monitoring steam. In the past we have relied upon continuous sodium analyzers, employing a sodium-sensitive electrode, as the best indicator of steam purity because they have proven to be rugged, sensitive, and relatively maintenance free. However, the best we could do about chloride was try to draw some inference from the sodium levels. This is a questionable procedure because the ratio of chloride to sodium in the steam is not necessarily fixed and, under certain circumstances, the chloride in the steam may exceed the sodium on an equivalent basis. Ammonium ion is almost always present in measurable quantities in high-pressure boiler water, and the amount may vary depending upon makeup quality and how well pH is controlled in the feedwater. If the ammonium ion is balanced by additional chloride, the chloride may very well exceed the sodium and the steam will become enriched with chloride because of the volatility of ammonium chloride.

The metal hydroxides, such as sodium hydroxide, promote stress-corrosion cracking of turbine alloys. There is no evidence that volatile alkalies, such as ammonia, cyclohexylamine, and morpholine enter into this phenomenon. Continuously recorded pH values, which are a measure of hydroxide alkalinity, therefore are not adequate because volatile alkalies are nearly universally used for adjustment of feedwater pH. In theory, if the concentration of volatile alkali were known, a correction could be made for its contribution to pH, but there are several factors that make this approach impractical. There is presently no direct way of monitoring the volatile additive continuously, and unless ammonia is the sole volatile additive, the chemistry becomes exceedingly complex because of the presence of cyclohexylamine or morpholine and the ammonia formed as a decomposition product.

If we were to rely on continuous sodium and pH measurements, we would have to assume that volatile alkalies make a fixed contribution to pH, and experience tells us this is a dubious assumption. As a practical matter, the problem of monitoring sodium hydroxide is so complicated that no one has been encouraged to guess at an acceptable level for turbine operation. Standard operating practice in high-pressure plants has been reduced to controlling boiler water chemistry, makeup preparation, and condenser integrity in a way that precludes the introduction of sodium hydroxide to the steam.

How and Where Steam Is Sampled

Steam cannot be sampled in a haphazard way if reliable data are to be obtained. As all of the impurities may not be in solution, great care must be taken to make sure that the condensed sample conveyed to the monitoring instrument is representative of the main steam. Twenty years ago an industry-supported program conducted at the Naval Boiler and Turbine Laboratory revealed that the two most important factors influencing the accuracy of steam sampling are proper nozzle design and a requirement that sample flow rate be adjusted to produce a steam velocity through the ports of the nozzle equal to the velocity of the stream being sampled [*8*]. Details of the nozzle in general use today are described in ASTM Standard Method of Sampling Steam [D 1066–69(1975)].

Since we are concerned about turbine damage, we need to know the level of contaminants in the superheated steam. Saturated steam, as it leaves the boiler drum, and superheated steam may differ in purity because of deposition in the superheater and the introduction of contaminants with desuperheating water. However, very few plants with drum-type boilers sample superheated steam because of the acknowledged difficulty in collecting and transporting the sample in a way that prevents the contaminants from adhering to the walls of the sample line.

The problem of sampling superheated steam has been investigated and a solution has been proposed [*9*]. This takes the form of a specially designed sampling nozzle that permits the reinjection of part of the cooled sample to desuperheat the steam as it enters the ports of the nozzle.

While the sampling of superheated steam is preferred, the procedure is generally considered to be too cumbersome for routine use. The procedure more commonly used is the monitoring of both condensate and saturated steam. Condensate monitoring is suitable for establishing the purity of feedwater used for desuperheating, provided there is no source of contamination to the cycle beyond the condensate sample point. Weighted averages for contaminants in feedwater and saturated steam provide a reasonably good picture of the steam going to the turbine.

The steam from supercritical, once-through steam generators is superheated. Therefore, the sampling of steam from these units is a waste of effort unless the reinjection nozzle is used. However, experience to date suggests that there is no deposition or release of critical contaminants within the steam generator, a fact that permits us to use monitored feedwater values as a measure of steam purity. In those plants where both feedwater and steam are monitored by conventional means, an indicated reduction in contaminants through the steam generator is more likely to be explained by loss of solids to the steam sampling line than by precipitation in the steam generator.

Carry-over

For a unit having a drum-type boiler, the boiler water can be a major source of steam contamination. At the drum pressures of 17.9×10^6 to 19.3×10^6 N/m^2 (2600 to 2800 psi), commonly used in modern large generating units, the densities of steam and water are not vastly different, and separation of the two phases by centrifugal action becomes difficult. Therefore, the elimination of the carry-over of boiler water with steam is never absolute. By present-day standards a boiler carrying over to the extent of 0.1 percent is considered to be performing well. If we put ourselves in the shoes of the water treatment chemist whose job it is to set water quality specifications, we are now at the point where we can establish boiler water limits.

Let us assume we have established a maximum sodium value for steam of 5 μg/litre. Dividing this value by the fraction carry-over, we arrive at the corresponding limit for boiler water. If the unit has not yet gone into service, how do we know what value to assign to carry-over? One might base this on experience with similar units, a risky procedure at best, or obtain an opinion from the boiler manufacturer. The best procedure is to run some controlled carry-over tests as soon as the unit can sustain full load. The best technique for doing this is to monitor sodium concentrations in the boiler water and steam under varying conditions of load, water level, and dissolved solids. If, for example, we find 0.1 percent carry-over by this procedure, we have established a sodium limit for boiler water of 5 mg/litre.

A factor frequently overlooked in calculations of this type is the volatility of boiler water constituents at high temperatures. The measured concentration of sodium in the steam represents the sum of that present in entrained boiler water and that present in vaporized salts. If the volatility of all constituents varied little, the sodium in the steam could be predicted from the sodium in the boiler water, but laboratory investigation has shown that this is not the case. Data by Martynova [*10*] indicate that 5 mg/litre of sodium in sodium chloride in the boiler water will produce 10 μg/litre of volatile sodium in the steam at 17.9×10^6 N/m^2 (2600 psi), while 5 mg/litre of sodium in sodium sulfate will produce only 0.02 μg/litre. Vaporous carry-over, therefore, varies with the anions present in the boiler water. We now arrive at the very important conclusion that it is always better to monitor the steam directly, rather than to draw inferences about its purity from the chemistry of the boiler water.

As imperfect as the best continuous monitoring schemes are, it is essential that purity be monitored in steam going to high-pressure turbines. Otherwise, the operator is flying blind and does not know if he is within the turbine manufacturer's guidelines. Unfortunately, this principle is not embraced with uniform enthusiasm throughout the utility industry. In a survey reported by General Electric [*6*] investigators found that among 50 once-through units at least 12 were without sodium analyzers, and among 60 drum-type boilers operating above 13.8×10^6 N/m^2 (2000 psi) at least 22 were without sodium analyzers. Some, but not all of these, were monitoring cation conductivity. None was monitoring chloride.

Because of its lack of sensitivity, cation conductivity is a poor substitute for sodium analysis. If, for instance, the steam contained 5 μg/litre of sodium, all attributable to sodium chloride, the theoretical cation conductivity would be 0.092 μmho. With the conductivity of water of 0.05 μmho added to this, the meter reading would be 0.14 μmho. If the sodium were increased to 7 μg/litre, the meter reading should rise to 0.18 μmho. It is not likely that anyone who has worked extensively with these instruments would put much credence in a 0.04-μmho rise. Of course, cation conductivity does not respond to the presence of sodium hydroxide at all, since sodium is replaced by hydrogen in the cation column to produce water.

The strongest argument for monitoring the cation conductivity of steam is that it is a second line of defense during periods when the sodium analyzer is out of service.

Boiler Water Chemistry

It is not the intention of this paper to discuss the theories of high-pressure boiler water treatment. Suffice it to say that in those plants in which there is concern about turbine cracking there is also concern about caustic corrosion in the boilers [*11*]. Almost without exception high-pressure boilers are run on essentially pure water or with phosphate treatment at a pH below that corresponding to the pH of trisodium phosphate.

For drum-type units operating on pure water, monitoring of the boiler water for pH and sodium or cation conductivity is desirable because these parameters provide a double check on condenser leakage and indicate when chemical treatment must be started. However, for boilers on phosphate treatment, continuous monitoring of pH may be helpful in pinpointing sources of contamination, but monitoring for sodium and cation conductivity is generally not warranted. This is because the smallest condenser leak that can be detected by monitoring condensate will affect boiler water conductivity and sodium only negligibly, even several hours after the leak has started, since a large background of solids and sodium is already present.

Condensate Polishing

All once-through units and some drum-type units have condensate polishing demineralizers. In these plants it is always necessary to monitor sodium downstream of the polishing unit. Should the cation resin in the polisher become exhausted, some sodium hydroxide may leak through. As we have seen, sodium hydroxide cannot be detected by means of cation conductivity.

Anion exhaustion before cation exhaustion in condensate polishers is rare. However, if the cation resin is permitted to ammoniate on line as a means of extending the length of runs, some means of detecting anion leakage is required. In this event, cation conductivity is useful for detecting the presence of chloride and sulfate, while ignoring the influence of ammonia.

Condensate Monitoring

As the largest single source of cycle contamination is condenser leakage, continuous monitoring of the condensate is vital in all plants. Devices for monitoring condenser leakage must be able to detect extremely small leaks because contaminants in the condensate may be concentrated many thousands of times in the boiler water of drum-type units and may pass through undiminished in quantity to the turbine in once-through systems. However, which monitoring scheme will detect the smallest leak depends upon the chemical composition of the cooling water and the inherent sensitivity of the monitoring device. At the moment, we believe that against the background levels normally encountered a 0.2-μmho change in cation conductivity, a 5-μg/litre change in silica, and a 1.0-μg/litre change in sodium can be detected reliably. Silica detection involves the use of an automatic colorimetric analyzer.

The first step in selecting the most sensitive monitoring scheme is calculation of the theoretical cation conductivity of the cooling water, which is done as follows

$$\text{cation conductivity} = 427\left(\frac{\text{mg/litre Cl}}{35.5} + \frac{\text{mg/litre SO}_4}{48} + \frac{\text{mg/litre NO}_3}{62}\right)\mu\text{mho}$$

Then we make our selection on the basis of the following relationships:

if

$$\frac{\text{cation conductivity}}{\text{mg/litre Na}} > 200$$

reject sodium.

Then if

$$\frac{\text{cation conductivity}}{\text{mg/litre } SiO_2} > 40$$

reject silica and use cation conductivity.

But if

$$\frac{\text{cation conductivity}}{\text{mg/litre } SiO_2} \leq 40$$

reject cation conductivity and use silica.

If

$$\frac{\text{cation conductivity}}{\text{mg/litre Na}} \leq 200$$

reject cation conductivity.

Then if

$$\frac{\text{mg/litre Na}}{\text{mg/litre } SiO_2} > 0.2$$

reject silica and use sodium.

But if

$$\frac{\text{mg/litre Na}}{\text{mg/litre } SiO_2} \leq 0.2$$

reject sodium and use silica.

It is possible that we will see chloride used for monitoring condensate in the near future. If we assume that a 1.0-μg/litre change can be seen reliably, chloride can be substituted for sodium in the foregoing relationships. If the analysis selects both chloride and sodium, the one with the higher concentration in the cooling water should be chosen.

Colorimetric Analyzers

Colorimetric analyzers are frequently used in power plants for the continuous monitoring of phosphate, silica, and hydrazine. These are based upon the development of color in a flowing sample by the continuous addition of appropriate reagents and the measuring of the color intensity by means of a photometric cell. These are very sophisticated instruments that perform very well under the conditions that exist in an analytical laboratory, where they receive relatively more attention than they do in a utility plant. Because plant personnel frequently fail to provide the amount of maintenance required, approximately 50 percent of the instruments installed in utility systems are not running at all or are not providing reliable data at any given time. However, those utilities that have recognized the need for maintenance have gotten very satisfactory results. Although these instruments require more attention than pH, conductivity, and sodium analyzers, the man-hours devoted to keeping them functioning are significantly fewer than the man-hours needed to perform an equivalent amount of analytical work at the laboratory bench.

A number of years ago several instrument suppliers offered to the utilities continuous iron and copper analyzers for monitoring condensate and feedwater. These processes were complicated by the need for acid digestion of the continuously flowing samples, and eventually the high level of maintenance required to keep them functioning led to their abandonment. It is unfortunate that efforts to perfect these analyzers were dropped because, of all colorimetric analyzers, they represent the greatest potential saving in labor.

The manual techniques currently used for the determination of iron and copper concentrations at low levels are tedious and lengthy and, consequently, are rarely performed with sufficient frequency for adequate surveillance of corrosion product release from piping and heat exchangers and the determination of iron and copper ingress to boilers. As the major objective of condensate and feedwater conditioning in all utility plants is the minimizing of the amount of corrosion products that enters the boiler, the supplier of reliable iron and copper analyzers would find a sizable market for his wares.

Summary

Because of the susceptibility of turbine alloys to stress-corrosion cracking and corrosion fatigue, the monitoring of steam for very low levels of contaminants is mandatory. Drum-type boilers operating on essentially pure water must be monitored with equal care because contaminants may cause wide swings in pH which lead to boiler tube corrosion. As condenser leaks are the most common source of contamination, selection of a monitoring scheme that will detect even minute condenser leaks is essential. Nearly instantaneous recognition of contamination is required because failure can be swift and catastrophic. Monitoring must, therefore, be continuous.

Figures 1 and 2 show how continuous, automatic monitoring devices are applied to drum-type units and to once-through units, respectively. These sketches are not intended to be typical but rather to show the author's conception of how plants operating above 13.8×10^6 N/m^2 (2000 psi) should be instrumented.

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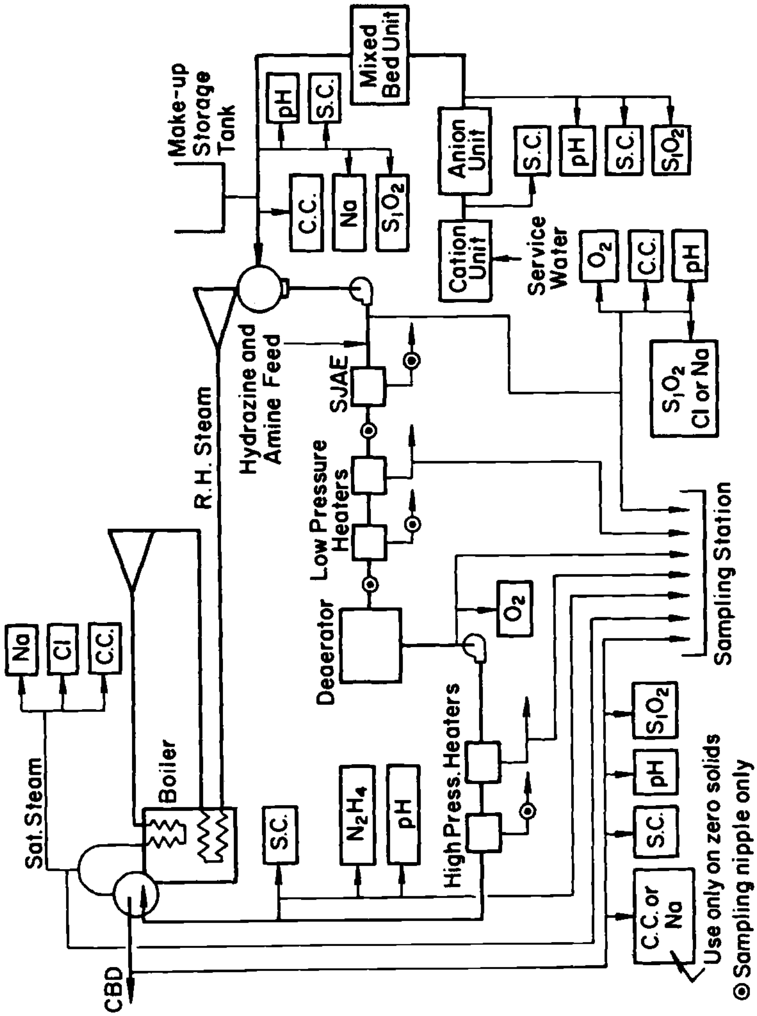

FIG. 1—*Suggested monitoring scheme for a high-pressure unit with a drum-type boiler.*

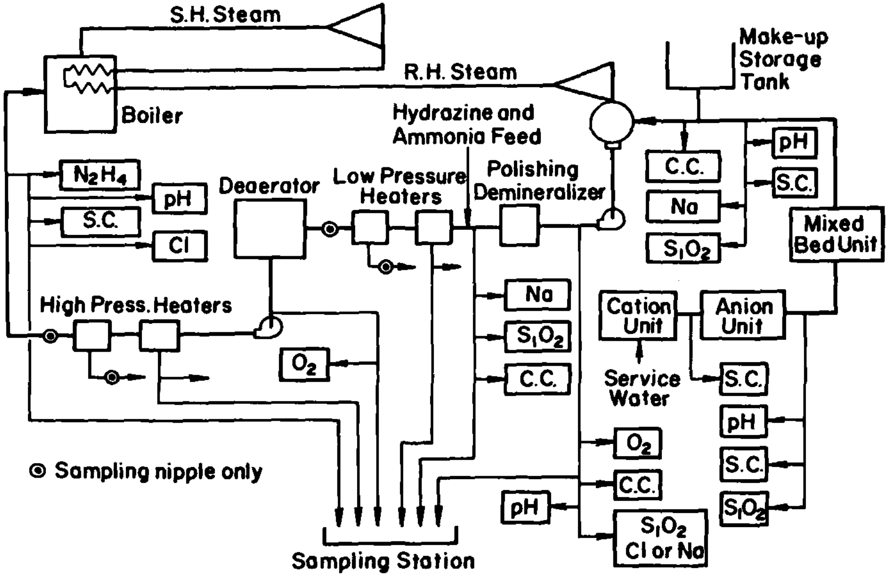

FIG. 2—*Suggested monitoring scheme for a once-through unit.*

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K. A. Selby[1]

Power Plant Water Quality Instrumentation: A Guideline for Operation, Calibration, and Maintenance

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REFERENCE: Selby, K. A., **"Power Plant Water Quality Instrumentation: A Guideline for Operation, Calibration, and Maintenance,"** *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 49–54.

ABSTRACT: The paper focuses on how the organizational structure within a power plant can help or hinder in the effort to obtain reliable data from water quality instrumentation. It also focuses on the education and training level required of personnel who operate such instrumentation and provides guidelines for daily attention to instrumentation and recommendations for the scheduling of routine maintenance and calibration procedures.

KEY WORDS: water quality, instrumentation, operation, calibration, maintenance, organizational structure, educational level, training level, power plants

Power plants of recent vintage are larger, more complex, and operate at higher pressures and temperatures than their predecessors. The increase in turbine size into the 800 to 1000 MW range has been accomplished through the use of materials of construction that are sensitive to inorganic, and possibly to organic, contaminants in the steam. Higher water quality is required. More water quality instrumentation is being used to document water and steam quality. This instrumentation is becoming more complex and more sophisticated.

In spite of this new level of importance of water quality instrumentation in the power plant, the approach within the plant to operating, calibrating, and maintaining this instrumentation has not changed significantly in recent years. Each utility has its own organizational structure within the plant, which may or may not provide for the increased importance of water quality instrumentation and water-treating equipment operation. To be effective, the organi-

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zational structure must create clear lines of responsibility for the operation, calibration, and maintenance of instrumentation.

This paper focuses on how the organizational structure in the power plant helps or hinders in the effort to obtain reliable data from water quality instrumentation. It also focuses on the education and training level required of those designated to operate such equipment. In addition, the paper provides guidelines for daily attention to instrumentation and scheduling of routine maintenance and calibration.

Organizational Structure

Most power plants in the United States utilize the same basic organizational structure of personnel. There are significant differences, however, regarding the personnel within the plant assigned to operate, calibrate, and maintain water quality instrumentation. This difference can be shown to have a significant effect on the reliability and accuracy of this instrumentation.

As part of the information gathering for this paper, ten electric utilities were questioned about power plant organization regarding water quality instrumentation and their success in keeping that instrumentation in good working condition. The utilities surveyed vary in size but all operate fossil fuel plants of recent vintage and have a variety of chemical instrumentation in those plants. The survey was limited to fossil fuel plants in order to reduce the complexity of the study. The lessons to be learned from this limited survey, however, should also be applicable to nuclear plants. The persons interviewed were generally responsible for overseeing power plant chemistry in one or more plants. The results of the survey are shown in Table 1.

This survey indicated that the operation, calibration, and routine maintenance of water quality instrumentation is the responsibility of one or the other of two different groups of technicians within the plant. In some plants instrument technicians are responsible for water quality instrumentation as well as for flow, temperature, pressure, and level-indicating instrumentation. In other plants water quality instrumentation is the responsibility of chemistry technicians. These people are also responsible for laboratory analyses, general plant chemistry, and sometimes the operation of demineralizers and chemical feed systems.

In most cases the plants that experience successful operation of water quality instrumentation are those in which the chemistry technicians are responsible for that instrumentation. Success, of course, is a subjective term but is meant here to include (1) maintaining the instrumentation in an operating condition and (2) keeping the instrumentation in calibration.

In the survey, most of the plants that assign the responsibility for water quality instrumentation to the instrument technicians are less successful by these criteria. This is not due to any lack of competence or commitment on

TABLE 1—*Utility survey. Operation, maintenance, and calibration of water quality instrumentation.*

Utility	Operation		Routine Maintenance		Calibration		Successful Experience with Water Quality Instrumentation
	By Chemical Technician	By Instrument Technician	By Chemical Technician	By Instrument Technician	By Chemical Technician	By Instrument Technician	
1	x		x		x		no
2		x		x		x	no
3	x		x		x		yes
4	x		x		x		yes
5		x		x		x	no
6	x		x		x		yes
7	x		x		x		yes
8		x		x		x	no
9	x		x		x		yes
10	x[a]			x	x[a]		yes

[a] Performed by chemical supervisor.

the part of the instrument technicians. Water chemistry instrumentation, however, often receives a lower priority than those plant instruments that control pressure, flow, or temperature. Another factor is that the instrument technician often has little or no chemistry training and therefore may not understand what the instrument is measuring or how it is making the measurement.

Successful operation of water quality instrumentation, therefore, is most likely to be achieved under an organizational structure in which there is a clear line of responsibility for the operation, calibration, and maintenance of that instrumentation.

Education and Training Level

The consistent operation of water quality instrumentation requires a certain minimum knowledge of the chemical principles by which that instrumentation operates. The desirable level of education is the equivalent of 2 years of college-level chemistry. Also desirable is training which acquaints the technician with the overall operation of the power plant. For example, one utility with a very successful program hires persons with the minimum education requirements and places them in a central chemical staff group. They are then trained in this group for a year in a variety of projects related to power plant chemistry. At the end of the training program the employee is qualified to bid on job openings as a chemical technician in the individual power plants. This program is successful because it combines the desirable minimum level of education with a formal and practical training program.

Regarding the education and training required for chemical technicians, it should be kept in mind that as water quality instrumentation becomes more sophisticated the required level of education and training will increase. Instrumentation such as ion-exchange chromatographs require highly skilled technicians for operation. The use of such instrumentation will necessitate more thorough training.

Operation, Calibration, and Maintenance of Water Quality Instrumentation

Water quality instrumentation must be operated and cared for on a systematic and scheduled basis. This means that each instrument must be given a certain minimum amount of daily attention and that calibration procedures and routine maintenance must be performed according to a prearranged schedule.

Daily Attention—At the beginning of each day the technician should survey the sample flows to all instruments. After sample flows have been verified or adjusted, each instrument will be examined individually. The chart paper in the recording device is to be marked with the date and time and rolled back to examine the data produced since the last examination. Trends and abnormal conditions should be noted. Also, the general condition of each instrument should be examined. This involves observing the cleanliness of the instrument, particularly its flow path, as well as any abnormal operation.

Routine Maintenance—Routine maintenance involves such tasks as adding reagents to analyzers, changing or reconditioning electrodes, replacing chart papers, and replacing other "consumable" items in the instruments. These tasks must be performed on a routine and scheduled basis. They must not be allowed to wait until the instrument is not working properly.

Buffer solutions must be changed in analyzers such as sodium or chloride monitors on a more frequent schedule than that recommended by the manufacturer. This may increase the cost of buffer solutions and consumable items, but it will ensure more reliable and accurate operation over the long term.

Analyzers that feed reagents to the sample stream must have reagents added before the containers become empty. The best way to accomplish this is to add these reagents on a scheduled basis.

Most chart papers provide advance warning, usually 24 h, that the end of the roll is about to be reached. If the water quality instrumentation is to be left unattended over a weekend, a 24-h warning is not sufficient. For this reason the quantity of available chart paper must be checked before the instrument is left unattended for periods longer than the warning period.

Calibration—Actual calibration schedules for water quality instrumentation will be determined by the following factors:

(*a*) The make, model, and general reliability of the particular instrument;
(*b*) the plant conditions under which the instrument operates;
(*c*) whether the instrument is being used to provide absolute values or for trending purposes; and
(*d*) the frequency of laboratory cross checks of data produced by the instrument.

The manufacturer of each instrument recommends the frequency at which calibrations should be performed. Although this can provide a guideline for preparing a calibration schedule, the technician should expect to schedule calibrations more frequently than recommended in the manufacturer's literature. One reason for this is to provide a greater safety margin for maintaining instrument accuracy. Another reason is that manufacturers often do not take into account the less than ideal conditions under which these instruments frequently operate. Therefore, the actual frequency at which an instrument must be calibrated may or may not coincide with the manufacturer's recommendations.

Because of the overall reliability of conductivity instrumentation, the need for scheduled calibration of conductivity cells is often overlooked. Conductivity cells are often left in place without attention until the conductivity values being produced are obviously "wrong." The cell constants of conductivity cells can change slowly over a period of time, especially if they are operating on an unfiltered sample stream containing metal oxides or other suspended solids. Cell constants should be checked twice a year, either by checking individual cells with a standard solution or by comparing their values with the values produced by a reference cell. In some cases several conductivity cells can be operated in series on a single source of water. The differences in readings produced by the test cells can be compared with the reference cell and inaccurate cells removed from service to be reconditioned or retired.

Summary

Experience in operating power plants has shown that water quality instrumentation should be operated, maintained, and calibrated by personnel directly responsible for plant chemistry functions. In this way a clear line of responsibility exists for the information produced by such equipment.

The personnel assigned to the water quality instrumentation should have an education level equivalent to 2 years of college chemistry and additional training that will acquaint them with overall power plant operations.

All instrumentation must receive daily attention. Routine maintenance and calibration procedures must be performed according to a set schedule to maintain consistency of operation.

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Program for Steam Purity Monitoring: 1. Instrumentation and Sampling

REFERENCE: Pensenstadler, D. F., Peterson, S. H., Bellows, J. C., and Hickam, W. M., **"Program for Steam Purity Monitoring: 1. Instrumentation and Sampling,"** *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 55–70.

ABSTRACT: For the past 3 years the Westinghouse Electric Corp. has conducted a major program of instrument selection and development and sample analysis to monitor the steam turbine chemical environment and to determine the source of corrodant species that contribute to turbine blade corrosion.

This paper describes the development and application of a continuous on-line analyzer; a grab sample analysis program, utilizing state-of-the-art ion chromatography, to measure steam impurity concentration at various locations throughout the steam-water cycle; and the combination of these techniques, in the form of a total plant survey, to assess total power plant chemistry.

The significance and usefulness of continuously monitoring parameters such as sodium, dissolved oxygen, conductivities, and chloride is discussed, as are the validity of the sampling procedures, the utility of a nozzle to extract steam, and the strengths and weaknesses of ion chromatographic grab sample analyses. Finally, the implementation of a data acquisition system on the continuous analyzer, to handle the ever-increasing amount of information being generated by seven of these field systems, is reviewed.

KEY WORDS: steam, purity, control, power, computers, ion, chromatography, chemistry, turbines, instrumentation, sampling, analysis–composition, cations, anion, conductivity, condensate, power plants, water quality

Throughout the steam–condensate cycle used for the conversion of thermal energy into electrical energy in power plants, the energy conversion fluid must be chemically controlled. Consequences of inadequately controlled chemistry include loss in plant efficiency and plant corrosion. All plants include components whose functions are to purify and chemically control the steam–condensate as it is cycled between the condensate and steam phases. During normal operation impurities are removed in the condensate phase and appropriate chemicals for boiler treatment and so on added.

The steam–condensate chemical control can be adversely affected as a re-

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sult of malfunction of plant components, loss of plant component integrity, erroneous chemical information, and operator errors. The improper operation or malfunction of a demineralizer, polisher, deaerator, exhaust pump, or a chemical feed system can result in plant exposure to an unwanted chemical environment. The loss in integrity of a condenser tube, air seals, or a pump can adversely affect the chemical control. The plant operator's decisions exert a major influence on chemical control, and his decisions demand constant vigilance of plant chemical conditions from a continuous flow of reliable information from the plant chemists.

In order to maintain proper plant chemistry control, and to recognize more quickly and diagnose any adverse change in the plant environment, plants are instrumented with continuous chemical monitors and maintain laboratory facilities and a chemical staff. It is desirable that plant instrumentation, laboratory facilities, and the chemical analysis methods and practices reflect changes in plant chemistry operating requirements and advances in chemical technology. During the normal lifetime of a power plant, chemical analysis methods and chemical instrumentation installed and used during the initial plant start-up can become obsolete. In addition, satisfying the chemical control requirements of recent plants and future plants demands that current chemical technology be an integral part of plant operations.

In recognition of present and future plant chemical control requirements, the Westinghouse Corporation initiated a major program on steam–condensate monitoring and analysis in 1977. This paper describes chemical instrumentation and chemical analysis developments achieved to date from this ongoing program. Included are grab sample analyses by ion chromatography, a continuous steam sampling and analysis system, procedures for conducting a total plant survey, and computer techniques for reducing plant chemistry data. The second paper on this program describes chemical results from power plant applications of these developments.

Grab Sample Analysis by Ion Chromatography

The steam–condensate produced in power plants is among the highest purity, large-volume gas and liquid produced in industrial systems. Rarely, if ever, are gas and liquid purities realized which are equivalent to those routinely achieved a large fraction of the time during normal operation of most power plants. Special sampling and analysis methods are required in grab sample analysis of the high-purity steam–condensate. Ideally, one would prefer to use continuous on-line analyzers in order to minimize the possibility of sample contamination in handling and analysis. However, on-line instrumentation which satisfies all plant analysis needs is not currently available, and, therefore, grab sample analysis must be an integral part of plant chemical practices. The ion chromatograph, along with recent developments for its use in the analysis of condensate, makes possible for the first time routine cation and anion analysis of grab samples at the 1-ppb level.

The ion chromatograph was first reported in 1975 by Small, Stevens, and Bauman [*1*][2] of the Dow Chemical Co. A recent review article by Maugh [*2*] describes the technique and identifies many of its current uses. Ion chromatography combines new separator ion exchange resins with a unique suppressor column–conductivity cell detection system to achieve cation or anion analyses. The electrical output consists of time-dependent conductivity signals, identifiable with specific cations or anions, for which the peak heights are a linear function of cation or anion concentration. The typical detection limit of the instrument is 1 ppm. Special sample concentrator columns can be used to extend the detection limit. In our grab sample analysis program we use the ion chromatograph in combination with concentrator columns to achieve detection limits of <1 ppb in condensate samples. Figure 1 is a photograph of the ion chromatograph. Early in the program, concentrator columns were used for sample storage and shipment. However, during the past

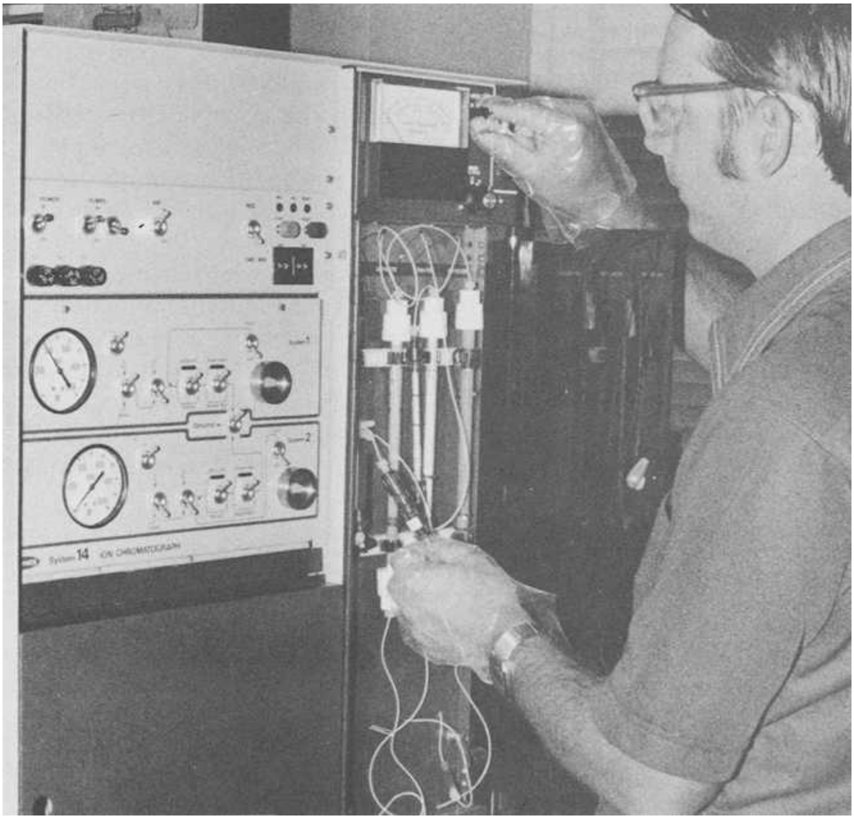

FIG. 1—*Dionex ion chromatograph.*

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

18 months concentrator columns have been used only during the analysis, and polystyrene bottles are used exclusively for sample storage and shipment. This change has contributed to simplifying sampling procedures, extending sample storage life, and reducing concentrator column expense.

Tested and proven procedures must be used in each step of the grab sample analysis method if reliable analyses are to be achieved. Acquiring a representative sample, avoiding sample contamination, and maintaining the sample compositional integrity until it is analyzed are requirements for achieving reliable and meaningful analyses. The same criteria must be exercised in carrying out the actual analysis. It is recommended that sample lines and valving be of stainless steel and be continuously flowing for a minimum of 24 h prior to the collection of grab samples. Sample conditioning condensers, cooler, and associated fittings and valving must be maintained leak free. Condensate temperature should be <50°C and preferably near ambient temperature.

A critical point in high-purity grab sample analysis is the collection and storage of the sample, whereby its composition remains unaltered until it is analyzed. Extensive tests were conducted for the purpose of identifying sample bottles which satisfied this requirement (see Table 1). Polystyrene bottles were selected because of their low absorption and leaching characteristics. Calibration standards, covering the concentration range of 1 to 50 ppb for sodium, chloride, and sulfate, were stored in preconditioned bottles and periodically analyzed. No significant sample compositional changes were noted during an 8-day test period.

Sample bottle preconditioning is essential for achieving reliable grab sample analysis. Our preconditioning procedure is to half fill the bottle with >15 MΩ water, replace the cap, shake, and empty the bottle. Repeat this procedure three times, and then fill the bottle completely and cap it. Allow it to soak for 12 h. Repeat the rinsing and filling operations and allow the bottle to soak for a second 12-h period. The bottle is then considered to be preconditioned for collecting samples. When sampling, the bottle is emptied, rinsed

TABLE 1—*Recovery of ions after storage in different types of plastic containers.*

	Polystyrene Container			Polypropylene Container		Polyethylene Container	
Ions Recovered, ppb	After 1 Day	After 3 Days	After 8 Days	After 1 Day	After 3 Days	After 1 Day	After 3 Days
Cl^-	22	22		22	22	18	24
Cl^-	5		5.7				
SO_4^{-2}	52.5	52.5		52.5	52.5	50	57
SO_4^{-2}	1		1				
Na^+	1	1	0.9			5	1
K^+	1	1	1				

three times with the sample (including the cap), filled, and then capped. In practice, duplicate samples are collected, but usually only one sample is analyzed. The duplicate is only for backup and is used to check a questionable analysis. Typically, less than 5 percent of the duplicate samples are analyzed. All sample bottles are used only once and then discarded. Any visible bottle crack will result in sample contamination.

The transfer of the sample from the bottle to the concentrator must be accomplished without sample contamination or loss of impurities. A small polyethylene beaker and the transfer syringe are rinsed with high-purity water. A sample is poured into the polyethylene beaker, and the syringe is filled by withdrawing a sample from the beaker. Polyethylene gloves are worn throughout this operation and the transfer of the sample to the concentrator column. Syringes and beakers are designated cation or anion and only used for the intended analysis type. Following a training session which includes the analyzing of 20 to 40 samples under supervision, both chemists and technicians have been able to perform the analyses with high reliability. Strict operator adherence to a tested and proven analytical procedure is essential, and procedure innovation or change cannot be tolerated in analyzing a series of samples. No evidence of organic ion sample contamination from the polystyrene sample bottle has been found.

Grab samples collected from power plants have been analyzed by ion chromatography both at the source and after shipping to the Westinghouse Research and Development Center. Special fiberglass shipping cases, equipped with molded polyethylene foam inserts, are used for shipping samples by common carrier. Figure 2 is a photograph of the shipping case. Its design reduces bottle breakage and provides thermal insulation to protect against sample loss as a result of exposure to freezing temperatures.

Calibration standards are used to periodically check the performance of the ion chromatograph. In general, little or no drift in calibration of the ion chromatograph has been found. Figure 3 compares chloride calibrations of an instrument prior to shipment from Pittsburgh and on arrival at a power plant in Oklahoma a week later. Figure 4 is typical of the linear response found for peak height versus impurity concentration.

A sufficient, reliable, and monitored supply of high-purity water is essential in high-purity water analysis, where the species being analyzed are similar to those found in water. Many of the needs for a high-purity water source were mentioned earlier in this paper. Figure 5 is a schematic drawing of a purification system developed for this purpose and used throughout the program. Ion chromatographic analyses are used to periodically check the purity of the water delivered by the system.

On-Line Continuous Steam Analyzer

In a typical power plant, the condensate phase is analyzed at more points than the steam phase. Analytical information based only on plant conden-

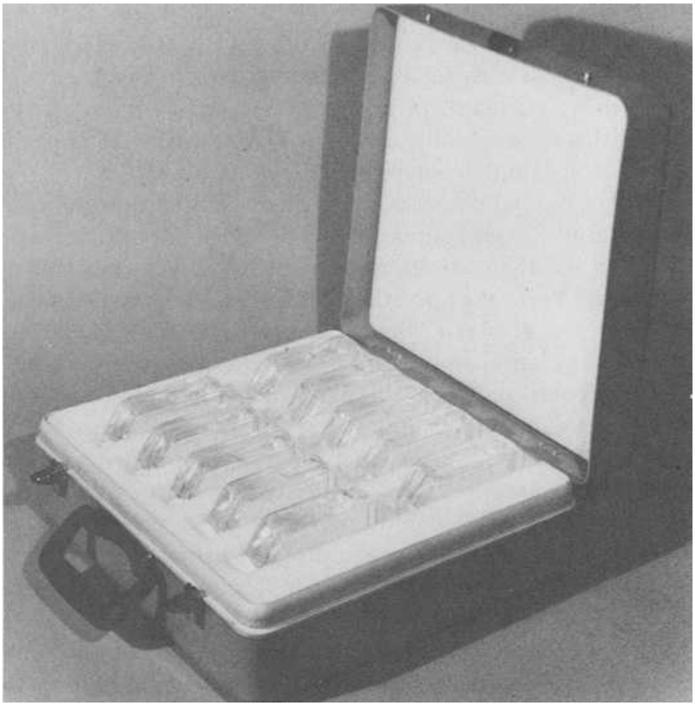


FIG. 2—*Photograph of a grab sample bottle shipping case.*

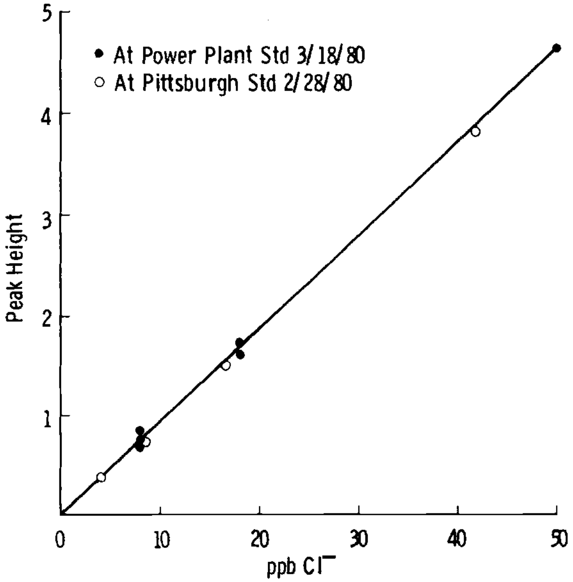


FIG. 3—*Chloride calibration curve prior to and after shipment.*

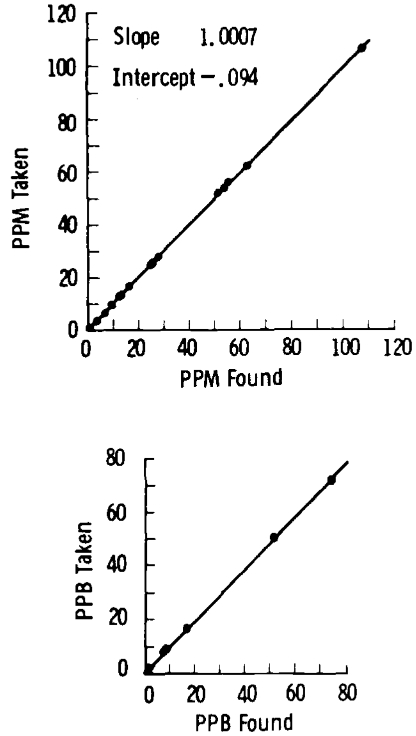


FIG. 4—*Recovery study curve for chloride.*

sate analyses is not sufficient to ensure the purity of the steam phase. This can only be accomplished by analysis of the steam. Ideally, one desires analytical instrumentation capable of directly monitoring the steam environment. Since chemical instrumentation capable of operating within the steam environment is not available, one must resort to a steam sampling system, steam condensation, and condensate analysis instrumentation.

An on-line, continuous steam analyzer system, based on condensate analysis, has been designed and field tested. A steam sampling nozzle is used to minimize possible sample contamination from the release of turbine piping deposits. Figure 6 is a schematic drawing of the sampling nozzle. The nozzle is inserted into the crossover piping between the intermediate pressure and low-pressure turbines. Steam from the nozzle is passed through a valve into a condenser and cooler to provide a continuous condensate flow (1 litre/min) for the analyzers. Thermocouples are incorporated to monitor the steam and condensate temperatures.

The analyzer system includes continuous analyzers for sodium, oxygen, pH, cation conductivity, and specific conductivity. The analyzer outputs and the thermocouple outputs are displayed on a multipoint recorder. Figure 7 is a photograph of the analyzer cabinet. To date, eight on-line steam analyzers

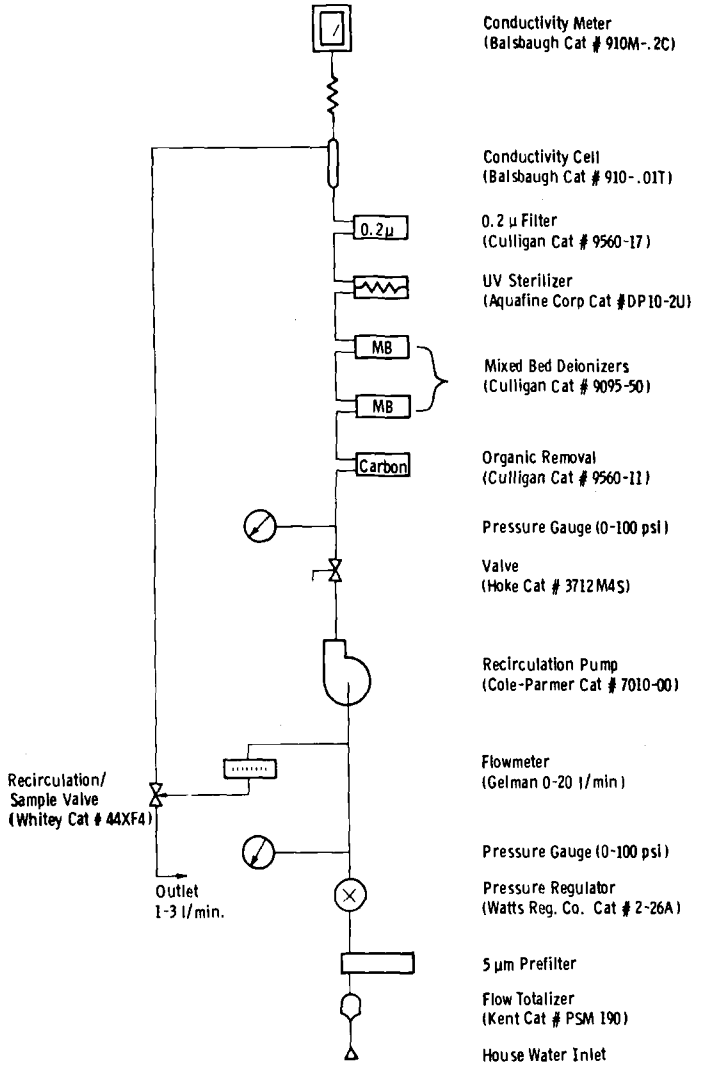


FIG. 5—*Laboratory water treatment system for Type I reagent-grade water.*

have been built and used in the monitoring of steam entering approximately 20 low-pressure turbines for periods of 3 to 6 months. The total accumulated turbine operation monitoring time is in excess of 10 years.

Date reduction from such an intensive monitoring program is a major undertaking. To aid in the data reduction and data flow process, data collection forms are used to record daily entries. The daily entries include high, low, and typical values of the monitored parameters along with other relevant plant information. These forms, along with the recorder charts, are returned to the Westinghouse Research and Development Center twice a

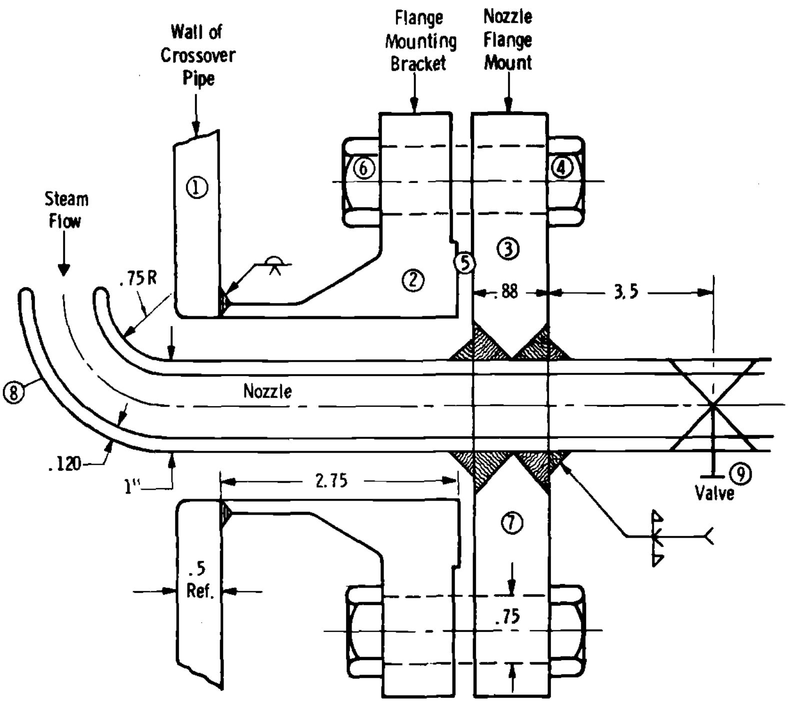


FIG. 6—*Steam sampling nozzle for low-pressure crossover pipe.*

month for processing and analysis. The data are computer processed and graphed. Figure 8 is a typical computer summary plot. If a specific information need is indicated, this can be obtained by examination of the original charts.

In order to facilitate future data reduction from on-line steam analyzers, the units are being equipped with magnetic tape recorders. Data recorded on the magnetic tapes can be readily processed, analyzed, and automatically graphed using computer programs developed for this purpose.

Total Plant Survey of Steam-Condensate

A total plant survey [*3*] is an intensive chemical assessment of the entire steam-condensate cycle covering a time period of approximately 1 week. Analysis methods used in the survey include grab sample analysis by ion chromatography, the on-line steam analyzer, existing plant chemical instrumentation, and plant laboratory analyses.

The survey examines the plant environment for influences of plant load. Typical test load conditions include base load, stepped load reduction, continuous load reduction, shutdown, and start-up. Auxiliary boiler steam used in start-up and stored condensate during shutdown also have been analyzed.

The planning efforts in preparation for a total plant survey include the

FIG. 7—*Westinghouse continuous on-line steam analyzer.*

scheduling of plant operations, the installation of equipment for grab sample collections, the installation of the on-line steam analyzer, the on-site installation of two ion chromatographs, the scheduling of work hours for approximately ten persons on two shifts, and the delivery to the plant site of many materials used in conducting the tests. Numerous planning sessions are required, and a degree of schedule flexibility is maintained to accommodate last-minute plant operating needs.

Six total plant surveys have been conducted on fossil fuel plants, including one in Japan. The data are gathered on a time schedule and under known plant operating conditions to provide meaningful chemical information over the test time period. The information gathered during a total plant survey includes the following:

1. Grab sample analysis by ion chromatography. Approximately 25 grab sample sets are collected in duplicate from 6 to 12 designated condensate

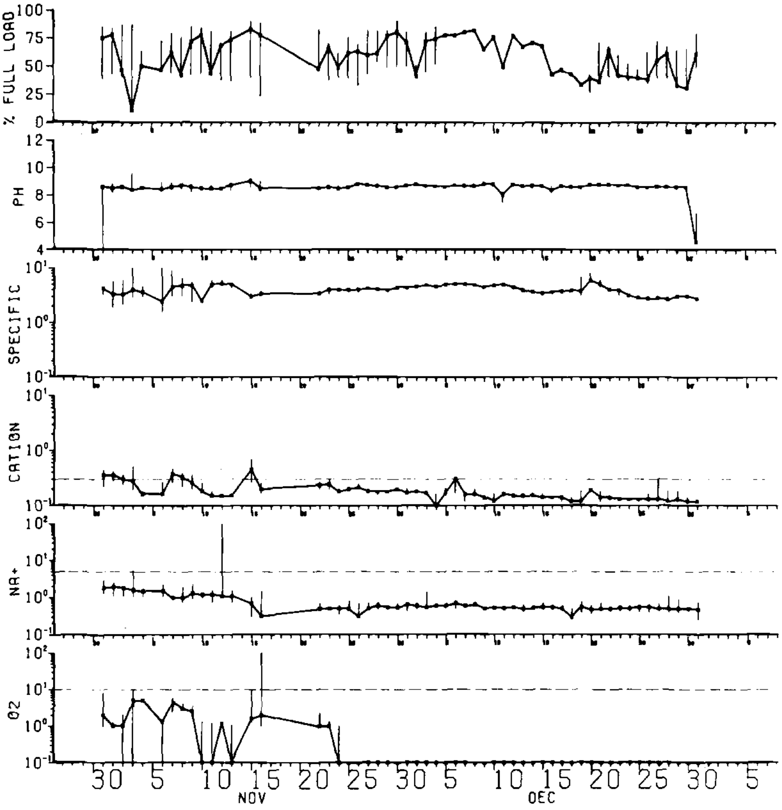


FIG. 8—*Computerized graph of on-line analyzer data for low-pressure steam. Conductivities are in microsiemens; Na^+ and oxygen are in parts per billion.*

flow points located around the plant cycle. The samples are analyzed on site for cation and anion impurities at a sensitivity of <1 ppb using two ion chromatographs.

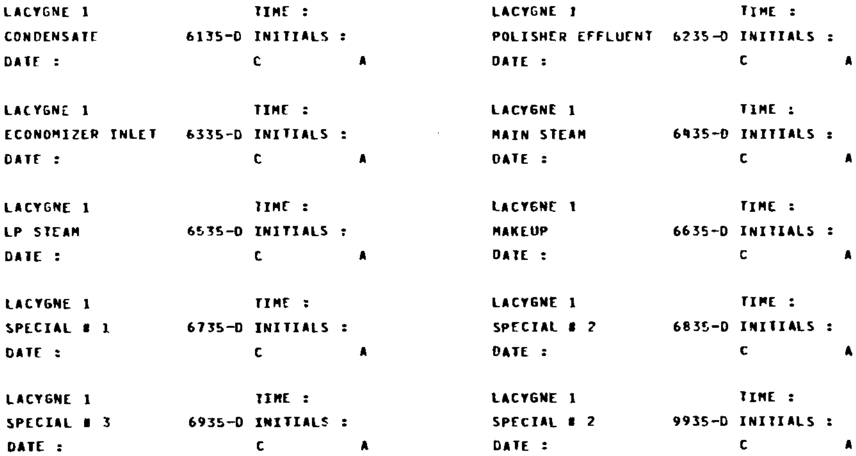
2. Continuous low-pressure steam monitoring with the on-line analyzer for oxygen, sodium, pH, cation conductivity, specific conductivity, steam temperature, and condensate temperature.
3. Periodic readings of some 25 plant chemistry instruments throughout the test period.
4. Listing of specific plant chemical control equipment, laboratory analyses performed, chemical staffing, and chemicals used in plant operations.

Data collected in a total plant survey are reduced and summarized in report form, including conclusions and recommendations, using both manual and computer techniques. The total plant survey is among the most comprehensive chemical examinations ever conducted at a plant. It provides information never before obtained, for example, sulfate and chloride analysis at the 1-ppb range around the plant cycle and direct continuous monitoring of several chemical parameters in nozzle-sampled low-pressure steam. The survey provides, often for the first time in many plants, the application of computer techniques in chemical information collection, interpretation, summarizing, and dissemination. In addition, the details of the chemical changes induced as a result of shutdown and start-up operations are obtained.

Computer Techniques in Plant Chemistry

Increased use of computer techniques in plant chemistry is needed. The computer can provide a systematized and organized means for data collection, data storage, data display, data reduction, data graphing, and data dissemination. The technique reduces chemical information to a format whereby it is readily available for use in chemical control, diagnostics, improving plant chemistry operations, and even for justifying new chemical instrumentation plant needs. The development of the necessary computer techniques for plant chemistry needs has been an integral part of this program.

Computers are also invaluable as a tool for planning and communicating work instructions involving shift changes. Its use in printing labels for plant-specific grab sample analysis bottles and data-recording forms for conducting total plant surveys has facilitated the conducting of these tests. Figure 9 is a photograph of a sheet of computer-printed grab sample bottle labels. The labels include plant identification, sample location, date, time, the initials of the personnel taking the sample, a C to indicate that cation analysis has been performed, an A to indicate that anion analysis has been performed, and a code number for sample identification. Labels for all total



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LACYGNE 1                  TIME :                LACYGNE 1                     TIME :
CONDENSATE          6135-D INITIALS :            POLISHER EFFLUENT      6235-D INITIALS :
DATE :                     C          A          DATE :                        C          A

LACYGNE 1                  TIME :                LACYGNE 1                     TIME :
ECONOMIZER INLET    6335-D INITIALS :            MAIN STEAM             6435-D INITIALS :
DATE :                     C          A          DATE :                        C          A

LACYGNE 1                  TIME :                LACYGNE 1                     TIME :
LP STEAM            6535-D INITIALS :            MAKEUP                 6635-D INITIALS :
DATE :                     C          A          DATE :                        C          A

LACYGNE 1                  TIME :                LACYGNE 1                     TIME :
SPECIAL # 1         6735-D INITIALS :            SPECIAL # 2            6835-D INITIALS :
DATE :                     C          A          DATE :                        C          A

LACYGNE 1                  TIME :                LACYGNE 1                     TIME :
SPECIAL # 3         6935-D INITIALS :            SPECIAL # 2            9935-D INITIALS :
DATE :                     C          A          DATE :                        C          A
```

FIG. 9—*Computer-printed bottle labels.*

SAMPLE POINT # 1 CONDENSATE

	6101	6102	6103	6104	6105	6106	6107	6108	6109	6110	6111	6112	6113	6114	6115	6116
TIME																
LOAD MW																
CATION RUN #																
ANION RUN #																
SODIUM ppb																
CHLORIDE ppb																
SULFATE ppb																
OTHER CATION-TIME																
-PEAK																
OTHER ANION-TIME																
-PEAK																
DUP CAT RUN #																
DUP ANION RUN #																
DUP SODIUM ppb																
DUP CHLORIDE ppb																
DUP SULFATE ppb																

FIG. 10—*Computer-generated data recording form.*

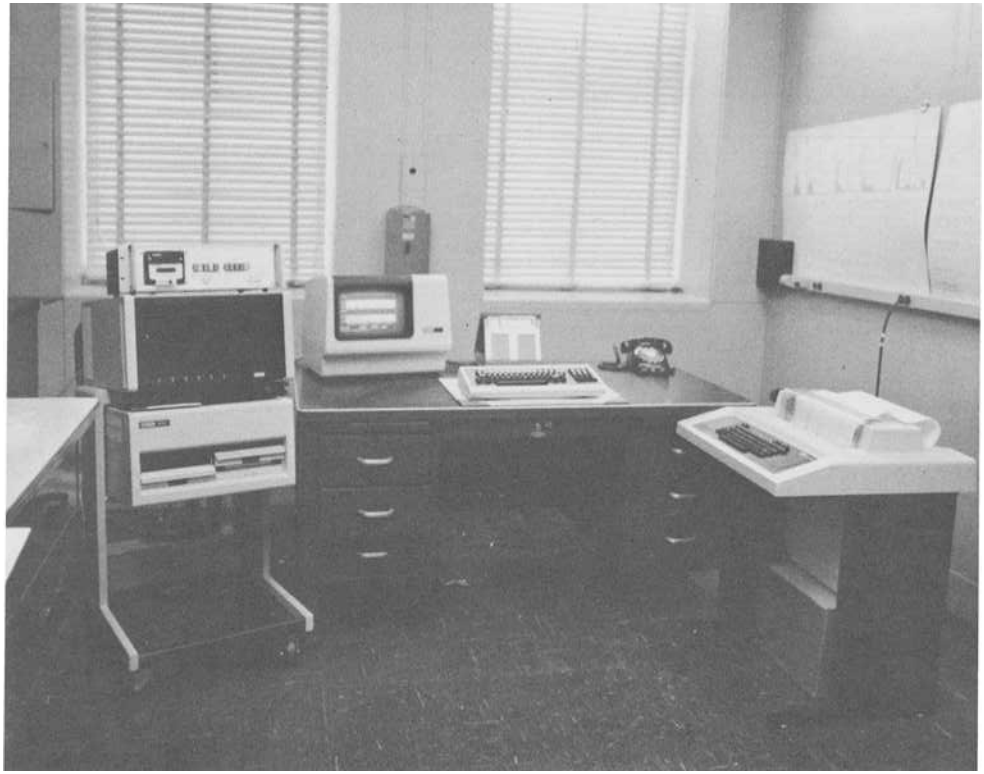

FIG. 11—*Steam purity data center.*

plant survey planned samples are preprinted along with a limited number of special sample labels to accommodate other possible sample needs.

Computer-printed forms are prepared for the recording of all analysis data from grab samples. Figure 10 is a copy of the form used for recording data for condensate. The same numbering code is used as is used for bottle labels. The data forms permit the rapid assessment of work completed, work remaining, and identification of the need for duplicate analysis, and provide for easy manual or computer data graphing and for communicating work requirements on shift changes. More important, they provide all information in a single condensed form for purposes of examination and filing.

The computer is an ideal tool for the analysis and graphing of large quantities of data. The continuous steam analyzer records seven parameters on a multipoint recorder. As previously noted, forms have been used for recording a daily high, typical, and low value of each monitored parameter. The data received on the forms are entered into a computer and graphed as a function of time or on the basis of statistical analysis. Reference must be made to the original charts for details of chemical excursions. This approach is time consuming, and it also limits the information extracted from the charts.

In order to facilitate data collection, data storage, data reduction, and data reporting for the on-line steam analyzer, all units are being retrofitted with magnetic tape cassette recorders. Each monitored parameter will be tape recorded once a minute. Data transfer from the plant to processing will be by cassette. A data center for retrieving and processing the information has been established at the Westinghouse Research and Development Center and is shown in Fig. 11. The equipment includes a tape reader, microcomputer, monitor, input terminal, output terminal, and hard copier. The microcomputer will have direct access to an on-site Univac 1100 computer. Screened data will be transferred to the Univac 1100 unit for storage, analysis, and graphing. When fully operational, this computer approach will greatly facilitate data collection, data anlaysis, and information dissemination for all operations of on-line steam analyzer systems.

Summary

Means of sampling and instrumentation for acquiring chemical information on steam–condensate in power plants have been presented. These include grab sample analysis by ion chromatography, a continuous on-line steam analyzer system, a total plant survey, and computer techniques in plant chemistry. The full benefits derived from incorporating these methods into power plant chemical analysis are illustrated in the second paper on the steam purity monitoring program.

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W. M. Hickam[1]

Program for Steam Purity Monitoring:
2. Results of Power Plant Testing

REFERENCE: Peterson, S. H., Pensenstadler, D. F., Bellows, J. C., and Hickam, W. M., **"Program for Steam Purity Monitoring: 2. Results of Power Plant Testing,"** *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 71–79.

ABSTRACT: The steam purity monitoring program of the Westinghouse Electric Corp. has accumulated a large data base on the chemical purity of water and steam in modern fossil fuel power plants. Three types of monitoring have been employed:

(*a*) grab samples taken during a plant visit and returned to the Westinghouse Research and Development Center for analysis by ion chromatography;
(*b*) continuous analysis of steam condensate, extracted from the low-pressure (LP) turbine cross-over pipe, using the Westinghouse prototype steam purity monitor; and
(*c*) total plant surveys of steam and water purity combining continuous analysis of LP steam and grab sampling of multiple locations to permit correlation of impurity levels throughout the plant during all essential operating cycles, including base load, load swings, and a shutdown and hot restart.

The plants that have been studied were selected to provide a variety of designs, including both drum and once-through boilers, various operating pressures, and different types of water treatment. Furthermore, care has been taken to study units that have experienced turbine corrosion and units that have operated for long periods without corrosion problems. Results are presented of this broad program of steam purity monitoring, with attention to the typical chemical environment of turbines in power plants in the United States.

KEY WORDS: steam, purity, power plants, sodium, oxygen, cations, pH, conductivity, chlorides, ion chromatography, sulfates, chemistry, turbine, instrumentation, water quality

A previous paper [*1*][2] in this volume has introduced the approach that the Westinghouse Electric Corp. has taken to develop instrumentation and analytical methods for identifying and measuring the concentrations of ionic impurities in power plant steam. A research program, involving the use of these analysis methods in actual plant testing, has been conducted since mid-

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

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1977 by the Westinghouse Research and Development Center. In this paper we present some results from nearly 3 years of plant testing.

Results and Discussion

Grab Samples

As discussed in the previous paper, a considerable investment in time and effort has been made to develop reliable grab sampling methods, including selection of bottles and analytical techniques. Since 1977, samples have been collected from more than 20 power plants, typically using samples available at the sample sink. The steam purity monitoring tests using the company's continuous analyzer (CA) have been conducted at some of these plants; in such cases low-pressure (LP) steam samples were available at the CA grab sample tap.

Grab samples returned from plants were analyzed by ion chromatography, and the results of analyses for Na^+, Cl^-, and $SO_4^=$ have been compiled to assess the current state of steam purity control in American power plants. Since the sampling and analysis procedures were developed as the program ran, we recently selected 1 Jan. 1979 as an arbitrary starting date for a grab sample data base. Some of the data collected before that date was of questionable reliability because of sampling technique or analytical procedure, so a "clean start" was made at a time when these procedures were set and reliable.

Figure 1 shows a summary of 112 grab samples collected at 14 turbine units. The number of results in certain concentration ranges is shown by vertical bars for Na^+, Cl^-, and $SO_4^=$ analyses. In addition, the type of sample is distinguished as water (shaded) or steam. The water samples include condensate, polisher effluent, economizer inlet, and others. At some plants, drum blowdown or makeup samples, or both, were collected, but these were excluded from the results shown. The steam samples included saturated (drum) steam, main steam, low-pressure (LP) steam, and extraction heater drains. The concentration ranges were based on the company's steam purity recommendations [2] for sodium and chloride, with each range subdivided into halves.

The results for these 14 turbine units show what we consider to be a general result of our testing program: namely, that sodium and chloride can be controlled, most of the time, within the recommended steam purity limits. Sulfate is also usually controlled within the 5 ppb limit. In the present case, Na^+ was less than 5 ppb in 84 percent of the samples, Cl^- in 94 percent of the samples, and $SO_4^=$ in 90 percent. However, some samples were found with ion concentrations above the 24-h limit, and other results indicate operation within the limited-time ranges. Spot grab samples such as those we obtained cannot provide definitive assessment of the risks that result from such operation.

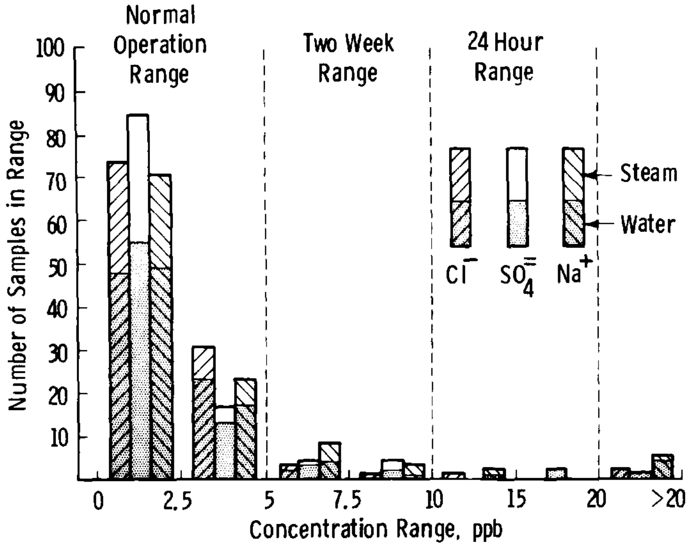

FIG. 1—*Summary of grab sample results in concentration ranges, with Westinghouse steam purity recommendations for Na^+ and Cl^- indicated. The results are subdivided according to sample type, water* (shaded) *or steam.*

We have also compared units that have suffered turbine corrosion and those that have not had turbine corrosion incidents (Fig. 2). The former, or "affected," category consists of five units that have had corrosion and in which analysis of turbine deposits has shown high concentrations of corrodents. This is, of course, an after-the-fact classification, and the results may not indicate the chemical environment of the turbine during the period when corrosive deposits were forming.

Although the sample sets are still fairly small, especially for affected units (5 units, 27 samples), there do seem to be differences in the distributions. In particular, the distribution for the unaffected units seems to be mostly in the lowest range while for the affected units it is weighted to somewhat higher concentrations. Since the largest single group ($SO_4^=$, <2.5 ppb) of steam results for affected units contains only seven results, these indications must still be considered preliminary.

Continuous Analyzer

Sixteen turbine units have had continuous analyzers installed for periods ranging from a few weeks to over a year, with the typical monitoring period being 3 to 6 months. Since the first instrument was installed in November 1977, seven more have been built, and the accumulated monitoring experience is now over 100 instrument months.

The continuous analyzer data represent a huge amount of data on a unit, but the amount of data can be reduced to manageable proportions by summarizing on a daily basis to low, typical, and high values. These summaries

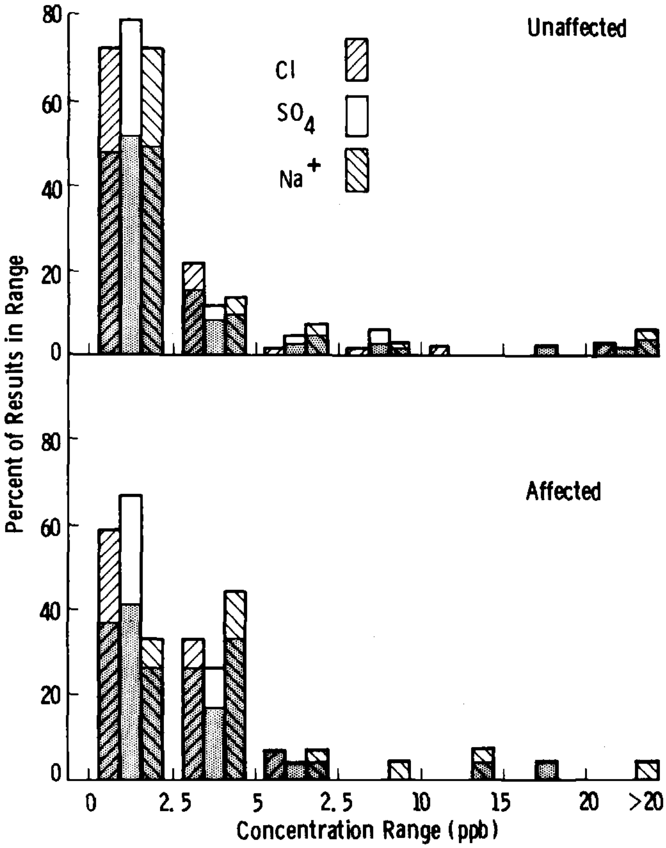

FIG. 2—*Summary of grab sample results for water* (shaded) *and steam* (open) *from 14 power plants.*

serve as a guide to the original data, establishing a base line of normal operation and indicating those occasions when there are significant departures from typical behavior. In addition, the summary data have formed the basis of statistical analysis of the data. Figure 3 shows how daily typical values for sodium concentration are distributed in various ranges, which are based on the recommended steam purity limits. The results are compared for affected and unaffected units, although these labels are still based on corrosion history and deposit analysis and, accordingly, describe the past environments of the units. With this provision, we note that the distribution for unaffected units has almost twice the percentage of results below 1 ppb as the distribution for affected units. In other words, the unaffected units typically operate well down in the recommended range, with a wide margin for error. The affected units show higher typical values and, accordingly, have less margin to work with.

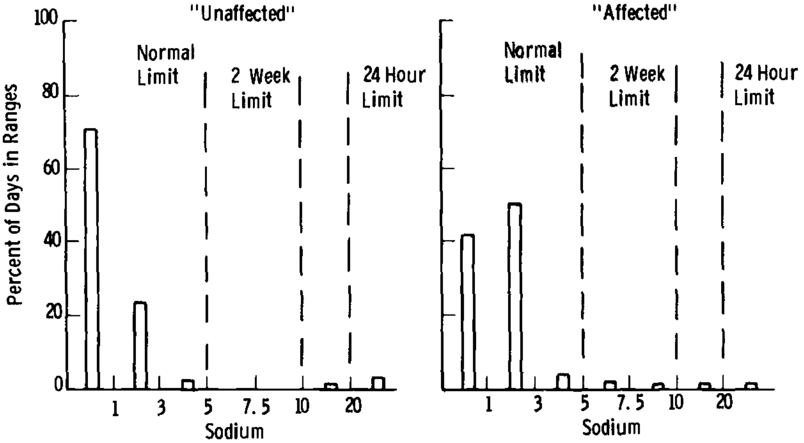

FIG. 3—*Summary of continuous analyzer results for Na⁺ monitoring, as of April 1980. The data are shown as percent of days that the typical sodium concentration (ppb) fell within particular ranges, for affected and unaffected units.*

These points are illustrated even more clearly in Fig. 4, which contains a distribution plot for cation conductivity. For this parameter, the results for affected units exceed the recommended value on 24 percent of the monitored days, whereas for unaffected units only 7 percent of the days had excess values. To allow some margin for error, the percent of results below 0.2 μS/cm can be compared, showing 84 percent for unaffected units and only 41 percent for affected units.

Further interpretation of cation conductivity results is greatly facilitated when grab sample analyses are available to confirm the identities and concentrations of anionic species. We have usually found that when the cation

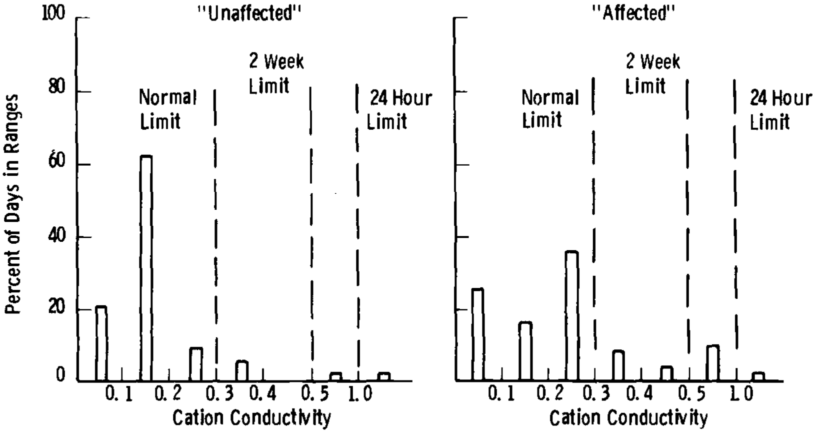

FIG. 4—*Summary of continuous analyzer results for cation conductivity monitoring as of April 1980. The data are shown as percent of days that the typical cation conductivity (μs/cm) fell within particular ranges, for affected and unaffected units.*

conductivity approaches or exceeds the 0.3-μS/cm recommended limit, it may not be due to very high chloride or sulfate levels and is often due to the presence of dissolved carbon dioxide, which indicates air inleakage. This point will be discussed in more detail later.

Total Plant Surveys

We have conducted six total plant surveys (TPS) combining extended periods of grab sampling and continuous team monitoring. These tests have provided opportunities to examine the effects of critical plant operations on steam purity, with samples collected from points all around the plant water–steam cycle. Among the units tested we have included both affected and unaffected units, with examples of drum and once-through boilers in both categories.

Total plant surveys generate so much data that it is difficult to discuss the tests in a short time. We previously presented results from a TPS conducted at a drum boiler unit with a 7-year history of confirmed corrosion-free operation [*3*]. The results indicated that the unit operated well within the steam purity recommended limits and that steam purity was independent of load over the range of normal operation. Only operation below about 10 percent of design load produced significant changes in system chemistry, but even then only in the water samples.

In September 1979, a total plant survey was conducted in Japan with the cooperation of Mitsubishi Heavy Industries (MHI).[3] The unit studied was a 450 MW, 24 MPa (3500 psig) once-through boiler unit with mixed-bed condensate polishers, using seawater to cool the condenser. This unit had had over 7 years of operation with no turbine corrosion incidents and had been recently inspected to confirm its unaffected status.

Our usual test procedure was modified to eliminate a shutdown but was extended to include a month of follow-up grab sampling by MHI after our departure. The MHI personnel were trained in the use of the ion chromatograph, and sampling procedures were taught to MHI personnel and to power plant operators. In all, over a 5-week period 42 sets of grab samples were collected at four sampling points: condensate, economizer inlet, main steam, and low-pressure turbine inlet steam (continuous analyzer). The results of the analyses for Cl^-, $SO_4^=$, and Na^+ in the LP steam samples are shown in Fig. 5. The results for the other sample points were virtually identical to those within the ±1 ppb scatter of results that is typical of the sampling and analysis procedures. It was particularly noteworthy that no sample had as much as 5 ppb of any of these species, and the most common result for Na^+ and Cl^- was <1 ppb. The typical result for $SO_4^=$ was a little higher, 1.5 ppb, which is consistent with its higher molecular weight.

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[3] Westinghouse licensee.

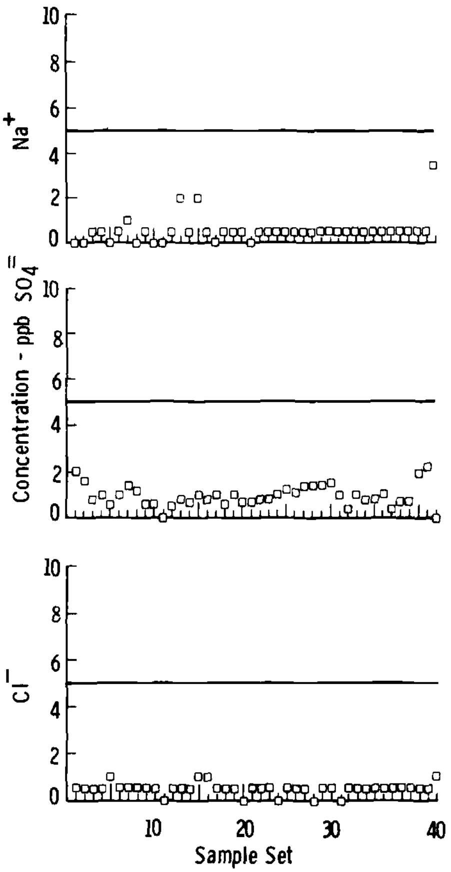

FIG. 5—*Low-pressure steam sample results: Na^+, $SO_4^=$, and Cl^- analyses for total plant Survey 4.*

Chemical purity in a once-through plant is primarily a function of polisher effectiveness, so we were particularly interested in what the continuous analyzer would show when a polisher was put into service after regeneration. In fact, the CA had no observable response to polisher changes. The reason polisher change gave no measurable effect on steam purity seems to be twofold:[4]

1. The criterion for taking a polisher out of service was gallon-count, so that breakthrough had not occurred.
2. Before going on stream, a newly regenerated resin bed was rinsed back to the condenser until its conductivity was <0.2 μS/cm.

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[4] We do not wish to imply that these two factors constitute a recipe for corrosion-free operation of a plant, but we use them as an example of operating procedures in a plant with a history of corrosion-free operation.

Among the important conclusions of this total plant survey were the following:

1. It is clearly possible to meet the recommended purity limits with a once-through boiler using condensate polishing.
2. The power plant was not using any special instrumentation. However, all the plant chemical instrumentation was functional and routinely calibrated, if appropriate.

Some Particular Results

Ion Partitioning in a Drum Boiler—In a drum boiler, equilibrium distribution of ionic impurities is supposed to keep levels of these ions in the drum steam to low levels by concentrating impurities in the water phase where they are removed as drum blowdown. Our evidence suggests that this partitioning may not be as successful as had been thought. In a total plant survey at a plant with a 16.6-MPa (2400-psig) drum boiler, the ratio of Cl^- in blowdown to Cl^- in steam was as low as 80:1, while the ratios for sodium and sulfate were greater than 1000:1. These results suggest that Cl^- may enter the steam as a volatile species, perhaps hydrochloric acid (HCl). In order to keep Cl^- in the steam within the recommended limits, it may be necessary to monitor Cl^- in blowdown and perhaps to increase the blowdown rate at times in order to control Cl^-.

Stoichiometry—Much of the time we have not observed mass and charge balance between Na^+ and $Cl^- + SO_4^=$. This is not particularly surprising since there is typically a large excess of ammonia (>1 ppm), some of which will be present in the ionized form, NH_4^+. It has been suggested that we analyze for NH_3, and in fact we often get such analyses. However, the experimental uncertainty in the measurements makes chemical balance calculations an unproductive exercise. For example, the grab sampling and ion chromatographic analyses for Cl^- and $SO_4^=$ are usually reproducible to about ± 1 ppb, which is 20 percent of the recommended value. In order to measure ammonia to this same ± 1 ppb, a precision of ± 0.1 percent must be obtained. If the ammonia measurement is only ± 1 percent, then the uncertainty of 10 ppb swamps the levels of the other ions.

Air Inleakage—With continuous analyzer monitoring we have observed several plants where air inleakage has caused high cation conductivity readings. The situation is illustrated by Fig. 6, which is a partial reproduction of the analyzer chart for a period of 32 h. We attribute the rise in cation conductivity to an increasing concentration of bicarbonate ion, formed by hydrolysis of carbon dioxide (CO_2). The specific conductivity rose at the same time because oxygen scavenging by hydrazine increased, leading to a greater rate of ammonia production. Finally, the pH also rose as the ammonia concentration increased. While all this was occurring, there was no noticeable increase in dissolved oxygen at the LP crossover, which presumably indicates

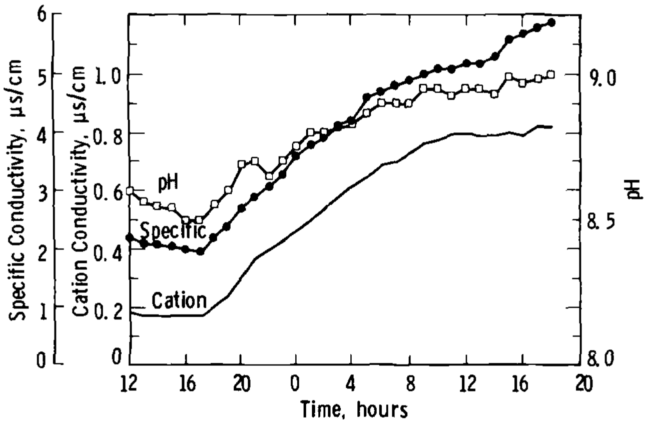

FIG. 6—*Continuous analyzer results, summarized hourly, for cation conductivity, specific conductivity, and pH during a presumed air inleakage incident.*

that oxygen was effectively removed. The unit had a drum boiler, so CO_2 buildup went on until a new equilibrium was established, while in a once-through boiler unit the condensate polishers would presumably have removed CO_2 from the system. We have no direct evidence that there is a harmful effect from the presence of such amounts of CO_2 in the system, but it certainly obscures any benefits from a cation conductivity measurement to determine acceptable levels of such ions as chloride.

Conclusions

1. We have studied units that achieve chemical purity in steam, much better than the recommended ranges, without requiring exceptional facilities or methods of operation.
2. Analytical procedures and instrumentation have been developed to ensure operation within the steam purity recommendations.
3. Both affected units and unaffected units appear to operate within the normal steam purity recommended ranges for sodium concentration and cation conductivity most of the time. However, unaffected units maintain lower values, and hence operate with larger margins of error.
4. Cation conductivity appears to offer a better indication of the likelihood of turbine corrosion than does sodium concentration.

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Newer Techniques and Instrumentation for Monitoring

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Quantification of Sodium, Chloride, and Sulfate Transport in Power-Generating Systems

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REFERENCE: Willhite, T. B., Sawochka, S. G., and Pearl, W. L., "**Quantification of Sodium, Chloride, and Sulfate Transport in Power-Generating Systems,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 83–91.

ABSTRACT: In the performance of several chemistry monitoring programs for pressurized water reactors sponsored by the Electric Power Research Institute (EPRI), integrating sampling devices are employed to concentrate low-level impurities present in the power-generation cycle. The devices employ a conventional Millipore membrane for collection of filterable species and separate cation and anion ion-exchange columns for ionic species. The preparation for the ion-exchange columns involves resin pretreatment aimed at complete regeneration of resins, and *in situ* regeneration to ensure resin cleanliness and uniformity following column assembly.

To complement and expand on results from the integrating ion-exchange columns, ion chromatography and specific ion electrode techniques were employed during short-term studies. These alternative techniques allow transient conditions to be monitored, whereas the integrated sampling system is deficient in this respect. Sodium, chloride, and sulfate concentrations determined with the different techniques were compared, and agreement was considered adequate for achieving program goals.

KEY WORDS: sampling, sample integration, sodium, chloride, sulfate, ion exchange, analytical procedures, power plants, instrumentation, water quality

It is becoming increasingly evident that water quality in steam-generating cycles is of critical importance to plant availability. This is particularly true in nuclear systems where component failures have necessitated unplanned outages with costly repairs and increased manpower exposure to ionizing radiation. Even though high-purity water is used in such systems, trace impurities are transported to the steam generators in gram-per-hour quantities [*1*][2] where they can be concentrated in crevices, incorporated in sludges, carried over with the steam, and so on. Numerous efforts are being made to

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

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quantify these impurities and address the relationship of such species to observed component attack. Once such relationships are established, plant operators will require relevant criteria and adequate measurement techniques to monitor and eliminate species of concern [*1,2*].

Experimental Procedure

Since concentrations of interest are typically 0.1 to 3 ppb and since direct measurement techniques at such levels are not available, a reliable method of sample preconcentration is required. The method of choice must concentrate impurities from a sufficiently large volume of sample to increase concentrations into the range of available analytical techniques. It also must minimize sample contamination and achieve reasonable sample collection efficiency. Concentration by evaporation is considered unreliable from the standpoints of impurity loss through steam solubility and steam carry-over and undue exposure to potential contamination. The sample concentration technique described here concentrates impurities on line with filters and ion exchange columns while allowing minimum exposure to the surrounding plant environment. Reagent-grade laboratory chemicals were used throughout the technique verification effort.

Sample Collection

The sample collection system design is shown in Fig. 1. A Millipore 0.45-μm membrane collects filterable species from a continuous sample flow of approximately 100 ml/min followed in series by a cation and an anion resin column operated at 1400 litres/min$\cdot$m^2 (34 gal/min$\cdot$ft^2). The sampling period extends from 3 to 7 days. A continuous bypass flow is maintained at approximately 1 litre/min to ensure representative flow in the plant sample line tubing with an outer diameter of 0.95 cm. Both sample and bypass flows are recorded and adjusted if necessary two to three times daily. Pressure regulation is employed downstream of the filter to maintain constant sample flow.

Ion-Exchange Columns

The ionic form of the ion-exchange resin and the elution scheme must consider sample collection and elution efficiency and must be compatible with analytical methods.

For cation preconcentration, a strong acid cation exchange resin is used (styrene-divinylbenzene copolymer). The selected resin is an 8-percent cross-linked, 20 to 50 mesh, nuclear-grade material purchased in the hydrogen form (typically 98.4 percent). The major impurities are sodium (0.7 percent), calcium (0.6 percent), and iron (0.2 percent). The resin is regenerated with 2 *N* nitric acid to remove most impurities. Then 40 ml of the resin is packed in a Lexan column of 9.5-mm inner diameter, and 61-cm length and regenerated

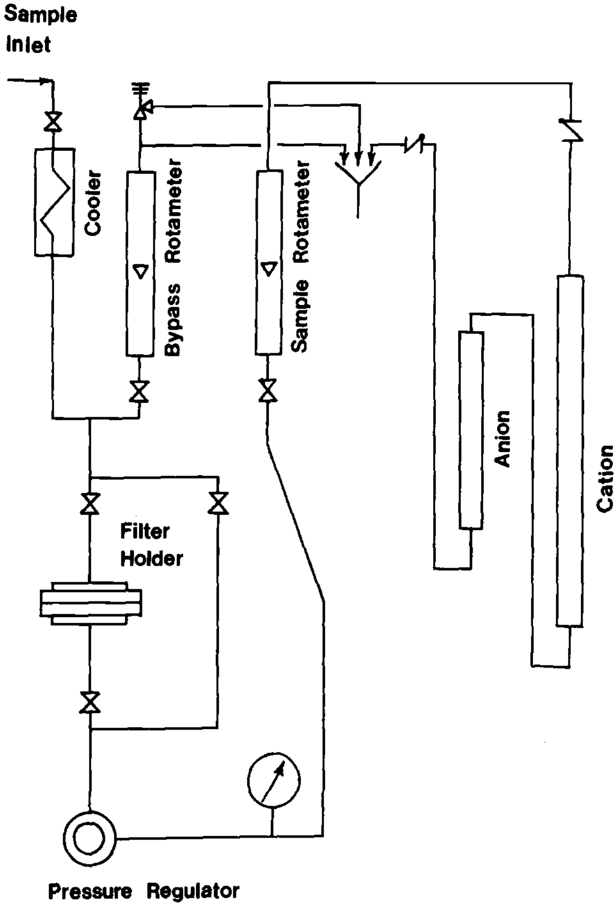

FIG. 1—*Schematic drawing of the sampling system.*

in situ with 2 *N* nitric acid. All column materials are prewashed in nitric acid. After sample collection, the column is inverted and eluted with 2 *N* nitric acid. The eluate is analyzed for sodium by atomic absorption spectrophotometry.

For anion preconcentration, a Type I strong-base anion resin (8 percent cross-linked and 20 to 50 mesh) is employed. This resin is typically 95 percent in the hydroxide form. The major impurities depend on the supplier. The impurities were chloride (2.5 percent) and carbonate (1.3 percent) for Manufacturer A and sulfate (3.5 percent), carbonate (1.5 percent), and chloride (0.5 percent) for Manufacturer B. The anion resin is pretreated in a two-step regeneration using a 4.5-weight percent solution of sodium bicarbonate followed by a 1 *N* nitric acid solution. Fifteen millilitres of resin are packed in a Lexan column of 9.5-mm inner diameter and 25.4-cm length and regenerated *in situ* in a two-stage regeneration using 0.72 *N* perchloric acid followed by 2 *N* ammonium hydroxide.

The perchlorate form of the resin is chosen in order to be compatible with the Central Electricity Research Laboratories (CERL) sulfate test [*3*] which is matrix dependent. Once the sample has been collected, the column is inverted and eluted with 0.72 *N* perchloric acid. The eluate is analyzed for sulfate using the CERL method and for chloride using the American Society for Testing and Materials ferric thiocyanate method [*4*].

Results and Discussion

Laboratory Testing

The concentration variations in the major contaminants during elution of a new cation resin column are shown in Fig. 2. A dramatic difference is apparent in the elution efficiency among the alkali metals, the alkaline earth metals, and the transition metals. These differences must be considered when metals other than sodium are to be analyzed. Ten column volumes are employed for the normal pretreatment step.

Previous work in the NWT Laboratory with anion exchange resins indicated that elutable chlorides increase during storage [*1*]. During *in situ* re-

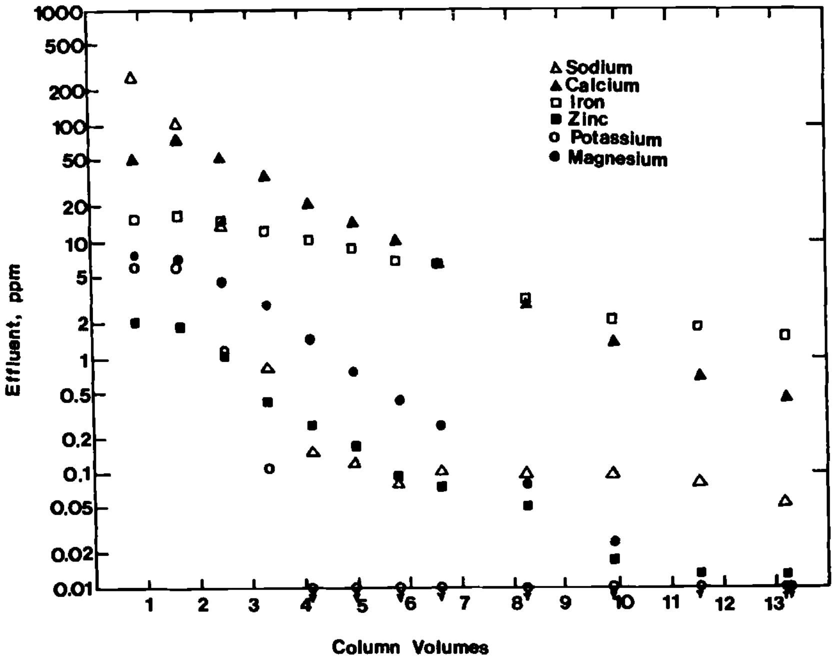

FIG. 2—*Cation resin pretreatment with 2* N *nitric acid; flow rate = 41 litres/min·m*^{2}*.*

generation, the chloride concentration in the eluate decreases rapidly until virtually no chloride is present. However, if the column is stored for several days and again regenerated, significant chloride return is observed. Each time the storage and regeneration steps are repeated, return occurs. To quantify the return, a series of 1 *N* nitric acid regenerations was performed. Even after 52 days, chloride return continued (Fig. 3).

A second matrix, chosen for its compatibility with the CERL low-level sulfate test [*4*], was 0.072 *M* perchloric acid. In this matrix, chloride return differed from that in the 1 *N* nitric acid matrix (Fig. 4). However, the return showed no sign of decreasing after 13 days.

Finally, a set of columns originally placed in the nitrate form with 1 *N* nitric acid and then rinsed with high-purity water was treated for chlorides after 13 and 14 days. Chloride returned at about a 35 percent lower rate than from unrinsed resins.

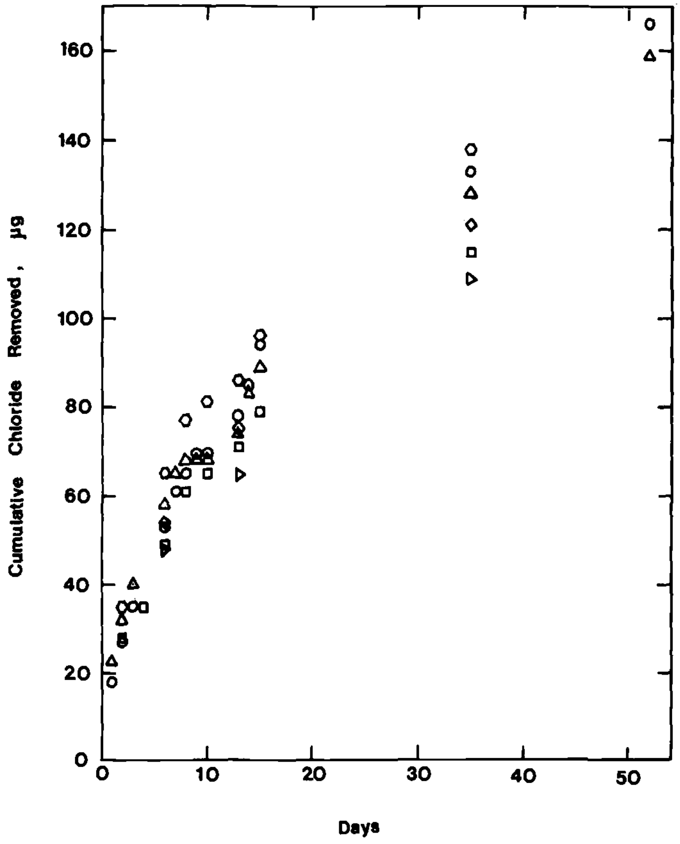

FIG. 3—*Chloride return from anion resin, 1* N *nitric acid (each symbol represents one test column).*

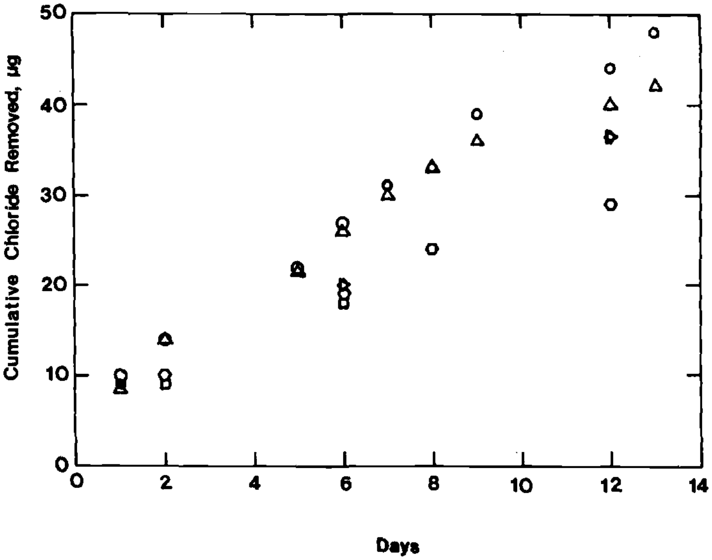

FIG. 4—*Chloride return from anion resin, 0.072* M *perchloric acid (each symbol represents one test column).*

To date, the source of the chloride has not been determined. Some possibilities are (1) slow migration of chloride from the interior of the resin beads, (2) gradual oxidation of residual resin substrate precursor, and (3) gradual oxidation of the resin substrate.

Despite the chloride return, meaningful results can be obtained with 100 to 1000-litre sample sizes if prompt analysis, careful process control, and concurrent field blanks are employed.

The results of laboratory recovery tests for sodium are shown in Table 1. The sodium solutions were spiked with 0.1 ppm ammonia to simulate plant conditions. The cation columns were as described previously. The recoveries generally are acceptable for achieving most program goals. However, signifi-

TABLE 1—*Laboratory recovery tests for sodium.*[a]

Test No.	Inlet, µeq	Overall Recovery, percent
A[b]	50.8	88 ± 3
B	51.0	87
C[b]	51.6	81 ± 12
D[b]	51.0	85 ± 3
E	57.0	82

[a] pH control = 0.1 ppm NH_3.
[b] Average of duplicates.

cant scatter was observed in the Test C results, and no explanation could be found. Field test data on sodium recovery will be discussed later.

Laboratory recovery tests also were performed for chloride and sulfate (Table 2). The test solutions contained no ammonia since, in the field application, the anion column follows the cation column, which removes ammonia from the stream.

The results for chloride indicate very good recovery, whereas those for sulfate indicate only fair recovery with significant variation between column fabrication lots. No correction was made for the sulfate or chloride recovery variations during the site test programs.

Field Testing

In field testing it is imperative that blanks be used to establish column background contaminant levels for all species of interest. In practice, columns are fabricated in lots containing 30 to 60 sets (one cation column and one anion column per set). Out of each lot, four to ten sets are picked at random to serve as blanks. The blanks are transported, eluted, and analyzed with the plant samples.

Column collection efficiency tests as a function of flow rate were conducted at a plant by passing a sample through two cation–anion column sets in series. Four such sample trains were operated simultaneously from a single manifold at different flow rates for the same length of time. The collection efficiency of the first set of columns was calculated based on the total amount of each species collected on both sets in the given sample train. The results are presented in Table 3. Two separate tests were performed. The first test ran for 1130 min and the second for 485 min. The low value of 45.9 percent for the second test for sodium at 25 ml/min probably resulted from the relatively lower sodium level in the sample column than that in the blank column for the 485-min sample time.

The sodium collection efficiencies for Test 1, which is considered more reliable because of the longer sampling period, are within the range of accuracy required for field measurements. The sampling times during routine

TABLE 2—*Laboratory recovery tests for chloride and sulfate.*

Lot No.	Overall Recovery, percent	
	Chloride	Sulfate
7A	92.8 ± 5.1	80 ± 5
4A	94.5	87
5B	97.2 ± 8.1	66 ± 18
5C	94.1 ± 16.3	58 ± 15
1C	102.0 ± 3.7	74 ± 17

[a] No pH control.

TABLE 3—*Field test of column collection efficiency.*[a]

Test	Time, min	Flow, ml/min	Sodium, %	Chloride, %	Sulfate, %
1	1130	25	76	99.6	100
		50	98	100.0	70
		75	92	99.9	100
		100	90	100.0	80
2	485	25	46	99.6	100
		50	78	98.0	100
		75	NR[b]	99.8	50
		100	80	100.0	87

[a] Percentage of total removed by the first column.
[b] NR = not reported.

field sampling range from 4 000 to 10 000 min. The results for chloride are more than adequate. The results for sulfate vary unsystematically. The reasons for this variability are not known.

Comparison of Methods

Results obtained by the column technique just described were compared with those obtained by ion chromatography (IC), on-line Orion sodium monitoring, and direct atomic absorption spectrophotometry (AA). Three sequential column samples were obtained from eleven sample points; during column sampling, three sets of grab samples were obtained at the same points. The sampling period for each set of column samples was approximately 6500 min. The sodium and sulfate results obtained by the different methods (Table 4) are in reasonably good agreement. The few deviations

TABLE 4—*Comparative methods study.*

	Sodium, ppb			Sulfate, ppb	
Sample Point	Column[a]	Orion	AA[b]	Column[a]	IC[b]
1	1.0	0.9		0.6	0.7
2	0.8	1.6		<0.6	0.7
3	4.3	5.0		0.4	0.8
4	6.4	6.0		<1.0	0.8
5	9.7	12.5		1.0	0.6
6	40.0		54	1.2	
7	40.0		55	3.3	2.8
8	0.3			<0.7	0.6
9	0.3			<0.6	0.6
10	0.3	0.5		0.5	
11	0.3			0.7	0.7

[a] Average of three column sets.
[b] Average of three grab samples interspersed during the column sampling period.

may be attributable to the variations in plant chemistry during the sampling period. Unfortunately, the IC chloride data were compromised by the presence of ammonium hydroxide in the sample during these tests. In subsequent tests, a cation resin column was employed to remove ammonium ion from the sample prior to IC analysis, thereby eliminating this source of error.

Summary

The validity of sampling by *in situ* preconcentration on ion-exchange resin columns has been demonstrated for sodium and chloride within the accuracy required in field measurements. Although reasonable recoveries of sulfate also have been obtained, the variability of results was greater than desired. Technique improvement is being investigated. Although this discussion has been limited to three major species of concern, that is, sodium, chloride, and sulfate, the technique has been applied successfully to several other cations and anions in power plant waters.

Acknowledgment

The sponsorship of the overall study by the Electric Power Research Institute is gratefully acknowledged.

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[*4*] *1975 ASTM, Annual Book of Standards, Part 31,* American Society for Testing and Materials, Philadelphia, 1975, Method C.

J. A. Rawa[1]

Determination of Anions in High-Purity Water by Ion Chromatography

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REFERENCE: Rawa, J. A., "**Determination of Anions in High-Purity Water by Ion Chromatography,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 92–104.

ABSTRACT: Characterization of high-purity waters is a classic analytical problem because of lack of sample integrity as well as inaccuracies in the analytical methods employed for measurement. For industrial process water applications, the purity of water with low dissolved solids content has been traditionally determined by on-line monitoring of specific conductance and sodium. Trace concentrations of cations (sodium, potassium, calcium, and magnesium) present in demineralizer effluents, condensates, and high-pressure boiler and boiler feedwaters have been determined by flame or flameless atomic absorption. Previously, there was no accurate method for measuring trace concentrations of anionic constituents. The introduction of a new analytical technique, ion chromatography (IC), has facilitated the identification and quantitation of several anions—chloride, nitrate, orthophosphate, and sulfate at the micrograms-per-litre level. The IC technique incorporates the concepts of ion exchange and conductimetric detection. Without sample pretreatment, these anions can be accurately detected down to about 50 μg/litre with a 100-μl sample injection. By concentrating the anions in the sample on a special low-capacity anion concentrator column (Dionex Corp.) prior to IC analysis, these same anions can be readily detected at $<$10 μg/litre. The anion concentrator column technique has been applied successfully to the analysis of high-purity waters from various industrial process water systems. The advantages and limitations of the IC method are discussed.

KEY WORDS: ion chromatography, trace anion analysis, anion concentrator column technique, high-purity waters, industrial process waters, steam, condensate, liquid chromatography, water trace impurities, sequential analysis, conductivity, demineralizers, electric utilities, water treatment, feedwater, water quality, quantitative analysis, instrumentation, power plants

Prior to 1960 the level of impurities in high-purity waters was quantitated by employing gross measurements such as conductivity. Sodium was often found to be the predominant cation in steam from boilers. Since sodium measurements were found to be reliable, on-line monitoring of sodium with an ion-sensitive electrode became prevalent in the early 1960s for assessment of boiler water carry-over. As atomic absorption and emission techniques

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became more popular in the late 1960s, more specific information about the contaminants in high-purity waters was disclosed. For example, other cations such as potassium, calcium, and magnesium could be readily detected by flame atomic absorption at the micrograms-per-litre level. Detection levels (<1 μg/litre) were further extended by the development of flameless atomic absorption in the early 1970s. As an increasing number of high-purity waters were more completely characterized, it became obvious that although conductivity and sodium measurements would often indicate whether there was a problem with water or steam purity, more specific information was required to isolate the source of a contaminant or contaminants.

While techniques for measuring trace levels of cationic impurities became increasingly sophisticated, there was a void in the number of proven analytical techniques for identifying and quantifying trace anionic constituents. Usually, samples were concentrated by evaporating large volumes of a water sample. Accepted methods for measuring anions at the milligrams-per-litre level were then applied. These concentration techniques are time-consuming and are easily influenced by environmental conditions.

The advent of ion chromatography (IC) [*1*][2] in 1975 and the availability of this specific instrumentation in 1976 revolutionized the approach to assessing ionic impurities in water, particularly high-purity waters. The sensitivity of IC without any sample concentration provided detection levels for sulfate (SO_4) and nitrate (NO_3) which were about ten times lower than those obtained for sulfate determined in accordance with the ASTM Tests for Sulfate Ion in Water and Wastewater [D 516–68 (1974)] and the ASTM Test for Nitrate Ion in Water [D 992–71 (1978)]. Ion chromatography also offers the advantage of sequential analysis which facilitates the detection of contaminants whose presence may not have been suspected.

The anion concentrator column technique [*2,3*] which was introduced in 1978 provided even lower detection levels [<10 μg/litre chloride, SO_4, NO_3, and orthophosphate (*o*-PO_4)]. The applications of IC to the determination of both trace anionic and trace cationic constituents has grown significantly in the past 2 to 3 years.

Ion chromatography has been successfully applied to the analysis of high-purity waters from various points throughout the industrial system [*4,5*]. It has been particularly useful to the power generation industry in the detection and evaluation of potentially corrosive species present in water and steam which could result in costly equipment damage [*6*]. The purity of condensates and demineralizer effluents has been better defined based on IC data.

Equipment

A Dionex Model 10 ion chromatograph equipped with a low-capacity anion exchanger (separator column) in the carbonate–bicarbonate form in

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

series with a high-capacity cation exchanger (suppressor column) in the hydrogen form and either a single or dual pen strip chart recorder were used for all analyses. An anion concentrator column (3 by 50 mm) containing a low-capacity anion exchange resin in the carbonate–bicarbonate form replaced the normal sample injection loop in the ion chromatograph when sample concentration techniques were required. An Orion Model 341 single-channel syringe loading device was used to pass a measured volume of sample from a sterile plastic syringe (available through Fisher Scientific Co., Pittsburgh, Pa., Catalog No. 14-831-40) through the concentrator column. The highest flow setting on the syringe loading device was used to maintain a flow of about 2 ml/min through the concentrator column.

A Perkin-Elmer Model 603 atomic absorption spectrophotometer equipped with a 10-cm burner head was used for cation analysis. The primary resonance lines were used for the determination of calcium, magnesium, sodium, and potassium. Calcium, magnesium, and potassium were determined by atomic absorption; sodium was determined by flame emission.

Reagents

Stock solutions (1000 mg/litre) for chloride, nitrate, sulfate, and orthophosphate and the carbonate–bicarbonate eluent were prepared from reagent-grade sodium salts. Combination anion standard solutions were prepared by serial dilution of appropriate aliquots of the stock solutions. The 1 *N* sulfuric acid–regenerant solution was prepared by dilution of concentrated sulfuric acid (specific gravity 1.84). Low-conductivity water (<1.5 μmho/cm), prepared by polishing demineralized carbon-treated water by passage through a 6 by 50-cm column of mixed-bed strong-base anion and strong-acid cation exchanger, was used to prepare standard solutions, eluant, and regenerant.

Atomic absorption calibration solutions for calcium, magnesium, sodium, and potassium were prepared by appropriate dilution of 1000 mg/litre stock solutions (available from Fisher Scientific Co., Pittsburgh, Pa.).

Description of Anion Concentrator Column Technique

The anion concentrator column is a 3 by 50-mm glass column which is packed with a low-capacity (approximately 0.03 meq/g) pellicular resin with 2 to 5 percent cross-linkage. The resin consists of an inert core of divinylbenzene which is surface sulfonated. The small aminated resin particles are electrostatically bonded to the sulfonated surface. The resin structure is shown in Fig. 1.

Because of the low exchange capacity of the resin, the type of sample preconcentrated by this technique is limited to those waters with low dissolved solids content. Anions are not quantitatively retained for samples that contain high levels of dissolved solids since the ions in the sample, if present in

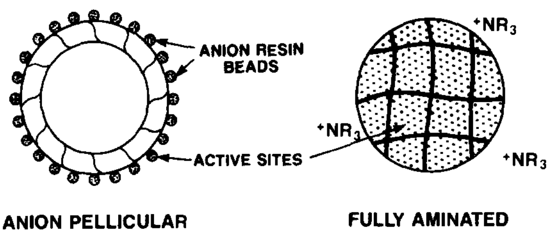

FIG. 1—*Description of the anion exchange resin in the anion concentrator column.*

sufficiently high concentrations, would act as an eluting phase when the sample is passed through the concentrator column.

A schematic drawing of the anion concentrator column is shown in Fig. 2. A female Luer adapter is used to connect a plastic syringe to a flanged fitting connected to one end of the concentrator column. Once the measured aliquot of sample has been eluted through the column, the syringe and adapter are disconnected and the concentrator column is placed in the injection valve of the ion chromatograph while eluant flow is bypassed.

The sample ions are retained on the anion exchange resin until the flow of the carbonate–bicarbonate eluant is directed through the injection valve. The concentrated anions are eluted onto the longer column of the anion exchanger (150 + 500 mm) to enable separation of the anions. The separated anions pass through a column of strongly acidic cation exchanger where the anions of interest are converted to their acid form. The anions in their highly conductive acid form are detected by conductivity against a low background conductivity of carbonic acid.

By this concentration technique levels of detection are improved approximately a hundredfold over detection levels achieved with the same instrumental conditions when only 100 μl of sample are directly injected (no sample concentration).

The concentrator column technique significantly improved the accuracy and precision of chloride measurements in the micrograms-per-litre range because the effect of the temporary decrease in conductivity response (re-

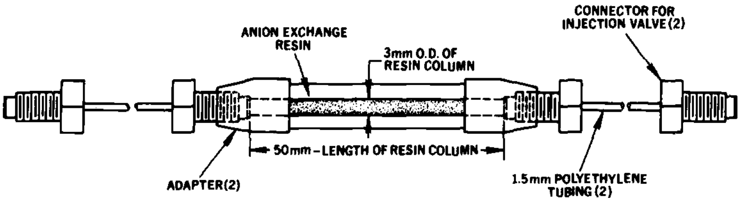

FIG. 2—*Schematic drawing of an anion concentrator column.*

ferred to as a "water dip") just prior to the elution of chloride is diminished by the large increase in the conductivity response for low chloride concentrations.

Procedure

Sample Collection

Samples were collected in duplicate in high-density polyethylene bottles with polyethylene-lined caps. The bottles and caps were preconditioned by rinsing them two to three times with low-conductivity water. The full sample bottles were permitted to stand at least 24 h to leach out contaminants. The water was discarded and the bottles were rinsed two or three times and then refilled with fresh aliquots of low-conductivity water. The preconditioned sample bottles were shipped to the sample collection site. The bottles were rinsed several times with the samples they were to contain and then filled. The samples were collected as described in the ASTM Specification for Equipment for Sampling Water and Steam [D 1192-70 (1977)]. The samples were stored at room temperature (25 ± 5°C) and analyzed as soon as possible after collection.

Instrument Calibration

The separator columns were conditioned daily with 0.1 *M* sodium carbonate (Na_2CO_3) solution, then rinsed with low-conductivity water. The suppressor column was regenerated as required by back flushing with 1 *N* sulfuric acid (H_2SO_4) solution and then rinsing with low-conductivity water. The separator and suppressor columns were equilibrated with 0.003 *M* sodium bicarbonate ($NaHCO_3$)/0.0024 *M* Na_2CO_3 eluant; then the background conductivity was electronically offset. The instrumental parameters used for sample analysis with direct injection and with sample preconcentration are listed in Table 1.

When sample concentration was required, the anion concentrator column was placed on line in the ion chromatograph by removing the normal sample injection loop from the injection valve and replacing it with the concentrator

TABLE 1—*Analytical conditions for analysis of trace anions (μg/litre) by ion chromatography.*

Eluant	0.003 *M* $NaHCO_3$/0.0024 *M* Na_2CO_3
Precolumn	3 by 150-mm anion separator
Separator column	3 by 500-mm anion separator
Suppressor column	3 by 250-mm anion suppressor
Flow setting	30% (approximately 138 ml/h)
Full-scale setting	10 μmho/cm
Recorder output	1000 and 500 mV

column. The carbonate-bicarbonate eluant was directed through the concentrator column to remove trace anionic impurities and to convert the anion exchanger in the concentrator column to the carbonate-bicarbonate form. The conditioned concentrator column was removed from the chromatograph, and a measured volume of low-conductivity water was passed through the concentrator column. The IC results obtained served as a blank. This procedure was repeated with the same measured volume (usually 10 or 20 ml) of a standard solution containing chloride, nitrate, sulfate, and orthophosphate. At least two different concentrations of calibration standards were analyzed each day to verify the linearity of the test. The concentration of the anion standard solutions and the volume of standard which was passed through the concentrator column depended on the level of detection required for the samples to be analyzed (see Table 2). The same volume of standard, blank, or sample was maintained for each calibration range. Ion chromatograms depicting the conductivity response obtained when a 10.0-ml and 20.0-ml sample is concentrated are shown in Figs. 3 and 4, respectively.

If the anions of interest were present at levels that could be detected by IC without sample concentration, the chromatograph was calibrated in the direct injection mode using a 250-μl sample injection loop. The concentration of anion standards prepared for test calibration with and without preconcentration are listed in Table 2.

A calibration curve was prepared by plotting peak height (millimetres) versus anion concentration (micrograms per litre) on linear graph paper.

TABLE 2—*Approaches to IC analysis for determining trace concentrations of anions.*

Nominal Range of Method,[a] μg/litre	Sample Pretreatment: Preconcentration	Sample Pretreatment: Direct Injection	Sample Volume: Preconcentrated, ml	Sample Volume: Injected, μl	Concentration of Standards Prepared for Instrument Calibration, μg/litre
100 to 5000 (Cl)	...	X	...	250	2000, 5000
500 to 5000 (NO_3)	...	X	...	250	2000, 5000
500 to 5000 (*o*-PO_4)	...	X	...	250	2000, 5000
500 to 5000 (SO_4)	...	X	...	250	2000, 5000
2 to 100 (Cl)	X	...	10.0	...	50, 100
10 to 250 (NO_3)	X	...	10.0	...	50, 250
10 to 250 (*o*-PO_4)	X	...	10.0	...	50, 250
10 to 500 (SO_4)	X	...	10.0	...	250, 500
1 to 50 (Cl)	X	...	20.0	...	25, 50
5 to 125 (NO_3)	X	...	20.0	...	25, 125
5 to 125 (*o*-PO_4)	X	...	20.0	...	25, 125
5 to 250 (SO_4)	X	...	20.0	...	50, 250

[a] Full-scale setting, 10 μmho/cm; recorder output, 1000 mV.

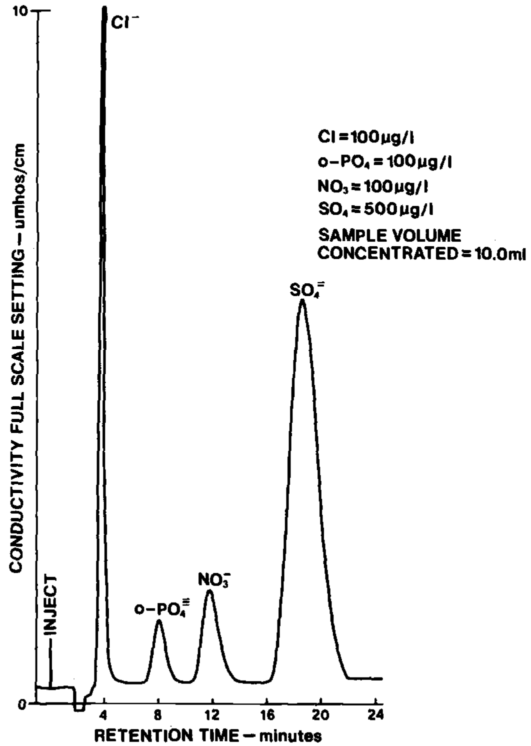

FIG. 3—*Trace anion analysis by IC with concentrator column technique—10.0-ml sample size.*

Approaches to Sample Analysis

The analytical approach to the ion chromatographic method may be varied to determine trace anions in waters with different impurity levels. The range of the method is extended by directly injecting the sample without any preconcentration. Detection levels are improved by increasing the volume of sample passed through the concentrator column. The lower limit of detection is limited by the dissolved solids content of the test samples. The method ranges listed in Table 2 have been found to be practical for analyzing different types (superheated steam to high-pressure boiler water) of high-purity waters from various sources.

On a given day with careful technique and stable instrument operating conditions, the actual detection levels for anions using either the anion concentrator column technique or direct sample injection may be lower. However, the nominal range of the method is defined to account for potential problems with blank correction, instrument stability, and variations in analytical technique that would occur when the IC method is universally applied.

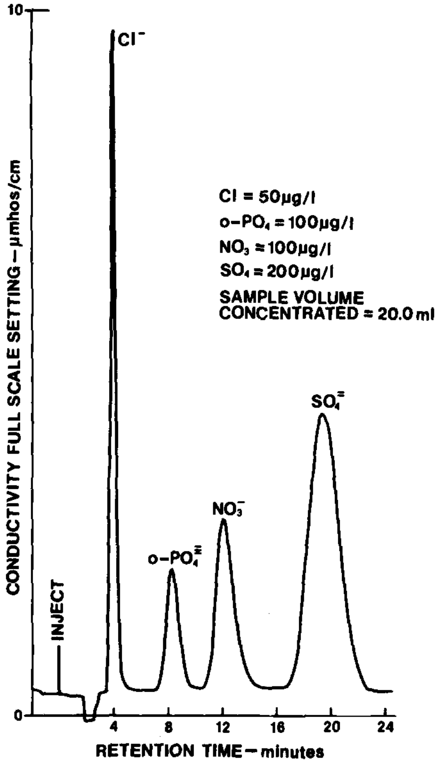

FIG. 4—*Trace anion analysis by IC with concentrator column technique—20.0-ml sample size.*

In practice, two separate anion concentrator columns may be used for analysis. While one sample is being concentrated on a concentrator column, another sample is installed in the chromatograph for analysis. Both concentrator columns are conditioned with eluant prior to use. Calibration is established with both concentrator columns.

Precision

The single-operator precision for sequential analysis of trace concentrations of chloride, nitrate, sulfate, and orthophosphate was determined by performing ten replicate analyses of combined standard anion solutions prepared with low-conductivity water. The same anion concentrator column was used for all analyses. A 10.0-ml aliquot of each standard solution was concentrated before analysis. The results of the precision study are listed in Table 3. The relative standard deviation was ≤ 10 percent at the 68 percent confidence level for each concentration of anion tested. All of the experimental data were included in the precision calculations.

TABLE 3—*Single-operator precision for determination of trace anions by ion chromatography with the concentrator column technique.*

Anion	Nominal Standard Concentration, μg/litre	Average Concentration, μg/litre	Relative Standard Deviation, 68 percent confidence level	Bias, percent
Chloride (Cl)	5.0	5.08	4.3	+1.7
	90.0	93.4	5.0	+3.8
Orthophosphate (*o*-PO_4)	25.0	21.8	10.0	−12.8
	100	99.4	1.8	−0.6
Nitrate (NO_3)	25.0	23.9	7.6	−4.4
	100	110.2	2.9	+10.2
Sulfate (SO_4)	25.0	22.7	5.5	−9.2
	400	405.3	1.6	+1.3

Collection of Sample Data

Waters from various industrial water systems were analyzed by IC using the concentrator column technique (10.0-ml sample volume) to determine anionic constituents. The chloride concentration of some of the samples was also determined by the manual colorimetric ferricyanide method in accordance with the ASTM Tests for Chloride Ion in Water and Wastewater [D 512–67 (1974)]. No chloride (<100 μg/litre chloride) was detected in any of the samples tested by the colorimetric method [*5*]. The results obtained are listed in Table 4. Note that sulfate and nitrate could be quantitated at levels which could not be approached by conventional water testing methods. Considerably more information was gleaned from IC analysis than could have been determined by traditional methods for these anionic constituents. The relative concentrations of chloride and sulfate are of interest in the evaluation of corrosion mechanisms on metal surfaces.

A study was undertaken to better characterize contaminant concentrations in two 183 kg/cm^2 (2600 psi) drum-type boiler systems. The only routine treatment of these systems is adjustment of the feedwater pH with cyclohexylamine. Congruent phosphate treatment of boiler water is prescribed only when contaminant inleakage is sufficient to cause the boiler water cation conductivity to exceed 10 μmho/cm.

Samples were collected in duplicate for the determination of trace anions by IC and in triplicate for sodium, potassium, calcium, and magnesium analysis by flame atomic absorption and emission (see Table 5). Replicate samples were collected to evaluate the effects of contamination due to sample collection, sample analysis, or both. Reproducible data were obtained for most replicate analyses, indicating good control of the sample collection and analysis procedures. Severe contamination problems were noted for calcium. Contamination of the sample during collection is suspected since the original calcium results were confirmed by reanalysis of the same samples by flame atomic absorption.

TABLE 4—*Trace anion results, in micrograms per litre, obtained for high-purity waters by ion chromatography with the concentrator column technique.*

Sample Identification No.	Sample Type	Chloride (Cl)	Sulfate (SO_4)	Nitrate (NO_3)	Orthophosphate (*o*-PO_4)
1	demineralized water	51	73	<10	<10
2	demineralized water	40	48	<10	<10
3	demineralized water	107	203	<10	<10
4	demineralized water	22	38	<10	<10
5	demineralized water	56	195	<10	<10
6	condensate	22	40	<10	<10
7	condensate	6	30	<10	<10
8	condensate and demineralized water blend	34	>500	<10	<10
9	saturated steam	<2	40	<10	<10
10	boiler feedwater	61	123	<10	<10
11	boiler feedwater	39	28	42	<10
12	boiler feedwater	<2	280	<10	<10
13	anion effluent	24	33	<10	<10
14	anion effluent	20	13	<10	<10
15	boiler water	80	<10	<10	<10

TABLE 5—*Analytical results, in micrograms per litre, obtained by ion chromatography and flame atomic absorption–emission spectrophotometry for high-purity water samples collected from one plant site.*

Sample Identification No.	Sample Type	Cl	SO_4	NO_3	o-PO_4	Na	K	Ca	Mg
1	boiler feedwater	2, 3	<5, 8	<2, <2	<3, <3	<1, <1, 1	<5, <5, <5	10, 30, 1	<1, <1, <1
2	boiler water	59, 57	152, 168	<4, <4	<6, <6	96, 97, 97	35, 35, 35	11, 84, 53	2, 2, 3
3	boiler feedwater	<1, <5	<5, <5	<2, <2	<3, <3	<1, <1, <1	5, <5, <5	13, 10, 3	<1, <1, <1
4	boiler feedwater	2, <1	23, 18	<2, <2	<3, <3	3, 1, <1	20, 10, <5	9, 69, 17	<1, <1, <1
5	boiler water	20, 19	109, 109	<2, <2	<3, <3	27, 27, 27	5, 15, 10	93, 54, 31	3, 3, 3
6	superheated steam	4, 4	<5, <5	<2, <2	<3, <3	1, 1, <1	10, 5, <5	10, 2, 17	<1, <1, <1

Where detectable concentrations of anions and cations were found, a reasonable cation-anion balance was noted. The lowest replicate value obtained for each set of data was used to establish this correlation. Higher values were assumed to be due to contamination.

Ion chromatography has provided a means of detecting chloride, nitrate, orthophosphate, and sulfate at concentrations <100 μg/litre. A practical and accurate method for identifying and quantifying low concentrations of these anions did not exist previously. The deleterious nature of various combinations of contaminants may be better evaluated with the additional information provided by IC analyses. Eventually, new contaminants may be identified by IC which were not previously considered as playing a role in equipment damage, particularly turbine stress-corrosion cracking.

Precautions Concerning the Method for Determining Trace Anions by IC

Sample Collection—Preservation of sample integrity is the first critical problem. We have found high-density polyethylene containers to be suitable for sample collection for analysis of trace levels of chloride, sulfate, nitrate, and orthophosphate as well as sodium, potassium, calcium, and magnesium if the containers are preconditioned with high-purity water to leach contaminants from the walls of the container. Replicate samples are collected and analyzed to eliminate questionable data that may be attributed to contamination during sample collection or analysis.

Resin Conditioning—When the concentrator column technique is required, the concentrator column must be conditioned before use. The column is placed on line in the injection valve of the chromatograph. When the eluant flow is directed through the column, impurities which may coelute with the anions of interest are removed and the resin is converted to the carbonate-bicarbonate form. Failure to condition the resin in the concentrator column will cause nonreproducible results to be obtained.

Blank Analysis—A measured volume of low-conductivity water must be treated in the same manner as the anion standards used for calibration and the samples to be analyzed to compensate for anionic impurities in the water used to prepare standards for calibration. Erroneous sample results will be obtained if anionic impurities are present in the blank which have not been compensated for when establishing calibration.

Preparation of Laboratory for Trace Analysis—The laboratory environment must be as clean as possible. Elimination of concentrated chemicals and minimization of atmospheric dust is advisable. All laboratory glassware (apparatus) must be preconditioned by soaking in low-conductivity water.

Sample Handling—Samples must be poured from the sampling container into the syringe after permitting some of the sample (at least 10 ml) to flow over the lip of the container to waste. The plastic syringe used for measuring sample aliquots for introduction to the concentrator column must be rinsed with low-conductivity water and then rinsed at least twice with the sample it is to contain. The male Luer adapters on the concentrator column must be rinsed with low-conductivity water just prior to insertion in the chromatograph to avoid contamination.

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Recent Advances in Ion Chromatography

REFERENCE: Girard, J. E. and Glatz, J. A., "**Recent Advances in Ion Chromatography,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 105–115.

ABSTRACT: The chromatographic separation and quantitation of highly ionic species was a difficult problem until recently. Ion chromatography (IC) represents a solution to this analytical problem.

Nonsuppressed IC offers a new alternative method to practitioners of IC. Since a suppressor column is not necessary for this method, the time required to regenerate the suppressor column is saved. Better chromatographic efficiency is achieved with the suppressor removed. Peak reversal, a problem associated with the suppressor column, is also eliminated. The sensitivity for Cl^- (0.5 ppm) is comparable to that of conventional suppressed IC. The sensitivities for NO_3^- (1.25 ppm) and SO_4^{2-} (1.25 ppm) are only slightly less than those observed for the conventional technique.

KEY WORDS: ion, chromatography, anion, power plants, instrumentation, water quality

Until the advent of the ion chromatography technique (IC) in 1975 [*1*],[2] a reliable, convenient method for the analysis of inorganic anions was not available. Many analytical methods have been used for the determination of common anions in aqueous solution. Some of the accepted methods used for sulfate, for instance, are listed in Table 1, and an equally bewildering variety of methods for nitrate are listed in Table 2. These techniques are complicated and difficult to perform.

The IC method uses a low-capacity ion exchange column to separate the ions of interest, which is followed by a suppressor column which removes the background elements in the eluent. Thus, the ions of interest leave the suppressor column in a background of deionized water and are monitored by a conductivity detector. Although this method is useful for the analysis of alkali metal cations [*2*], inorganic anions [*3,4*], ammonia and alkylated amines

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

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TABLE 1—*Methods of analysis for sulfate.*

- Precipitation methods
  - Gravimetry
  - Turbidimetry and nephelometry
  - Colorimetry
    - Direct (measure color increase)
    - Indirect (measure color decrease)
  - Fluorimetry
    - Direct
    - Indirect
  - Ring oven, visual
  - Polarography
  - Atomic absorption
  - Ion-selective electrodes
  - Titrimetry
  - Radiometry
- Direct analysis of solutions
  - Ion chromatography
  - Ion-selective electrodes
    - Direct
    - Indirect
- Direct nondestructive particulate methods
  - X-ray fluorescence
  - Electron spectroscopy chemical analysis (ESCA)
- Reduction methods
  - Colorimetry
  - Fluorimetry
  - Gas chromatography
  - Coulometric polarography
  - Oscillographic polarography
- Thermal methods
  - Flame photometry
  - High-resolution mass spectrometry

[*5*], and some organic acids [*6*], it has not been extended to the heavy metal or rare earth cations or to anions of weak acids ($K_a < 10^{-7}$). Ion chromatography and its application to environmental pollutants has been reviewed recently by Sawicki, Mulik, and Wittgenstein [*7,8*]. We believe that the IC method is superior to the analytical methods previously mentioned and that it will eventually supplant most of these methods in the analysis of a wide variety of mixtures.

Experimental

Apparatus

A Varian Model 5020 high-pressure liquid chromatograph with a Valco injection valve with a 100-μl calibrated injection loop was coupled with a Wescan Model 213 conductivity detector. The conductivity cell was placed

TABLE 2—*Available methods of analysis for nitrate.*

- Nitration methods
  - Colorimetry
  - Fluorimetry
  - Gas-liquid chromatography
  - High-pressure liquid chromatography
- Reduction to nitrite and assay
  - Colorimetry
  - Fluorimetry
  - Gas-liquid chromatography
- Reduction to ammonia and assay
  - Colorimetry
  - Gas chromatography
- Thermal decomposition
  - Chemiluminescence
  - Mass spectrometry
- Enzymic methods
  - Colorimetry
  - Fluorimetry
- Chemical decomposition
  - Manometry
  - Chemiluminescence
  - Gas chromatography
- Oxidation methods
  - Colorimetry
  - Fluorimetry
- Complex formation and extraction into organic solvents
  - Colorimetry
  - Atomic absorption spectrometry
- Direct methods
  - Electron spectroscopy chemical analysis
  - Spectrophotometry
  - Ion-selective electrode
  - Ion chromatography

next to the column block heater, and it was insulated with Styrofoam insulation. The column used for all separations was a Vydac 302 IC column (Separations Group, Hesperia, Calif.). All separations were performed at 30°C at a flow rate of 2.0 cm^3/min.

Reagents

The eluents used for the separations described were prepared from analytical reagent-grade phthalic acid dissolved in conductivity water. The pH was adjusted by the addition of a 1-*M* potassium hydroxide (KOH) solution. The phthalic acid concentration was varied from 5×10^{-4} *M* to 5×10^{-3} *M*, while the pH of the solution was adjusted from 4.6 to 5.4.

Standard solutions of the various anions were prepared from analytical-grade reagents and conductivity water. Potassium salts were used in all cases except for CO_3^{2-}, which was prepared from the sodium salt.

Results and Discussion

The principal advantage of IC is that it makes possible direct determinations of ions that do not absorb in the ultraviolet or visible region. Conductivity is measured in micromhos and is generally a simple function of species concentration, particularly in the ranges handled by IC (10 μg/litre to 1 g/litre). It is therefore a simple matter to quantitate the ions of interest by use of external standards. Because of its exceptional selectivity, sensitivity, and speed, IC is particularly suited to applications involving direct analysis of anions in water.

The IC we describe is marketed by Dionex Corp. (Sunnyvale, Calif.). For anion analysis, a proprietary latex-agglomerated low-capacity anion-exchange resin is used as the separating column and a strong cation-exchange resin in the hydrogen form as the suppressor. Small and Solc [*9*] were the first to use carbonate and bicarbonate as an eluent. This eluent was chosen because the carbonate and bicarbonate are so conveniently neutralized to low-conductivity species, and different combinations of CO_3^{2-}/HCO_3^- will give buffers with variable pH. This allows one to separate the ions of interest in a large range of affinity. As a result of reactions in the suppressor column, the sample ions flow into the conductivity detector as the protonated anion (HA), not in the highly conducting background of CO_3^{2-}/HCO_3^-, but rather in the low-conductivity background of carbonic acid (H_2CO_3).

Ion chromatography using the two-column separator–suppressor arrangement (suppressed-anion IC) has found many applications, as already noted. A major disadvantage of this technique is that the suppressor column accumulates the ions from the eluent stream and must be regenerated periodically to remove unwanted ions. Another drawback is that the eluent must be a base, so that after neutralization by the suppressor column it will have low conductivity. Anions of very weak acids are difficult to determine by this technique since their acid form is too weakly conducting.

A simpler IC system has been recently described by Fritz and co-workers [*10,11*] and Harrison and Burge [*12*]. Both of these systems are similar in that they are both designed to work without a suppressor column (nonsuppressed IC). A specially designed conductivity detector [*13*], which tolerates some conductivity of the eluent without undue background noise or drift, is used. The circuit and cell design permit up to 100 times full-scale suppression without the significant drift normally caused by temperature variations. Under these conditions, conductivity changes of 1 part in 5000 per minute can be detected.

Several different ion exchange materials are now available which are capable of performing high-resolution separations of inorganic anions. Table 3 lists the physical properties of these materials and their manufacturers.

Fritz and co-workers [*10,11*] have developed a low-capacity ion-exchange resin which was made from macroporous polystyrene–divinylbenzene co-

TABLE 3—*Column materials used for anion separations.*

Material	Particle Shape	Capacity meq/g	Particle Size, μm	Manufacturer
Latex agglomerated	spherical	0.02 to 0.05	20 to 30	Dionex Corp., Sunnyvale, Calif.
Surface aminated microporous resin	irregular	0.007 to 0.07	44 to 75	not yet commercially available
Pellicular silica	spherical	0.1	20	separations group Vydac 302 Hispernia, Calif.

polymer beads (Rohm and Haas, XAD-1,2,4). The starting resin is swollen in chloromethyl methyl ether, methylene chloride, and nitromethane. Zinc chloride is added to produce a quaternary ammonium functional group. The capacity of the resin can be controlled by varying the time of chloromethylation reaction [*14*]. Since these materials were not commercially available at this time, we did not investigate their performance.

Harrison [*12*] has developed an interesting low-capacity ion-exchange material (Vydac 302) which is produced by chemically bonding the proper functional groups to a silica substrate by means of silane reactions [*15*]. This results in a thin shell of ion exchange material surrounding the silica particles. The silica substrate is of a spheroidal shape, having a high mechanical strength. The particles have an average area of 86 m^2/g with an average pore diameter of 330 Å and a capacity of 0.1 meq/g. The selectivities of this material seem to be somewhat different from those obtained on conventional organic-based resins. For example, large polarizable anions such as SCN^- and I^- are more easily eluted from a silica-based material than from an organic-based material.

The single most important requirement of the eluent-selected nonsuppressed IC is that its conductivity is sufficiently low to permit the use of a conductivity detector. Fritz and co-workers [*11*] have reported that salts of aromatic acids such as benzoic or phthalic acid were suitable eluting agents. Phthalic acid is employed in combination with the pellicular silica resin (Vydac 302) to obtain good separations of many anions.

We have investigated phthalic acid eluents at concentrations of 5×10^{-4} M, 1×10^{-3} M, and 5×10^{-3} M. The pH of the eluent was also varied from 4.6 to 5.4. In this concentration range the background conductivity of the eluent is low, generally in the 75 to 200 μmho range. The H^+ and OH^- ions have unusually high conductance (350 and 190, respectively). The result is that the pH must be adjusted to minimize the concentration of these highly conductive species. On the other hand, the organic acid which is present in the eluent must compete for active sites on the column with the anions of interest in the sample. To do this, it must be sufficiently ionized to perform the separation. Because of these constraints, the working pH of the system must be kept in the 4.0 to 6.5 pH range.

Very sharp separations of anions in phthalate eluent are easily achieved on the Vydac column. Figures 1 and 2 are examples of separations of Cl^-, NO_3^-, and SO_4^{2-} achieved in 1×10^{-3} *M* phthalate at pH values of 4.6 and 5.0, respectively. A common feature of all nonsuppressed IC chromatograms is the first peak, which is related to the total concentration of the sample salt and is commonly referred to as the "pseudo peak." When a sample is injected onto the column, anions present in the sample replace the eluent anions which are occupying active sites at the top of the column. The displaced eluent ions, together with sample cations, move with the solvent front to the conductivity detector. If the concentration of these cations and anions is such that the conductance is greater than that of the eluent background, there will be a positive peak. If the concentration is less than the eluent background, a negative peak will result.

Listed in Table 4 are the retention times and detection limits of various anions as a function of pH and phthalate concentration. The retention time of Cl^-, NO_3^-, and SO_4^{2-} decreases as the pH increases (with phthalate concen-

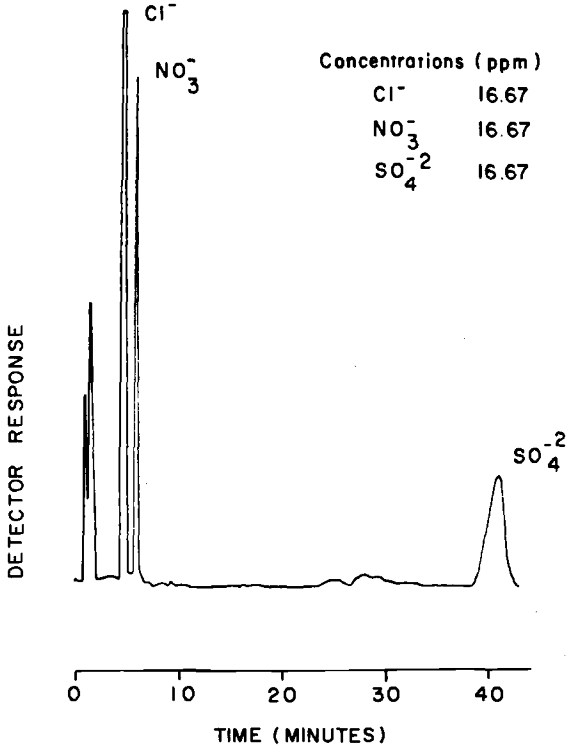

FIG. 1—*Separation of* Cl^-, NO_3^-, SO_4^{2-}: *the eluent is* 1×10^{-3} M *phthalate, pH is 4.6, and flow rate is 2* cm^3/min.

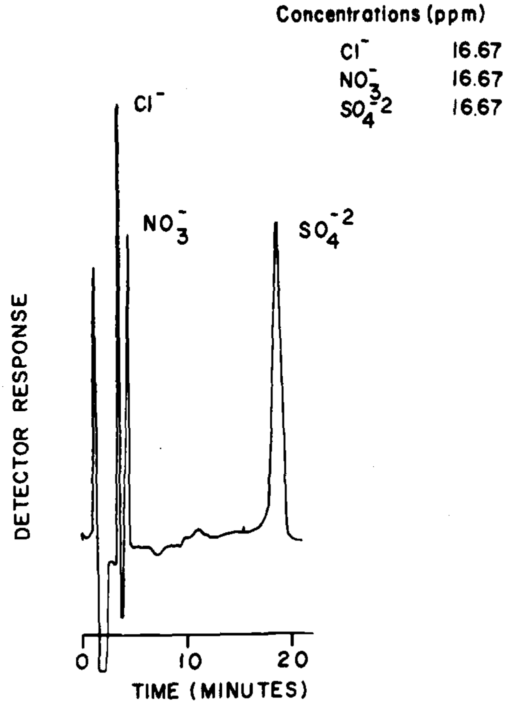

FIG. 2—*Separation of* Cl^-, NO_3^-, SO_4^{2-}: *the eluent is* 1×10^{-3} M *phthalate, pH is 5.0, and flow rate is 2* cm^3/min.

tration remaining constant). Figure 3 shows graphically the retention time dependence in relation to pH. Since the rate of movement of individual ion peaks appears to be an exponential function of pH, the pH of the eluent must be carefully adjusted to ensure reproducible retention times.

Changes in phthalate concentration have little effect on the resolution of weakly retained sample ions. For those ions with longer retention times, however, resolution degrades as the phthalate concentration is reduced. At lower concentration of phthalate, sample anions become attached to active sites for long periods without competition from phthalate anions for these active sites, and resolution is degraded.

The sensitivity we have observed for nonsuppressed IC is comparable to that of suppressed IC. Detection limits of 0.5 ppm for Cl^-, 1.25 ppm for NO_3^-, and 1.25 ppm for SO_4^{2-} are very respectable. As a general rule, we have noticed that at constant phthalate concentration, detector response increases as the pH of the system is decreased. Figures 4, 5, and 6 show detector response as a function of concentration for Cl^-, NO_3^-, and SO_4^{2-}, respectively, at two different pH values. As the pH is increased, the signal-to-noise ratio increases and there is more suppression required of the detector circuit.

TABLE 4—*Retention times and detection limits of various anions as a function of pH and phthalate concentration.*[a]

Ion	Retention Time pH 4.6, min	Retention Time pH 5.0, min	Retention Time pH 4.6, min	Detection Limit pH 4.6, ppm	Detection Limit pH 5.0, ppm	Detection Limit pH 5.4, ppm
		Eluent concentrations 5×10^{-3} *M*				
Cl^-	2.5	2.5	<2.5	2.5	5	
NO_3^-	3.1	3.1	<3.1	5	12.5	
CN^-	8.75	8.75	10.09	5	2.5	2.5
SO_4^{2-}	7.19	5.63	4.06	2.5	5	5
CO_3^{2-}	8.75	8.75	10.06	12.5	12.5	2.5
CrO_4^{2-}	8.75	8.44	10.06	2.5	2.5	5.0
PO_4^{3-}	8.75	8.44	10.06	2.5	12.5	2.5
		Eluent concentration 1×10^{-3} *M*				
Cl^-	4.69	3.44	<3.44	0.5	0.5	
NO_3^-	5.63	4.38	<4.38	1.25	1.25	
CN^-		21.56			5	
SO_4^{2-}	41.88	18.13	11.56	5	1.25	2.5
CO_3^{2-}		21.56			12.5	
		Eluent concentration 5×10^{-4} *M*				
Cl^-		5.0			0.5	
NO_3^-		6.56			1.5	
SO_4^{2-}		34.06			2.5	

[a] Column: Vydac 302 IC. Flow rate: 2.0 cm^3/min, 100 μl injection loop.

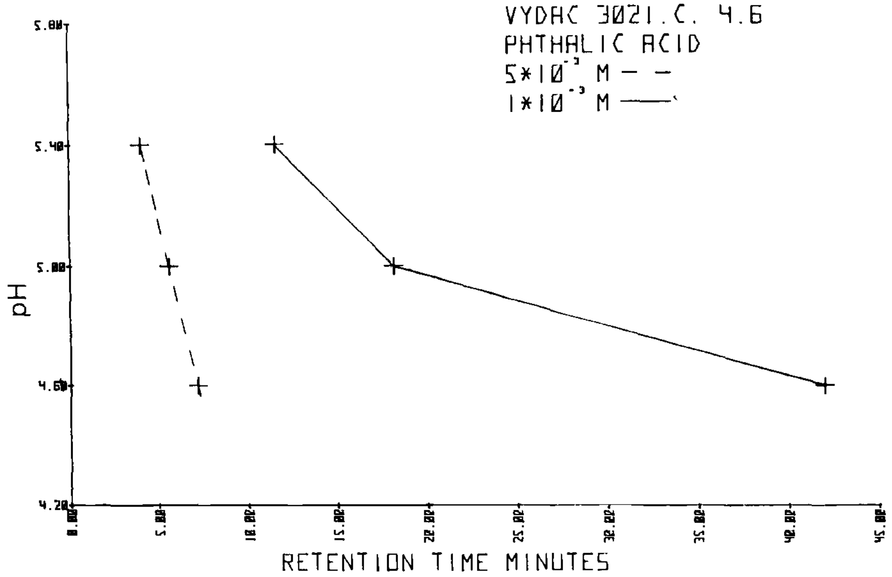

FIG. 3—*The relationship between retention time and pH at a constant phthalate concentration for* SO_4^{2-}.

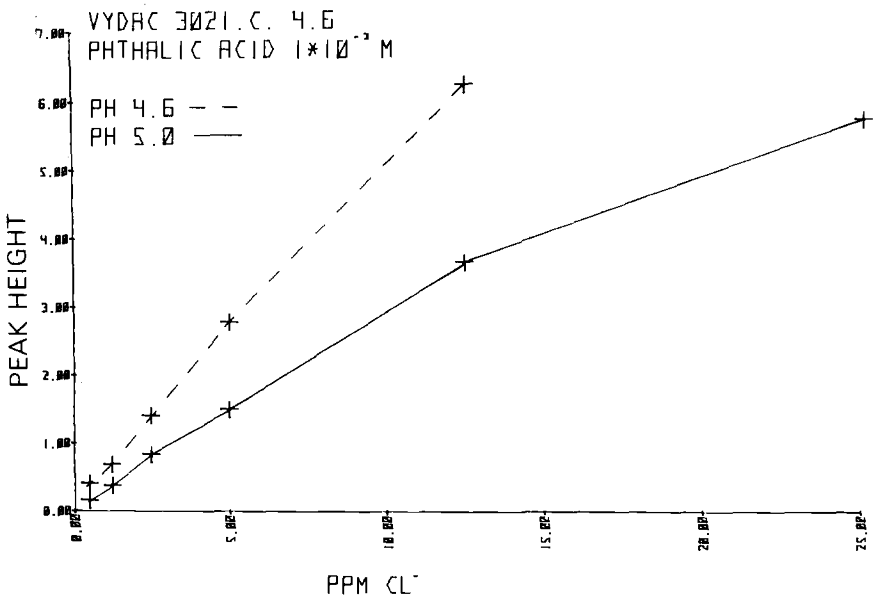

FIG. 4—*Linearity and dynamic range of nonsuppressed IC for Cl^- at pH 4.6 and 5.0.*

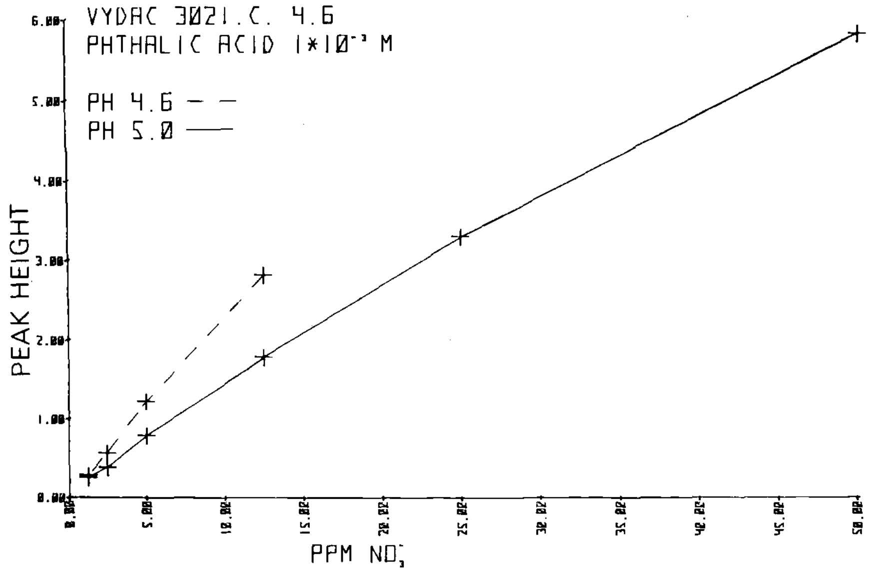

FIG. 5—*Linearity and dynamic range of nonsuppressed IC for NO_3^- at pH 4.6 and 5.0.*

The detector response is linear over a wider concentration range at the lower (4.6) pH.

It is generally assumed that a decrease in phthalate eluent concentration will increase detector response since the background conductivity will be lowered. The detection limits listed in Table 4 indicate that, at constant pH, lowering the phthalate concentration from 5×10^{-3} *M* to 1×10^{-3} *M* greatly increases the detector response by a factor of 10, as one would expect. Lowering the phthalate concentration even further to 5×10^{-4} *M*, on the other hand, does not increase sensitivity for Cl^- or NO_3^-, and for SO_4^{2-} it raises the detection limit from 1.25 to 2.5 ppm. It appears that 1×10^{-3} *M* phthalate is an optimum concentration.

As a general rule, to optimize conditions for low-level determinations of Cl^-, NO_3^-, and SO_4^{2-} on the Vydac 302 column in a nonsuppressed mode, we suggest a phthalate concentration of 1×10^{-3} *M* at pH 5.0. Although we have noted that detector response increases with decreasing pH, we feel that operation at pH 4.6 greatly increases the retention time for SO_4^{2-} (18.1 to 41.9 min). This makes the determination take twice as long and also makes the SO_4^{2-} peak much less sharp and more difficult to measure.

Summary

The chromatographic separation and quantitation of highly ionic species was until recently a difficult problem. Ion chromatography represents a solution to this analytical problem.

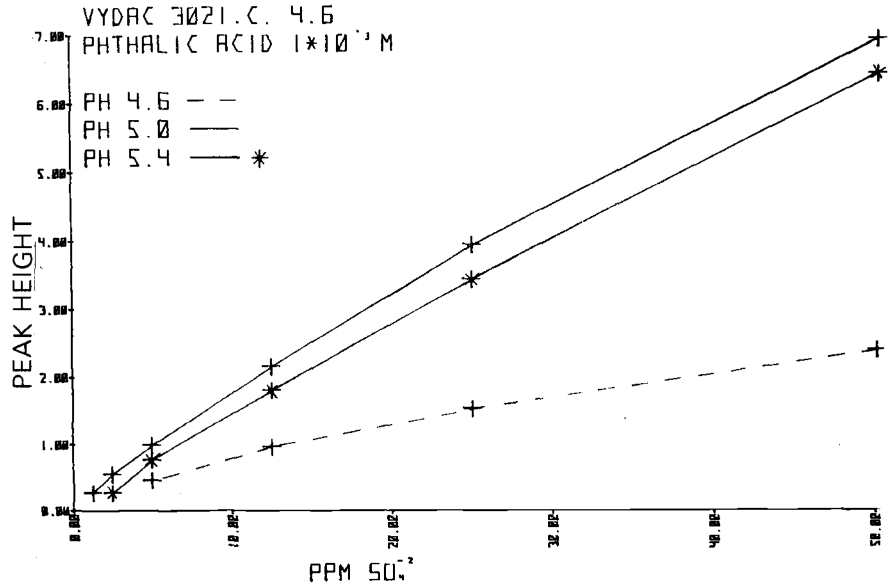

FIG. 6—*Linearity and dynamic range of nonsuppressed IC for SO_4^{2-} at pH 4.6, 5.0, and 5.4.*

Nonsuppressed IC offers a new alternative method to practitioners of IC. Since a suppressor column is not necessary for this method, the time required to regenerate the suppressor column is saved. Better chromatographic efficiency is achieved with the suppressor removed. Peak reversal, a problem associated with the suppressor column is also eliminated. The sensitivity for Cl^- (0.5 ppm) is comparable to conventional suppressed IC. The sensitivities for NO_3^- (1.25 ppm) and SO_4^{2-} (1.25 ppm) are only slightly less than those observed for the conventional technique.

Acknowledgments

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J. L. Simpson,[1] *M. N. Robles,*[1] *and T. O. Passell*[2]

In-Plant System for Continuous Low-Level Ion Measurement in Steam-Producing Water

REFERENCE: Simpson, J. L., Robles, M. N., and Passell, T. O., "**In-Plant System for Continuous Low-Level Ion Measurement in Steam-Producing Water,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 116–130.

ABSTRACT: This paper describes the development of an on-line analytical instrument to measure selected anions and cations over the sub-parts-per-billion to several parts-per-million concentration range. The system has been designed and is being installed in an electrical generating power plant. Laboratory evaluations and limited in-plant experiences will be discussed regarding measurements of nonhydrolyzable anions and cations, transition metal ions, and organic acids. The system will accommodate multiple sample line inputs with computer-controlled options to provide sample averaging, automated sample point selection, and system standardization and calibration. The data acquisition capabilities, including storage and report generation, will also be addressed.

KEY WORDS: measurement, chromatography, ions, water, on-line, power plants, instrumentation, water quality

It is becoming increasingly evident that the chemical ionic content of steam generating water plays a key role in the performance of electric power generating plants. Because of high flow rates and concentrating mechanisms, part-per-billion concentrations of impurities can accumulate in kilogram quantities in the turbine or steam generator. Power plant availability can be affected by these corrosive ionic species, and it is often difficult to set alarm criteria for corrective action, due to lack of reliable, on-line analytical instrumentation.

In order to provide adequate water impurity monitoring, the Electric Power Research Institute (EPRI) has funded a program to characterize the power plant application of a commercially available analytical system. The

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main objective of this program is to provide a field test, a validated method, and an instrumentation system capable of detecting and recording a wide range of ionic impurities in the sub-parts-per-billion to parts-per-million range of concentrations. The instrument is designed to sample on-line, power plant steam-producing water.

In this paper, we will describe the efforts taken in planning for this program. The tasks included are the evaluation of a basic measurement system to monitor anions, cations, organic acids, and corrosion products. Sampling system design, utility interface, and preliminary analyses at the plant are also included. The methodology selected was ion chromatography through the use of ion separation columns, eluent suppression columns, and conductivity detectors. The instrument design includes sampling, calibration, and data acquisition subsystems.

The measurement system is to be field tested on two power generating plants. Initial plant selection was narrowed to the secondary systems in pressurized water reactors (PWR). The experience acquired is expected to be applicable in other steam electric power plants, such as boiling water reactors (BWR), the breeder reactor, and fossil-fired stations.

Experimental

Ion chromatography is a relatively new technique based on the work of Small, Stevens, and Bauman. [*1*][3] Instruments based on their work are commercially available.[4] The instrument we are using is a modified ion chromatograph.

The basis for the operation of the instrument is physically straightforward. A pump capable of generating pressures of at least 7000 kPa (1000 psig), delivers a liquid eluent at a known and constant rate to the ion exchange columns in the instrument flow path. A sample aliquot injected into this stream is delivered to the first column, the separator. This column contains a low-capacity ion exchange resin with which sample ions establish equilibria in proportion to the strength of individual ion affinities for the resin–eluent system used. The stronger the affinity, the longer it will take for that ion to elute from the separator column. From the separator, ions pass into a suppressor column where the ionic background of the eluent is neutralized or suppressed by conversion to a low-conductivity substance such as water or carbonic acid. The separated ions of interest are eluted from this column in the form of highly ionized acids or bases [*2*] (see Fig. 1). Detection is achieved conductimetrically with a flow-through cell at the exit of the suppressor column. The output of the detector can drive a strip chart recorder pen, which traces peaks having areas and heights proportional to the quantity of the corresponding ion. However, in this on-line application, computerized data

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

[4] From Dionex Corp., Sunnyvale, Calif.

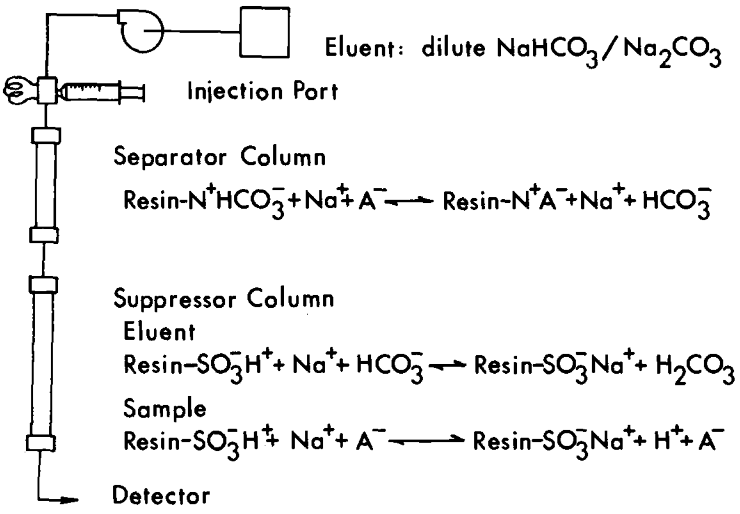

FIG. 1—*Anion system flow and chemistry diagram.*

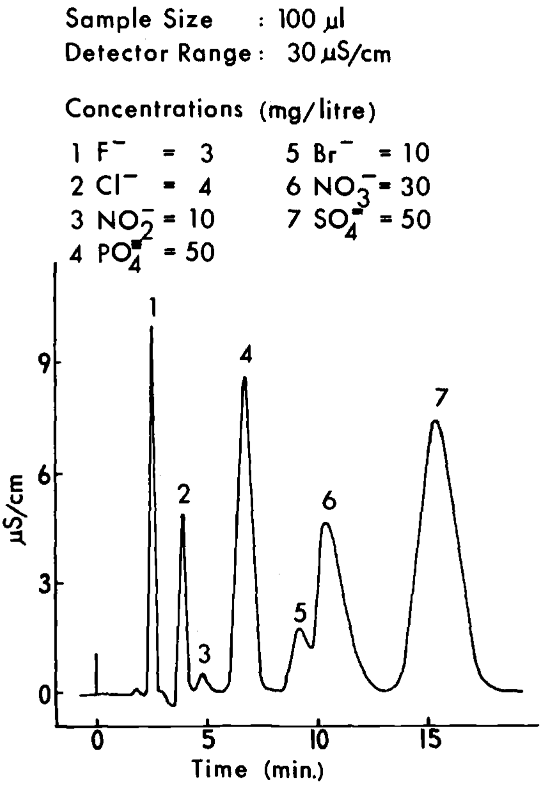

FIG. 2—*Anion chromatogram.*

TABLE 1—*Ion measurement capabilities.*

Ions	Estimated Detection Limit[a] ng/ml injected
Anions	
F^-	<1
Cl^-	<1
NO_2^-	10
$PO_4^{\equiv}$	5
Br^-	5
NO_3^-	5
$SO_4^=$	5
Cations	
Li^+	<1
Na^+	<1
NH_4^+	<1
K^+	1
Ca^{++}	<1
Mg^{++}	<1

[a] Detection limits expressed as concentration are variable depending on sample size. Nominal sample size is 10 ml.

acquisition and processing is required. Detection limits for many ionic species are in the low parts-per-billion region [*3*].

Anion Detection Capability

The initial phases of developing an on-line ion chromatography system consisted of the analysis of standard solutions. Known amounts of fluoride (F^-), chloride (Cl^-), phosphate ($PO_4^{\equiv}$), sulfate ($SO_4^=$), and several other ions were analyzed to determine system detection limits and sample size requirements. A typical chromatogram for these anions is shown in Fig. 2. Calibrations for all of these ions were linear over at least 3 orders of magnitude.

A detection limit for each anion can be found in Table 1, and these are typically <1 to 5 ppb for a 1-ml sample aliquot. Through the use of concentration techniques, such as a concentrator column [*4*], larger sample aliquots can be injected into the chromatograph; thus, detection limits can be reduced as sample size is increased. Figure 3 shows concentrator column response when increasing amounts of an anion, in this case chloride, are loaded onto a column and injected. Figure 4 demonstrates that these concentrators respond in a linear way to increasing anion loads, but they also have a finite capacity, approximately 10 μg for chloride. Capacity can be increased by increasing column volume or resin capacity. However, the capacity obtained is more than adequate for our application, as it exceeds the detection limit for Cl^- by 4 orders of magnitude, covering even intense transients. Figure 5 shows a chromatogram of a water sample with concentrations for Cl^- and $SO_4^=$ resembling PWR secondary water. $PO_4^{\equiv}$ and nitrate (NO_3^-) were also

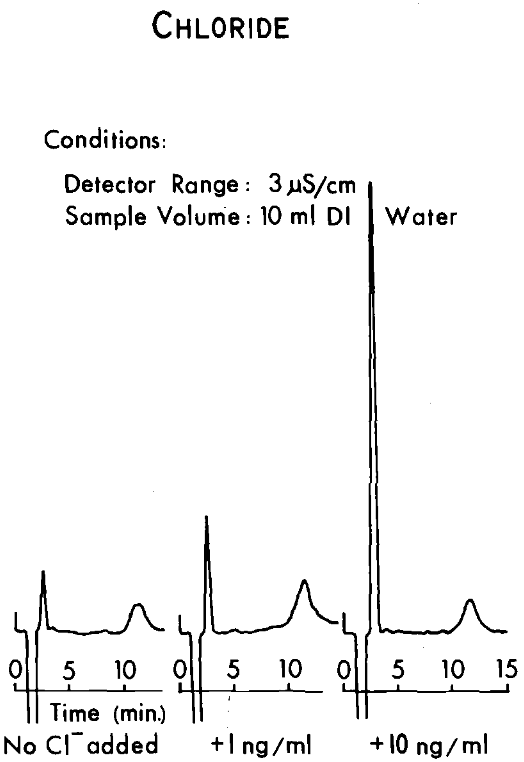

FIG. 3—*Concentrator column response.*

added. An actual measurement at one power station matched this chromatogram except that a reduced $SO_4^=$ peak was observed.

Cation Detection Capability

Known amounts of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), and lithium (Li^+) ions were analyzed to determine system detection limits. A typical chromatogram for these monovalent cations is shown in Fig. 6. As with the anions, calibrations were linear over several orders of magnitude.

Detection limits for these cations can be found in Table 1 and are typically <1 ppb for a 1-ml sample aliquot.

Concentrator columns can be used to increase detection limits as with the anions. For our application, they have insufficient capacity, especially when trying to concentrate a less tightly held minor ion in the presence of a major ion, for example, sodium in the presence of 1000 times more ammonium, which is typical of PWR secondary water when ammonia is used for pH control. In this situation, the capacity of the concentrator is exceeded and sodium ion is partially eluted from the concentrator by the more tightly held ammonium ion. As a result, the use of concentrator columns must be dis-

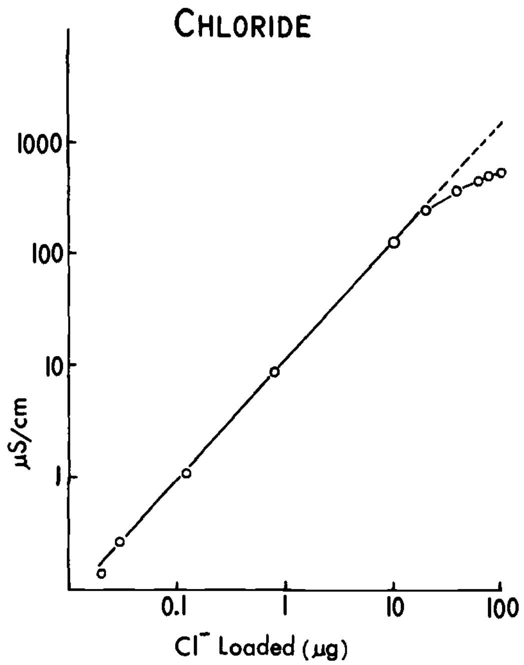

FIG. 4—*Concentrator column loading study.*

carded in favor of large-volume sample injections directly onto the separator column, which has ten times the capacity of the usual concentrator column. The use of this technique has been demonstrated with a PWR water sample (Fig. 7).

This technique is practical because we are dealing with relatively pure water samples, and the cations present form a band at the top of the separator column in the absence of eluent. Once the eluent flushes the sample through the column, normal partitioning occurs. We have achieved this through the use of a reservoir in the form of a 10-ml sample loop.

Through the use of concentration techniques, the capability for analyzing various anions and monovalent cations has been demonstrated. Two different column–eluent subsystems are required and comprise half of the analytical systems envisioned for the final on-line instrument. Two additional systems will be chosen from among the following: divalent cations, organic acids, carbonates, and corrosion products.

Divalent Cations

The divalent cations magnesium and calcium were evaluated and found to exhibit detection limits of <1 ng/ml. These ions are analyzed with the same resin columns used for the monovalent cations, but with a different eluent. As a result, the monovalent cations elute as a single peak very early in the

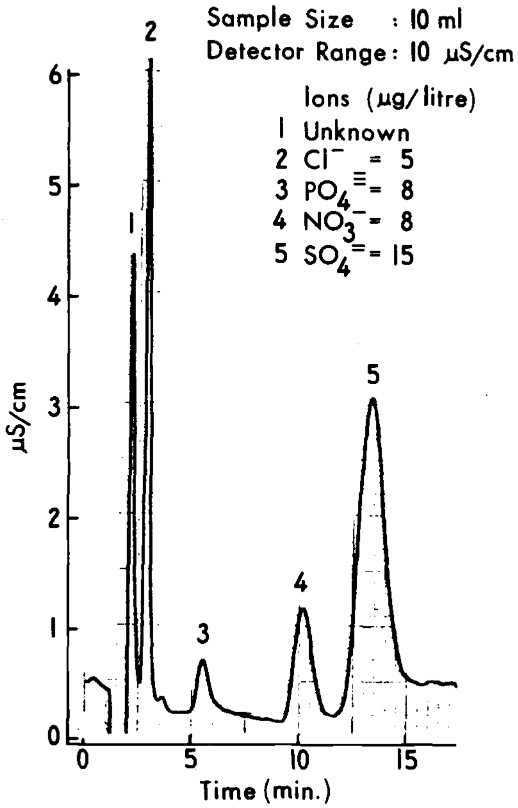

FIG. 5—*Anions in synthetic PWR secondary cooling water.*

analysis, followed by magnesium and calcium. The relatively large amount of ammonium found in most PWR secondary water systems does not significantly interfere with this analysis (see Fig. 8). Concentrator columns can be used to lower detection limits without having to worry about ammonium exhausting the concentrator's limited capacity since the divalent cations are retained more strongly.

Organic Acids, Carbonates, and Corrosion Products

Evaluation of several other subsystems is currently underway. Organic acids, such as formic and acetic, may also be present in PWR water systems as a result of thermal degradation of polisher resin beads or nonionic organics passing through the makeup water system. Preliminary evaluation of an ion chromatography exclusion (ICE) technique to detect these organic acids appears promising in that we can demonstrate sensitivities down to 100 ppb for formic, succinic, and acetic acids. Lower detection levels can be achieved

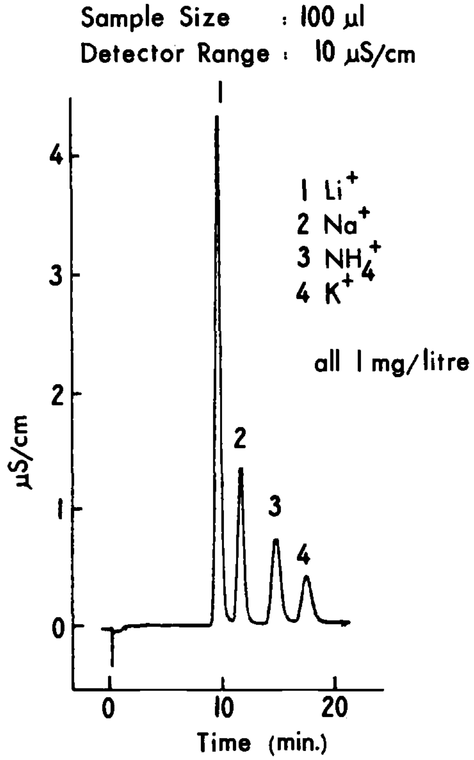

FIG. 6—*Cation chromatogram.*

through the use of concentration techniques. Carbonates have been analyzed using another ICE technique. Limited data on detection limits are available, and more work in this area is being conducted. Boric and silicic acids are other possibilities that will be investigated.

A literature search was made to determine the feasibility of measuring transition metal corrosion products by adapting an electrochemical detector (coulometry or amperometry) to an ion chromatograph. A great deal of work, and many papers have been published by Takata et al in Japan [*5*]. In the United States, Girard applied a coulometric detector to an ion chromatographic system and demonstrated acceptable sensitivities for many of the metal ions in which we are interested [*6*]. Amperometric techniques are also applicable, and claims of higher sensitivities than are obtainable by coulometric methods have been noted [*7*].

These techniques are promising enough to warrant further investigation; thus, an effort will be made to apply one of these electrochemical techniques to the on-line ion chromatograph. It is clear that preanalysis dissolution will be required for corrosion products not in solution.

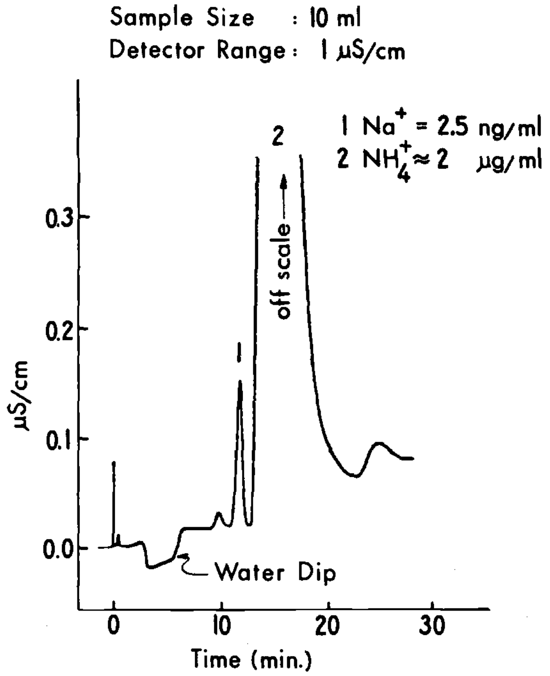

FIG. 7—*Monovalent cations in secondary cooling water.*

Measurement System Components

The measurement system being developed consists of calibration, sampling, and control–data acquisition systems in addition to four ion chromatograph systems. A block diagram (Fig. 9) shows how these systems are interconnected.

On-Line Sampling

The instrument is designed to be connected to ten sampling lines. This will enable continuous on-line sampling and circumvention of contamination problems commonly encountered with grab sampling systems. The sampling points selected in the PWR secondary cooling system include the following:

(*a*) condensate pump, combined discharge;
(*b*) condensate polisher, combined effluent;
(*c*) single polisher bed effluent;
(*d*) makeup water inlet;
(*e*) third-point heater drain from low-pressure turbine;
(*f*) mixed final feedwater;
(*g*) OTSG outlet steam;

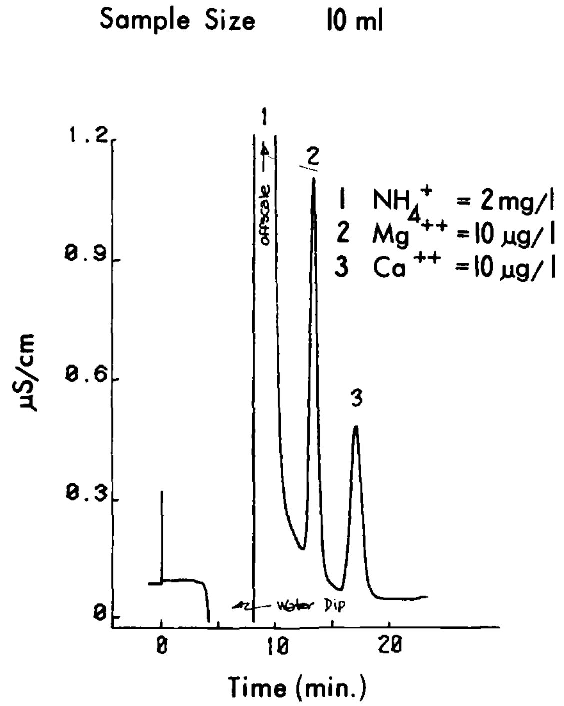

FIG. 8—*Divalent cations in synthetic PWR secondary cooling water.*

(*h*) moisture separator reheater drains (C or D);
(*i*) high-pressure turbine exhaust; and
(*j*) low-pressure turbine inlet steam.

These points were selected to allow a mass balance to be performed for each impurity.

Flow rates to the instrument sampling system will be at a minimum of 1 litre per minute with a Reynolds number greater than 4000. Initial cooling will be made at the sample location, and temperature control for instrument stability will be achieved at the analytical system. All sample lines will have sampling capability after the initial coolers and as close to the sample outlet location as practical. This will allow investigation of sample line adsorption and release effects as well as the possible need to clean the lines chemically. Sample line lengths will be minimized by locating the instrument central to all sampling points.

A reasonable temperature environment for the instrument will be provided by housing it in a small air-conditioned room. The absolute necessity of ambient temperature control has not been established. Sample water temperature can be accepted at the instrument at 24 ± 10°C. This is possible because the sample volume is smaller than the eluent volume.

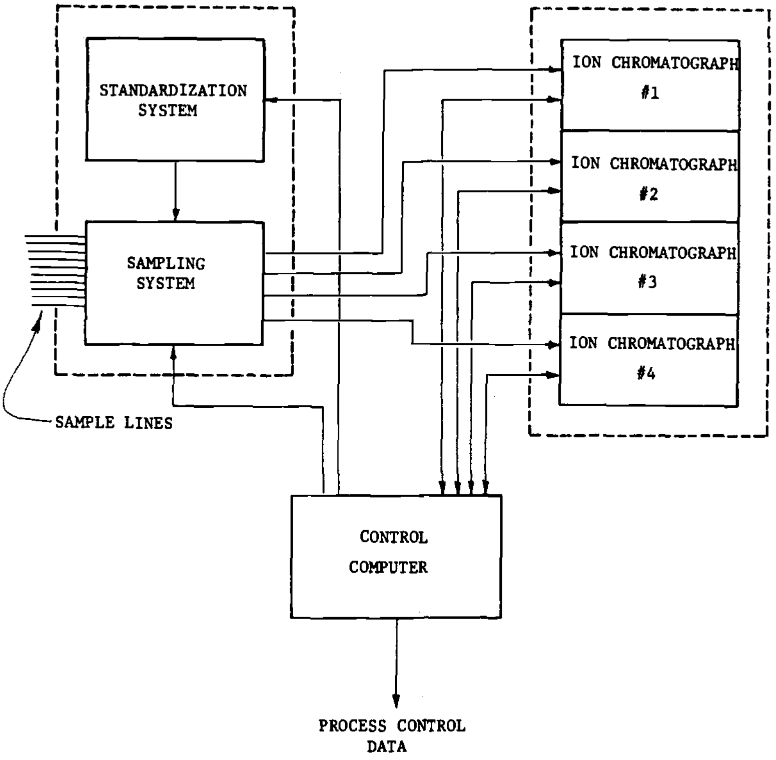

FIG. 9—*System block diagram.*

Sampling System Design

The on-line instrument will be interfaced with the power plant through a sampling system. This system will provide for sample averaging by allowing water to slowly fill a reservoir from which a small portion will be injected periodically into each chromatographic system. After the injections are completed, the reservoir will be emptied automatically and a new fill cycle initiated. The fill cycle will continue until the next time the reservoir is selected for analysis, as much as 5 h later. Filtration of sample water will be provided to prevent solids from entering the chromatographic systems. Through the use of constant volume metering pumps, sample injection volumes will be set by computer-timed pump operation. Sample point and chromatograph selection will be determined by the computer program. A schematic diagram of the sampling system is shown in Fig. 10.

Calibration

To provide current calibration data and automatic updating of instrument response factors, a system of preparing standards of various concentrations and injecting them into the chromatographs in a manner similar to routine

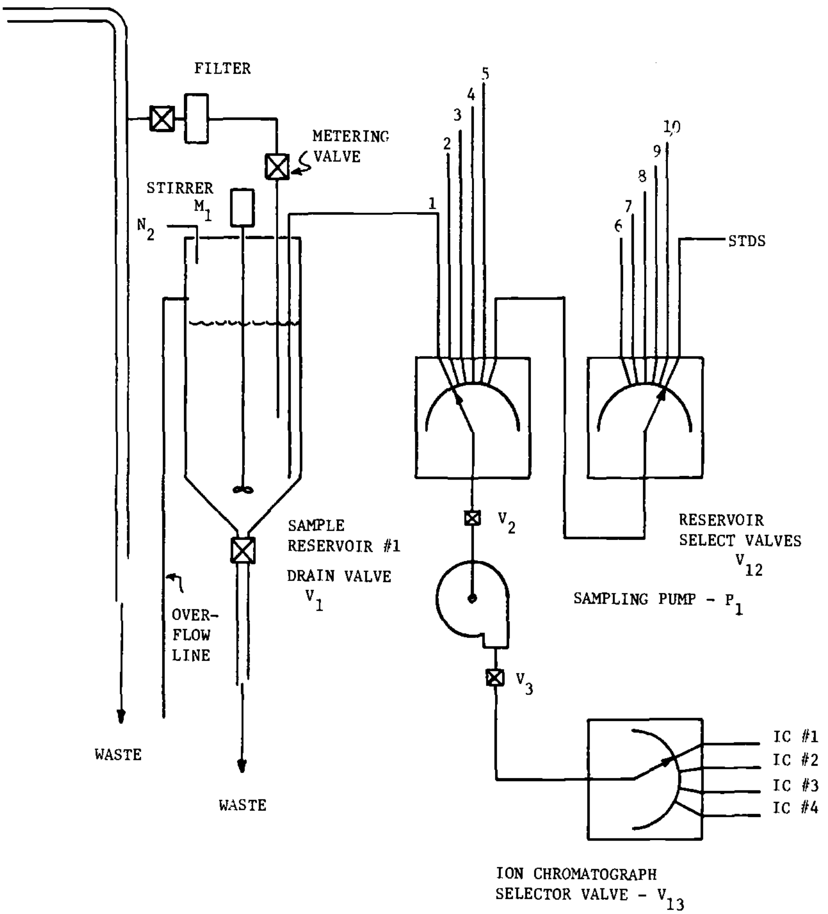

FIG. 10—*On-line ion chromatograph sampling system.*

water samples has been designed. Stock standard solutions are accurately metered into a mixing reservoir, and ultrapure (0.1 μS/cm) water is added to achieve a suitable dilution. After mixing, the reservoir is sampled for injection into a chromatograph. The reservoir is emptied and rinsed prior to the preparation of the next standard solution. Standardization of the chromatographs is based on a frequency programmed into the computer. A schematic diagram of this system is shown in Fig. 11.

Initial recalibration frequency is once per 6-h cycle. This frequency may change as experience is gained. Replacement of the 100-ppm standard stock solutions is at a maximum interval of 2 weeks.

Instrument Control and Data Acquisition

To provide automatic operation for the instrument, a computer system has been installed to provide time-based control of system valves and pumps

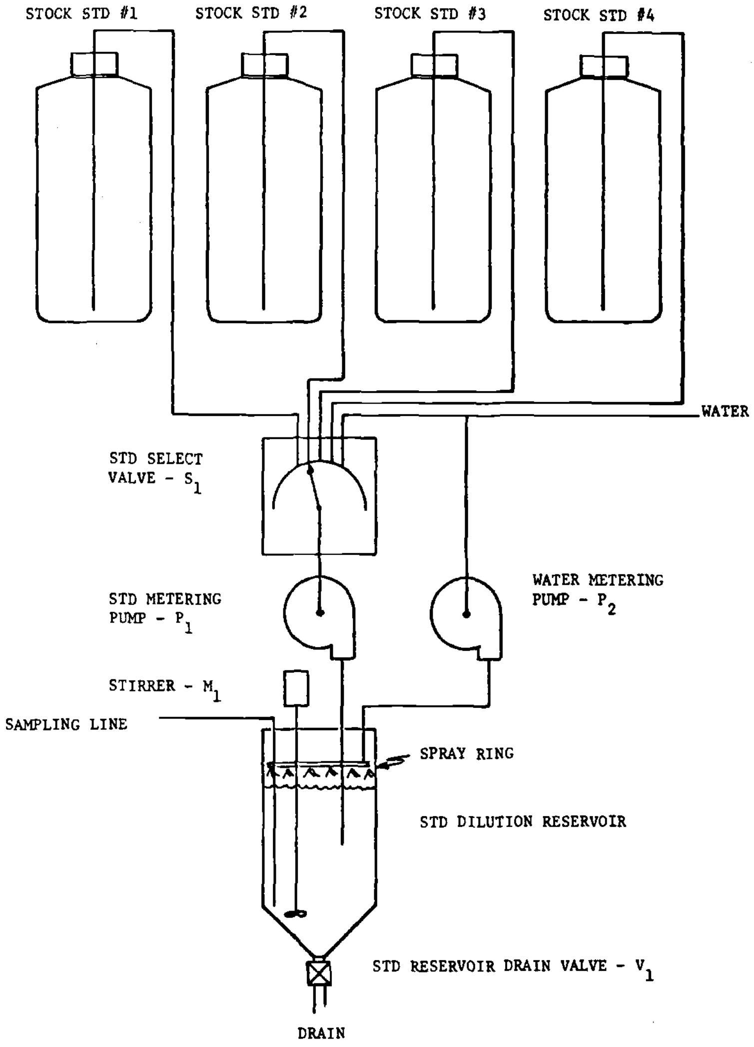

FIG. 11—*On-line ion chromatograph standardization system.*

to obtain sample or standard aliquots, inject them into the proper chromatograph, and initiate the regeneration of suppressor columns at predetermined time intervals. Data acquisition from each chromatograph detector and reduction for reporting of results is provided by the same computer system.

The algorithms needed to obtain peak areas accommodate fused peaks of equivalent magnitude and minor peaks on the leading or trailing edges of a major peak, as well as completely resolved peaks. Rejection of negative peaks, for example, the "water dip" seen with the anion subsystem, is another feature of the software. Through computer control of the standardization system, calibration factors will be updated and verified four times during a 24-h period.

Standard recovery data obtained by the instrument is analyzed by a linear regression routine to determine if these response factors are changing. If a large change (~20 to 30 percent) is noticed in the response factors, the data report will contain a comment, and no file update will take place.

The comment section of the results report will initiate operator intervention for remedial action.

All result and peak information data output by a sample or standards data report, except for the chromatogram raw data, are stored on a magnetic tape cassette.

Field Testing

Field testing of the instrument will be carried out in two electric power plants, which have been selected on the basis of availability of space, type of cycle (recirculating, once-through, or other), and cooperation of the utility management and operation personnel. It is planned to engage the power plant operating personnel in all phases of on-site work in order to share costs, demonstrate the practicality of the method, and obtain acceptance of the technique by the utility operators.

Rancho Seco, a PWR operated by the Sacramento Municipal Utility District (SMUD), was selected as the initial test facility. This nuclear plant operates with all-volatile treatment (AVT), full-flow condensate polishers, and freshwater cooling. It has four sample lines available, and sampling from these sources was initiated during the first 6 months of 1980. Seven additional lines were designed to be included with the instrument sampling system. The total system should be completed by June 1981. The second plant selected is the Baltimore Gas and Electric Calvert Cliffs reactor. This reactor differs from the first plant in that it features a recirculating steam generator and brackish water cooling.

Prototype Testing

To validate the on-line sampling system and obtain preliminary performance information on the ion chromatograph, an instrument and single-reservoir sampling device was installed at Rancho Seco. Three sampling points were made available, the polisher effluent, final feedwater, and condensate pump discharge. Chromatograms were obtained shortly after plant start-up and provided initial qualitative data.

Conclusion

A measurement system has been developed based on an on-line application of ion chromatography for the analysis of a comprehensive list of anions, cations, organic acids, and corrosion products. Thorough field testing will prove the capabilities of the instrument system and provide an invaluable tool for the analysis of ultrapure water. The introduction of this new technology in power plant operations will provide the reliable and essential information necessary for trouble-free production of electricity.

Acknowledgments

This work is being funded by the Electric Power Research Institute as RP 1447 as part of the Reliability Availability and Economics Program of the Nuclear Power Division, directed by Milt Levenson. The cooperation of Roger Miller and Arshad Alvi at the Rancho Seco plant of Sacramento Municipal Utility District is gratefully acknowledged.

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S. J. West[1]

High-Purity Water Quality Monitoring Based on Ion-Selective Electrode Technology

REFERENCE: Diggens, A. A., Lichtenstein, Susan, Synnott, J. C., and West, S. J., "**High-Purity Water Quality Monitoring Based on Ion-Selective Electrode Technology,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 131–138.

ABSTRACT: Power industry requirements for pure water demand instrumentation capable of detecting contaminants at very low levels. Moreover, precision and accuracy of measurement should be improved to allow reliable control. Although ion-selective electrodes have been employed successfully in the laboratory, certain problems have inhibited their utility in on-line monitoring applications. Recent work, briefly reviewed here, discusses these problems as encountered in the development of a sodium monitor. This effort has resulted in a second generation of ion-selective electrode-based devices which are less complex and, therefore, more reliable. Among these are monitors that measure chloride, chlorine, calcium, and sulfide in the parts-per-billion range. Hardware and chemistries are described, and data resulting from in-house and field evaluations are discussed. Work in progress for other parameters is presented.

KEY WORDS: ion-selective electrode, on-line monitors, power generation, dynamic calibration, low-level analysis, power plants, instrumentation, water quality

Power industry requirements for pure water call for instrumentation capable of detecting contaminants at very low levels. In addition, such instrumentation must be extremely reliable and must measure with a high degree of accuracy. As these considerations become more stringent, analytical techniques must be reviewed, but, perhaps more important, the means by which the technique is applied must be included in the evaluation. Any monitor for on-line use must be an integral part of the process, where successful operation of one depends on successful operation of the other.

The usefulness of ion-selective electrodes in the laboratory has long been recognized, but certain problems have inhibited their application to on-line measurement. Early attempts to build "monitors" by simply inserting elec-

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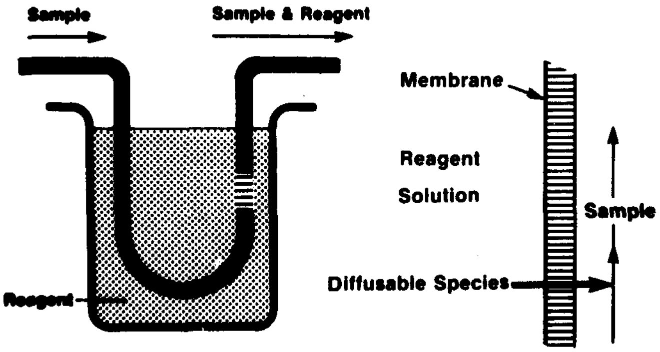

FIG. 1—*Sample and reagent.*

trodes into a pipe were largely failures in that a number of parameters affecting electrode measurement were not considered. Among these are temperature, sample conditioning, and calibration, all of which are easily dealt with in the laboratory. However, in flowing systems, the problems are much less trivial. As these problems were addressed in the past, the hardware necessary became more and more complex and, of course, more and more unreliable. The problems got worse as lower levels of detection, exemplified in the following limits set by Westinghouse and General Electric, were sought:

Sodium not to exceed 3 to 5 μg/litre (ppb) in high-pressure steam to turbine.

Chloride not to exceed 3 to 5 μg/litre (ppb) in high-pressure steam to turbine.

Turbine most critical component in power generation.

With these things in mind, we set out to design monitors as integrated measuring systems, eliminating as much as possible excess parts that might fail.

In earlier work [*1*],[2] we described in some detail the development of a trace sodium monitor. To meet the design constraints mentioned previously, the instrument would have to be capable of low-level detection, temperature compensation, passive reagent addition, dynamic calibration and elimination of background interference to that calibration. The first two of these design features were addressed by designing a trace sodium electrode whose isopotential lies in the region where measurement is made. This simplifies the amount of temperature correction required and thus simplifies the hardware. Passive reagent addition (Fig. 1), solves three major problems:

1. Since there is no volume change, as in the case of liquid reagent addition, there is no need to correct for dilution.

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

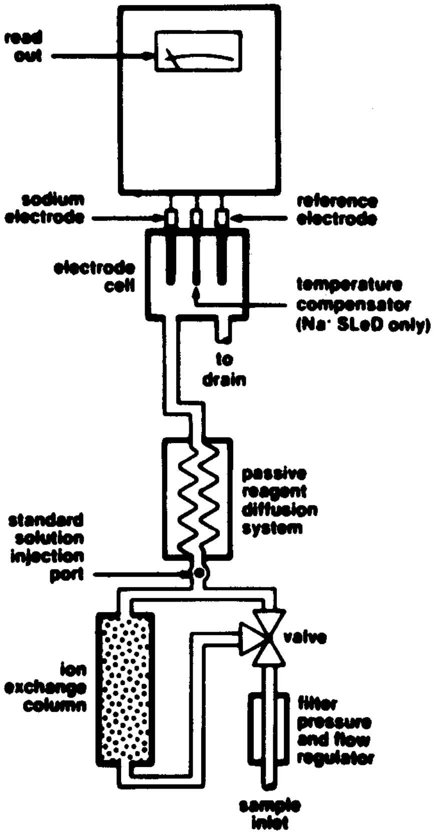

FIG. 2—*Fluidic system trace sodium monitor.*

2. Unreliable pumps or other mechanical devices are avoided.
3. Problems with reagent contamination are eliminated. This, of course, helps improve detection limits.

Calibration of any chemical measuring system should be carried out in the region of measurement interest and under the same conditions as a sample. To accomplish this, we use the sample stream itself, after it is passed through a polisher, as a diluent for dynamic calibration. The standard's needs can therefore be prepared at reasonable [~1 mg/litre (ppm)] levels for low [microgram per litre (ppb)] calibration. Mechanically, this requires only a valve and a syringe pump.

The design features discussed are shown schematically in Fig. 2. Figure 3 shows some data taken on an actual instrument. As can be seen, our approach results in an instrument that accomplishes its task. That is reason enough to start applying the same approach to other parameters affecting water purity.

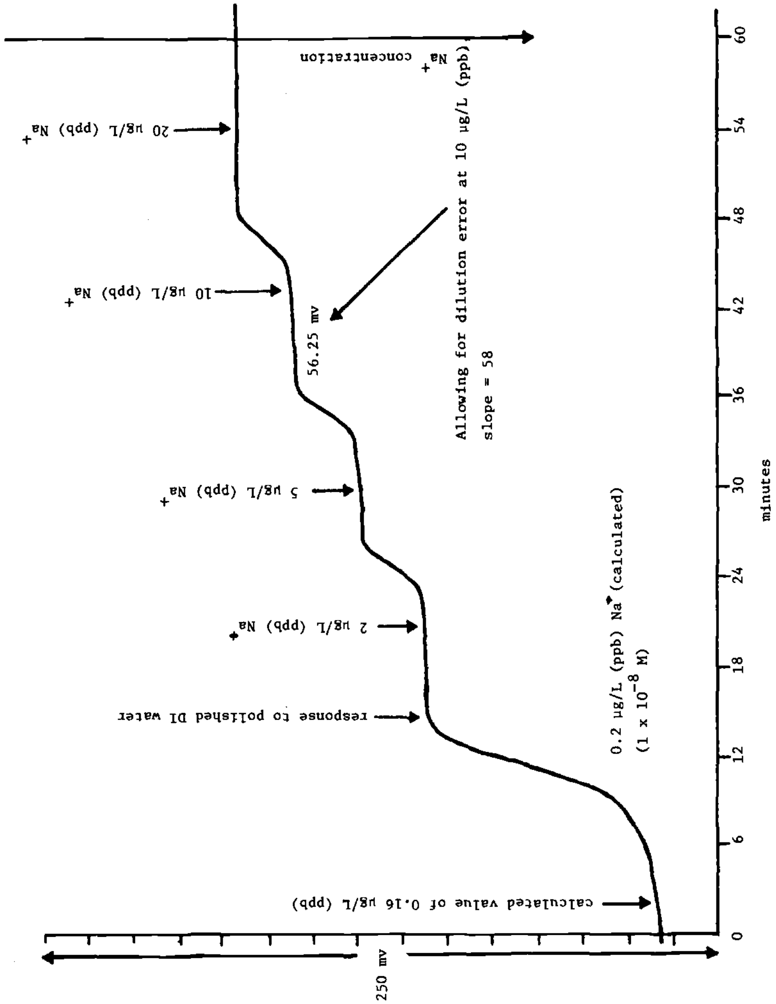

FIG. 3—*Sodium electrode response—decrease in ammonia vapor concentration.*

Low-Level Chloride

In the management of corrosion in steam-water circuits of electric generating plants, the monitoring of trace levels of chloride is a valuable capability. Chloride at micrograms-per-litre (ppb) levels can contribute to stress-corrosion cracking of turbine materials, resulting in extraordinarily expensive maintenance and downtime.

The recent development of solid-state ion-selective electrodes based on mercurous chloride [*2,3*] has permitted the development of an on-line instrument capable of monitoring low-level chloride in high-purity waters in the range of interest, zero to 50 μg/litre (ppb) [*4,5*]. Like the trace sodium monitor [*1*], the chief aspects of the chloride instrument design which allow measurement at low levels are the use of a low-level measuring electrode, passive reagent addition, and dynamic calibration.

The limit of detection of the low-level chloride electrode is determined by the solubility of mercurous chloride. A theoretical analysis of the electrode's response in the range of 0 to 50 μg/litre (ppb) chloride indicates a linear response (correlation coefficient 0.9997) with a sensitivity of 0.25 mV/ppb at 5°C [*3,4*]. In a flowing sample, a still greater sensitivity is achieved because the dissolving mercurous chloride is swept away from the electrode surface before equilibrium solubility can be attained. In the present instrument, a linear response of 0.4 mV/ppb is observed. The electrode and sample are held at 5°C with a cooling bath. Figure 4 is a schematic diagram of the system.

The low-level chloride electrode will respond to hydroxide ion at a pH of greater than 3.5. It is therefore necessary to acidify boiler water samples which typically have pH values of about 8.0. Addition of a reagent to a sample undergoing trace analysis for chloride is a potential problem, since contamination of the analate may occur. This difficulty was circumvented in the present work by the use of passive diffusion of formic acid into the sample. The sample simply flows through a length of silicone rubber tubing immersed in a bottle of formic acid solution. The formic acid diffuses through the tubing which is not permeable to chloride and thus prevents chloride intrusion. Passive diffusion offers, in addition, the advantages of negligible sample dilution and the absence of a pump or compressed gas.

The problem of calibrating a system at such low concentrations is solved by dynamic calibration. The sample is shunted through a deionization column before entering the formic acid bottle. This provides a blank so that the meter reading can be set to zero. A known chloride solution is then pumped at a known dilution into the blank stream, and the meter span is then adjusted.

Our experience in the application of the described instrument in power plants has demonstrated the utility of low-level chloride monitoring. Breakthrough of industrial demineralization systems has been detected by the chloride analyzer as much as 30 h prior to its indication by conductivity or sodium measurement. Also, it has been demonstrated that chloride levels in

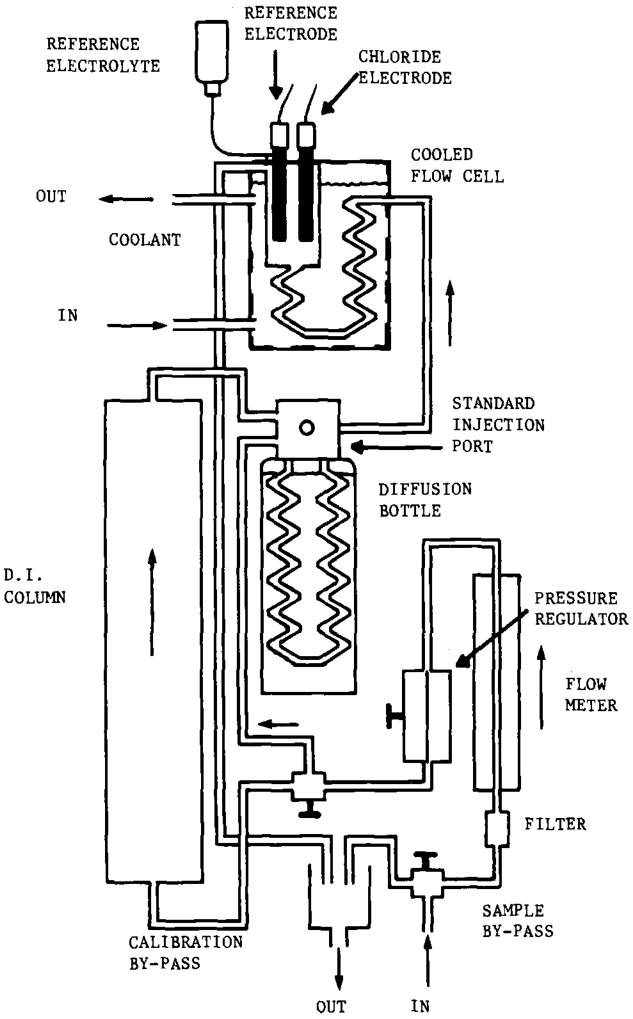

FIG. 4—*Low-level chloride analyzer.*

steam condensate do not necessarily track sodium levels, and thus the independent measurement of chloride is required for comprehensive corrodent control.

Hydrazine—Sulfite

Another aspect of corrosion prevention is the removal of dissolved oxygen. Reducing agents such as sulfite or, more often, hydrazine are added to the steam-water loop of utilities for this purpose. In order to maintain the optimum reductant level, periodic or continuous measurement of its concentration is necessary. Most power plants attempt to maintain hydrazine in the

50-μg/litre (ppb) range. The concepts of passive reagent addition, dynamic calibration, and ion-selective electrode measurement combine here, as in the cases of sodium and chloride, to result in a simple system for hydrazine or sulfite monitoring.

Hydrazine and sulfite react with iodine to produce iodide ions.

$$N_2H_4 + 2I_2 = N_2 + 4I^- + 4H^+ \tag{1}$$

$$SO_3^= + I_2 + H_2O = SO_4^= + 2I^- + 2H^+ \tag{2}$$

Iodide can be measured with an iodide-selective electrode with good sensitivity. The iodine can be added by passive diffusion through silicone tubing, resulting in a very simple system. A diffusion reagent consisting of glacial acetic acid, saturated with iodine crystals, provides sufficient sample conditioning for either measurement. Hydrazine instruments of this design are currently in use at power stations for the determination of 10 to 500 μg/litre (ppb) hydrazine. Sulfite instruments are finding use in the water treatment industry for control of the sulfite-dechlorination process in reverse-osmosis feedwater where a measurement range of 50 μg/litre (ppb) to 100 mg/litre (ppm) is encountered.

Sulfide

The measurement of sulfide ion is not routine in the power industry. However, under the reducing conditions and high temperatures and pressures in steam-water circuits, breakdown of sulfite or sulfate to sulfide has been suspected. As a result, the desire to measure sulfide has been expressed by plant operators, since sulfide is a known corrodent.

Sulfide can easily be measured with instrumentation like that described earlier. Sulfide-selective electrodes are extremely sensitive, and when used in conjunction with a pH electrode, rather than a conventional reference, a measuring cell with a response directly proportional to hydrogen sulfide, independent of pH, is obtained. Since virtually all of the sulfide present in a water sample below pH 5 exists as hydrogen sulfide, acidification of the sample is the only treatment required to allow measurement of total sulfide with this system.

Passive diffusion of acetic acid into the sample lowers the pH sufficiently for this measurement. Instruments utilizing the combination of sulfide and pH electrodes with diffusion of acetic acid are presently in use for the control of the Girdler–sulfide heavy water manufacturing process [*6*] as well as the sulfide abatement process in geothermal power generation. Evaluation of sulfide contamination in boiler water with this instrument will occur in the near future.

Calcium Hardness

One of the most widely applied forms of water treatment is "zeolite softening." In this process, natural or recycled water passes through a cation exchange column, generally in the sodium form, and calcium and magnesium ions are removed from the sample to then be replaced by sodium ions. This operation is performed in many industrial applications and may be the only form of treatment applied or the precursor to further purification.

Early detection of exhaustion of the zeolite columns is important to economical water treatment and, in turn, to economical operation of whatever industrial process it serves. The calcium ion-selective electrode is ideally suited to this purpose. Calcium ions are known to leak from the column with magnesium, though at much lower levels, and before the overall effectiveness of the columns is severely diminished. Calcium hardness breakthrough can be monitored very simply because no reagent addition is required in the range of pH 2.5 to 10 and because of the electrode's greater selectivity for calcium over magnesium. Levels as low as 5 μg/litre (ppb) calcium carbonate ($CaCO_3$) can be detected in the flowing stream of the monitor. Calcium hardness monitors are now being used in numerous industrial situations and may be expected to become standard equipment in critical softening processes.

Conclusions

Corrosion management in power generation is critical for reliable plant operation and is critically dependent upon the systems used to monitor that operation. Only by addressing this interrelationship can reliable monitors be designed. The initial design criteria for a sodium monitor have provided the basis for design of a second generation of instruments which can be integrated into the overall operation. The result is reliability.

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R. F. Eherts[1]

Evaluation of Power Plant Measurement of Sodium Ions in High-Purity Main Steam and Feedwater Utilizing In-Line Continuous Specific-Ion Electrodes

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REFERENCE: Eherts, R. F., "**Evaluation of Power Plant Measurement of Sodium Ions in High-Purity Main Steam and Feedwater Utilizing In-Line Continuous Specific-Ion Electrodes,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 139–155.

ABSTRACT: This paper discusses the measurement of trace-level sodium concentrations in aqueous solutions. A comparison between the specific-ion electrode analyzer and other analytical methodologies is presented. The techniques include atomic absorption spectroscopy, flame emission spectroscopy, and ion chromatography. The data were obtained over approximately a 300-day period utilizing combinations of the aforementioned analytical techniques. The evaluation was performed at Calvert Cliffs Nuclear Power Plant (CCNPP), Lusby, Md., a pressurized water reactor owned and operated by Baltimore Gas and Electric Co. (BG & E). The data revealed that significant perturbations in the indicated sodium concentrations on the specific-ion electrode analyzers existed during the study period. Based upon the comparison data obtained by other analytical methodologies, the indicated sodium level variances were not considered to be representative of the actual system concentration variances. The perturbations in the indicated sodium levels were correlated with flow–pressure fluctuations in the specific-ion electrode sample lines. In addition, the accuracy of the instrument was diminished as the actual system sodium concentration varied outside the calibration limits of the analyzer.

KEY WORDS: sodium ions, specific-ion electrode, power plants, instrumentation, water quality

Calvert Cliffs Nuclear Power Plant (CCNPP) has two units, each 850 MW. Both units are pressurized water reactors (PWRs) manufactured by the Combustion Engineering Co. Unit 1 was placed into operation on 1 May 1975; Unit 2 was placed into service on 1 April 1977. Baltimore Gas and

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Electric Co. owns and operates the dual-unit facility located on the Chesapeake Bay in Lusby, Md.

In an effort to determine moisture carry-over in the main steam system, Orion specific-ion electrode continuous sodium analyzers (Model 151102) were installed at Calvert Cliffs Unit 1. The sampling points for the in-line sodium analyzers were the following locations:

(*a*) turbine moisture separator reheater drain tank No. 11 (MSRDT),
(*b*) first-stage reheater drain tank No. 11, and
(*c*) No. 11 steam generator bottom blowdown sample line.

The analyzers were installed in late May 1979 and have run continuously to monitor sodium concentration in the main steam and steam generator water. Each sodium analyzer has input to an associated chart recorder which is periodically reviewed by plant personnel to evaluate the performance of the instrumentation. In an effort to determine the accuracy and reproducibility of recorded data, as part of the program to monitor the performance of the sodium analyzers, data were generated by comparative analytical methodologies. The results of the in-line analyzers were compared by plant personnel to values obtained by (1) flame emission photometry, (2) atomic absorption spectrophotometry, and (3) chromatography ion elution. The comparison work was performed both by Baltimore Gas and Electric Co. laboratories (Calvert Cliffs Nuclear Power Plant and Westport) and by an independent vendor laboratory (Environmental System Inc.).

System Descriptions

Reheated Steam System

The purpose of the reheat steam system is to increase turbine blade efficiency and to enhance the reliability and life of the low-pressure blading. The system consists of piping and components from the high-pressure turbine exhaust to the low-pressure turbine inlet. The steam exhaust from the high-pressure turbine (cold reheat) passes through the moisture separator–reheaters to remove moisture and increase the enthalpy of the steam. The slightly superheated, dried steam (hot reheat) leaves the moisture separator–reheater and is piped to the low-pressure turbine stop valves.

The moisture separator–reheater consists of a moisture separator and two reheater sections combined in a single shell. Steam, after entering the shell, passes first through the moisture separator section. This section consists of positive entrainment chevron separators to remove most of the moisture from the passing steam. After leaving the moisture separator section of the shell, the steam enters the first-stage reheater. This stage consists of a finnedtype heat exchange tube in which third-stage extraction steam, used as a heating medium, passes through the tubes and cold reheat passes around the tubes. The reheat steam leaves the first stage. The construction of this stage is identical to that of the first stage except that the steam used as the heating medium is from the main steam system. Drains from the two reheat stages and moisture separator drain to individual tanks. The drains are collected in these tanks and cascaded to feedwater heater shells (reheat drains) or feedwater drain tanks (moisture separator drains). All drain tanks on a high level pass directly to the condenser. The two Orion sodium analyzers monitoring the Unit 1 reheat system are located to obtain samples from the No. 11 moisture-separator drain tank and the No. 11 first-stage reheater drain tank.

Steam Generator Blowdown

The steam generators are vertical shell and U-tube heat exchangers with reactor coolant on the tube side and secondary water on the shell side. A steam generator blowdown system is maintained to remove impurity-laden water from the vessel. The bottom blowdown consists of a 5-cm (2-in.) nozzle connected to a collection header just above the tube sheet and is useful in removing both particulates and dissolved solids.

A low flow rate [approximately 0.02 litre/s (0.3 gal/min)] is maintained through the steam generator continuous sampling system equipment located in the nuclear steam supply system (NSSS) monitoring panel. The NSSS blowdown sampling system consists of a permanent in-line monitor and recorders for pH and conductivity. The interior components of the panel consist of a primary cooler, a pressure regulator, and an isothermal bath. Chilled water, cooled by a mechanical water chiller, with a capacity of 0.4 litre/s (6 gal/min), is circulated through the bath to regulate the sample temperature. The chill-water flow rate through the bath is regulated by a pneumatic temperature controller valve. The exchange coils in the bath are designed to be long enough to allow the sample to reach an equilibrium temperature with the bath. The bath adjusts the sample temperature to 25 ± 0.5°C (77 ± 1°F). The Orion sodium analyzer monitoring the No. 11 steam generator obtains a sample from the effluent of the isothermal bath.

Comparative Analytical Methodologies

In order to evaluate the precision and accuracy of indicated levels of sodium concentration observed on the Orion instrumentation, comparison was made with values obtained by other analytical techniques. The techniques utilized are listed here, together with a general discussion of the actual instrumentation involved.

Flame Photometry

A Beckman Model DU-2 ultraviolet spectrophotometer with an associated flame photometry attachment was utilized to provide the bulk of data for comparison purposes [*1*].[2] It is a single-beam, null-balancing model, which has been extensively utilized at the Calvert Cliffs laboratory to monitor for sodium impurities on secondary plant systems. A schematic illustration of the internal components of the system is given in Fig. 1.

Measurements with the spectrophotometer were produced utilizing site-specific chemistry procedures [radiation safety and chemistry procedures (RCP) 2-204 and 1-908] based on associated recommendations of the American National Standards Institute and the American Society for Testing and Materials [*2*]. This method is applicable to the determination of trace amounts of sodium ions in waters with low solids content, such as condensate and deionized water. It is specifically applicable to concentrations of sodium from 0.25 to 1000 mg/litre. The precision of the method may be expressed as follows

$$s_T = 0.006x + 0.09$$

where

x = concentration of sodium (mg/litre), and
s_T = overall precision.

Atomic Absorption Spectrophotometer

Comparative data were produced by means of the atomic absorption method of analysis for sodium utilizing a Perkin-Elmer Model 303 unit. The measurements were performed in compliance with approved procedures [*3*] by an independent laboratory under contract to Baltimore Gas and Electric Co. For the standard conditions involved in the method, the sensitivity was about 0.015 mg/litre for 1 percent absorption. A minimum reading of 0.1 percent was detectable, so the detection limit for the parameter was 0.0015 mg/litre, or 1.5 ppb. Standard solutions containing 0.8 mg/litre of sodium gave absorbance readings of 0.23 units (approximately 41 percent absorption), the working range being linear up to concentrations of approximately 1 mg/litre in aqueous solution.

Ion Chromatography

A Dionex Model No. 14 ion chromatographic unit was utilized to provide additional comparison data for the indicated sodium levels observed on the specific-ion electrode analyzers. The flow scheme of the system is indicated in Fig. 2. Basically, the unit combines the separation capabilities of ion-exchanger resins with conductimetric detection.

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

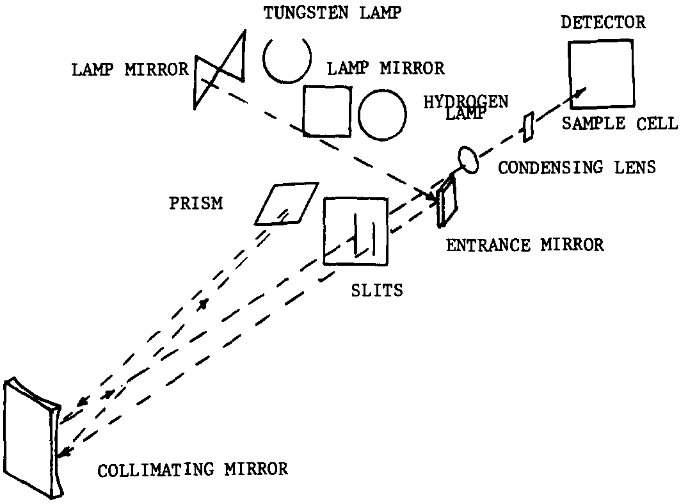

FIG. 1—*Spectrophotometer schematic.*

Measurements utilizing the technique of ion chromatography were performed in accordance with approved guidelines contained in the manufacturer's instruction booklet [*4*]. When using peak heights for quantitation, the relative standard deviation is usually 3 to 5 percent. For trace level analysis using the 0.3-μmho full-scale sensitivity and a 250-μl sample loop, the min-

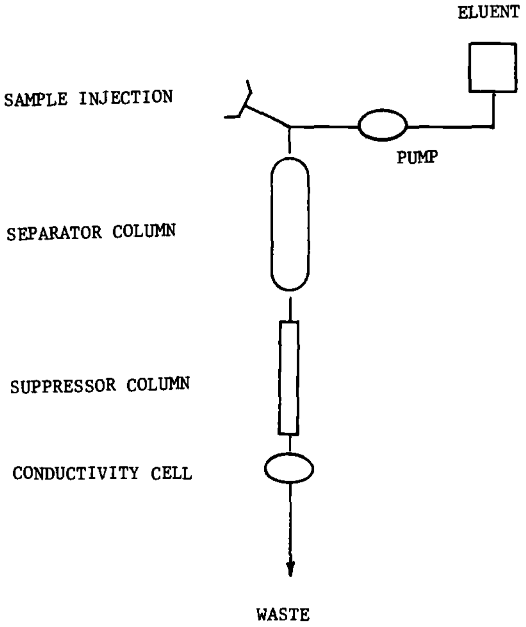

FIG. 2—*Dionex schematic.*

imum detection limit (MDL) for sodium is in the range of 5 to 20 ppb. The MDL is defined as twice the noise level.

Sampling Techniques

The sampling techniques utilized in the determination of comparison data were those outlined in site-specific procedures (RCP 1-501) based on standard practices for sampling water as outlined in the ASTM Practices for Sampling Water (D 3370-76) [*5*]. Control practices were established to ensure that representative samples were obtained while potential sources of contamination were minimized to the extent practical.

Orion Specific-Ion Electrode Sodium Analyzers

The Orion sodium analyzers installed at Calvert Cliffs Nuclear Power Plant were Model 151102 units, which continuously report the sodium concentration in a single sample stream. This is referred to as the absolute mode of analysis, and the instrument is referred to as the a/SLeD. The a/SLeD gives a continuous analysis of sodium from 0.1 to 1000 ppb in steam and feedwater applications. A thermistor automatically compensates for changes in sample temperature. The need for compressed gases and extravagant reagents has been eliminated by a unique system for pH control. The SLeD was designed with a minimal number of moving parts to eliminate maintenance input and increase reliability. A description of the instrument is provided as Fig. 3 [*6*].

Experimental Procedures

Analytical Techniques

The following analytical techniques were used:

(*a*) Flame 1 (flame photometry apparatus operated by Calvert Cliffs Nuclear Power Plant chemistry laboratory);

(*b*) Orion (continuous specific-ion electrode sodium analyzers installed and calibrated by General Electric personnel, operated and maintained by Baltimore Gas and Electric Co. personnel);

(*c*) Flame 2 (flame photometry apparatus operated by Westport Chemistry Laboratory personnel);

(*d*) Atomic absorption instrument (AA) (owned and operated by an independent contract laboratory); and

(*e*) Dionex (ion chromatographic apparatus operated by Baltimore Gas and Electric Co. personnel).

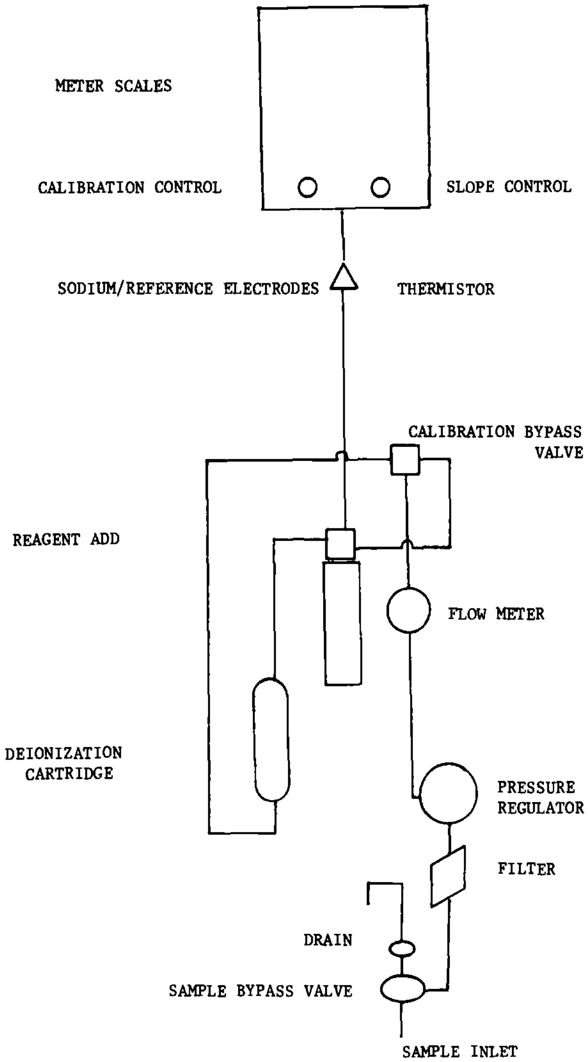

FIG. 3—*Specific ion electrode analyzer.*

Time Span

Data were collected for a time period of approximately 1 year utilizing various combinations of analytical techniques.

Data

Figures 4 through 11 compare sodium levels generated by (1) routine (daily) flame photometric analysis performed by CCNPP chemistry personnel as part of the chemistry surveillance program and (2) specific-ion elec-

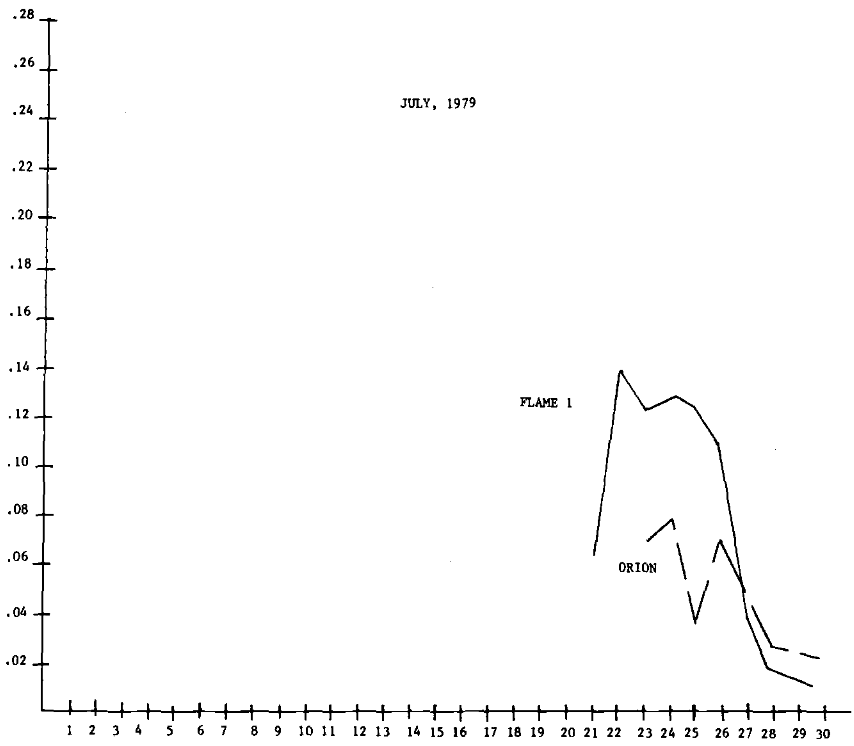

FIG. 4—*Steam generator sodium (parts per million) versus time (days) in July 1979.*

trode measurements recorded by the Orion sodium analyzer. The sampling location was the No. 11 steam generator blowdown system. The vertical axis represents the sodium concentration in parts per million (0.0 to 0.30), and the horizontal axis is the time in days. The study period is illustrated for a duration of approximately 250 days.

Figure 12 characterizes a comparison of sodium levels as monitored at the sampling location of the No. 11 steam generator blowdown. The methodologies utilized include (1) two separate flame photometry analyses performed by CCNPP chemistry personnel and Westport laboratory chemistry personnel. Both laboratories are owned and operated by Baltimore Gas and Electric Co.; (2) atomic absorption spectrophotometry analysis performed by Environmental Systems Inc., an independent laboratory under contract to Baltimore Gas and Electric Co.; and (3) specific-ion electrode measurements as recorded by the Orion sodium analyzer. The study period lasted for approximately 20 days.

Figure 13 illustrates a comparison of sodium levels monitored at the No. 11 steam generator blowdown location. The samples analyzed by ion chro-

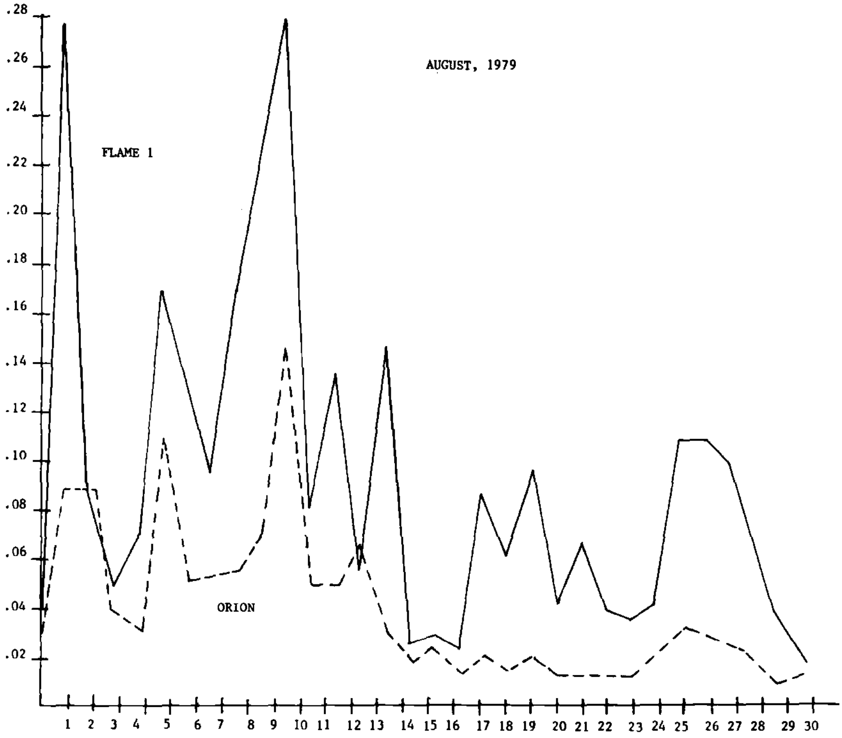

FIG. 5—*Steam generator sodium (parts per million) versus time (days) in August 1979.*

motography are compared with levels recorded by the Orion analyzers. The study was performed for approximately a 10-day period.

Discussion

It is readily apparent from examination of the graphs in Figs. 4 through 11 that there were significant disparities between the sodium levels monitored by the Orion analyzer and those monitored by the flame instrumentation. In general, the sodium trends established by the flame unit and supported by additional plant chemistry data (feedwater sodium, condenser cation conductivity, tube plugging information, and so on) are reflected by the Orion analyzer. However, in numerous instances the Orion instruments reflect deviation from the normal trend established. These perturbations show marked increases and, at times, decreases from the flame data. The following examples illustrate both situations: (1) on 25–27 July 1979 (Fig. 4), the Orion analyzer shows a marked and abrupt decrease from the general trend established by the flame unit and supported by the overall plant chemistry. The

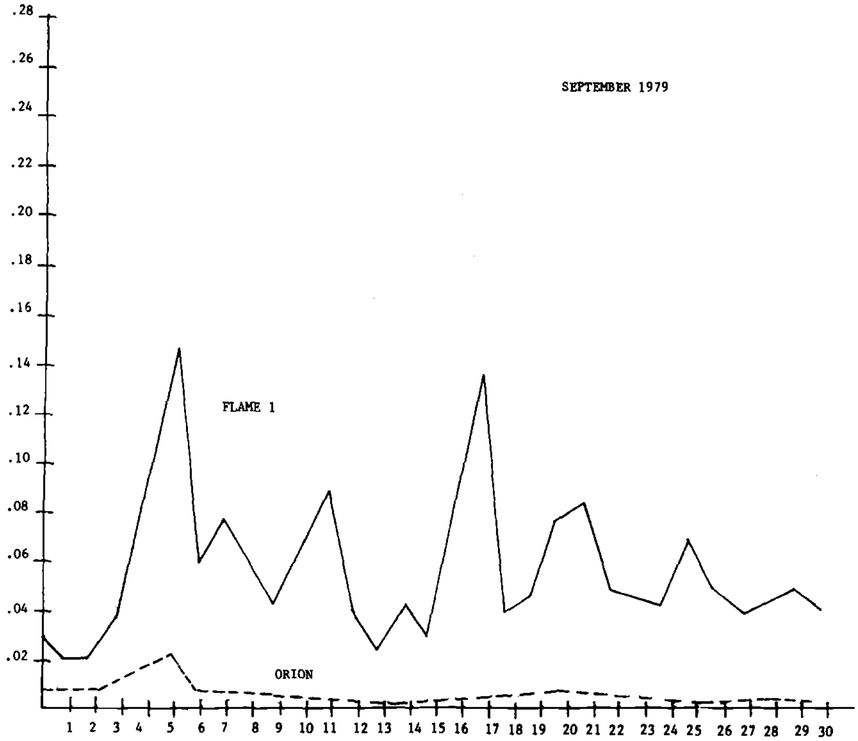

FIG. 6—*Steam generator sodium (parts per million) versus time (days) in September 1979.*

decrease on 26 July from 0.080 to 0.030 ppm sodium does not correlate with the 0.125-ppm level observed by the flame unit; (2) on 3-6 March 1980 (Fig. 10), the Orion unit displayed a significant and sudden increase in sodium levels from the trend established by the plant chemistry. The increase from 0.040 to 0.090 ppm is not observed in the flame data.

There were many other instances of sodium concentration deviations observed on the Orion instruments that did not correspond to the general sodium trend established by the flame instrumentation and supported by the overall chemistry and operation of the nuclear facility. It was observed by plant personnel that the "unexpected" changes in sodium levels were accompanied by significant fluctuations in the Orion analyzer flow and pressure. In numerous situations, the Orion instrument pressure was observed to decrease from 1000 to <300 g/cm^2 (15 to <5 psia) over a 24-h period. In addition, flow fluctuation from the "normal" 40 ml/min to <10 ml/min, as well as changes to >50 ml/min, were observed. It has been previously documented [7] that sample flow fluctuations of 1 ml/min have resulted in reading variances in the sodium level of as much as 30 percent on the Orion in-

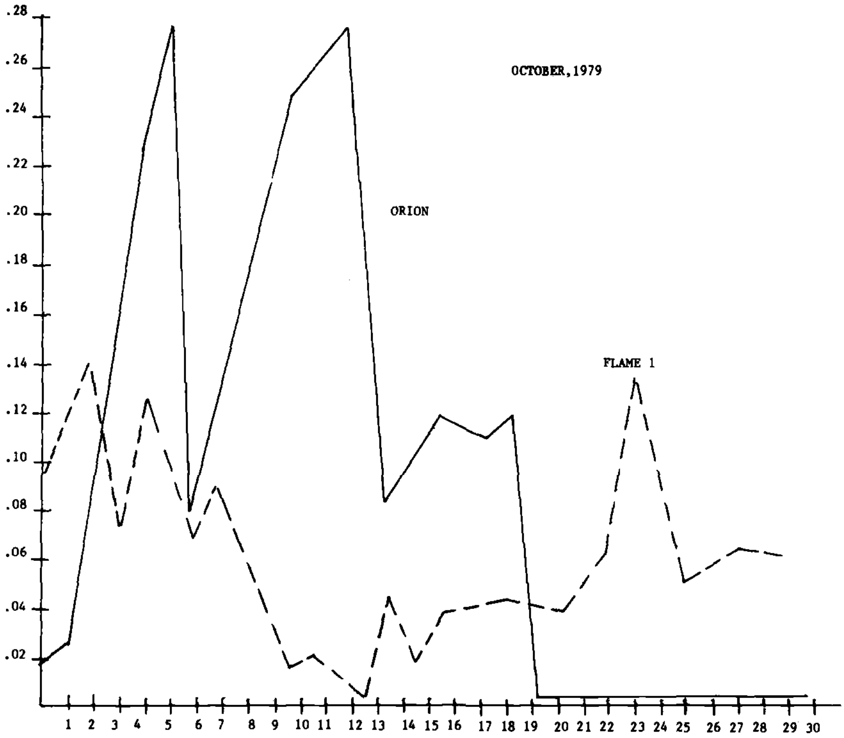

FIG. 7—*Steam generator sodium (parts per million) versus time (days) in October 1979.*

strument. The data generated in this section supports the assumption that transient sodium level variances recorded by the Orion analyzer, which were either in excess of or below anticipated levels, resulted from observed flow transients in the analyzer rather than "real" changes in sodium concentrations in the steam generator.

The graphs in Figs. 12 and 13 compare the Orion analyzer data with the sodium levels monitored by a number of additional analytical techniques. Examination of the data indicates the following observations concerning Orion analyzer data accuracy and reproducibility: (1) During those periods of time when indicated levels of sodium ions (0.010 to 0.040 ppm) are well within the range of calibration (10 to 100 ppb), the accuracy of the Orion data is greatly enhanced. Comparison of the data generated from 9–15 April 1980 illustrates this point clearly. (2) However, during periods of time of seawater ingress (due to loss of condenser integrity), as the indicated level of sodium concentration approached or exceeded the outer limit of calibration, the accuracy of the Orion unit became significantly diminished. Comparison of data generated on 25–29 March 1980 illustrates this point markedly.

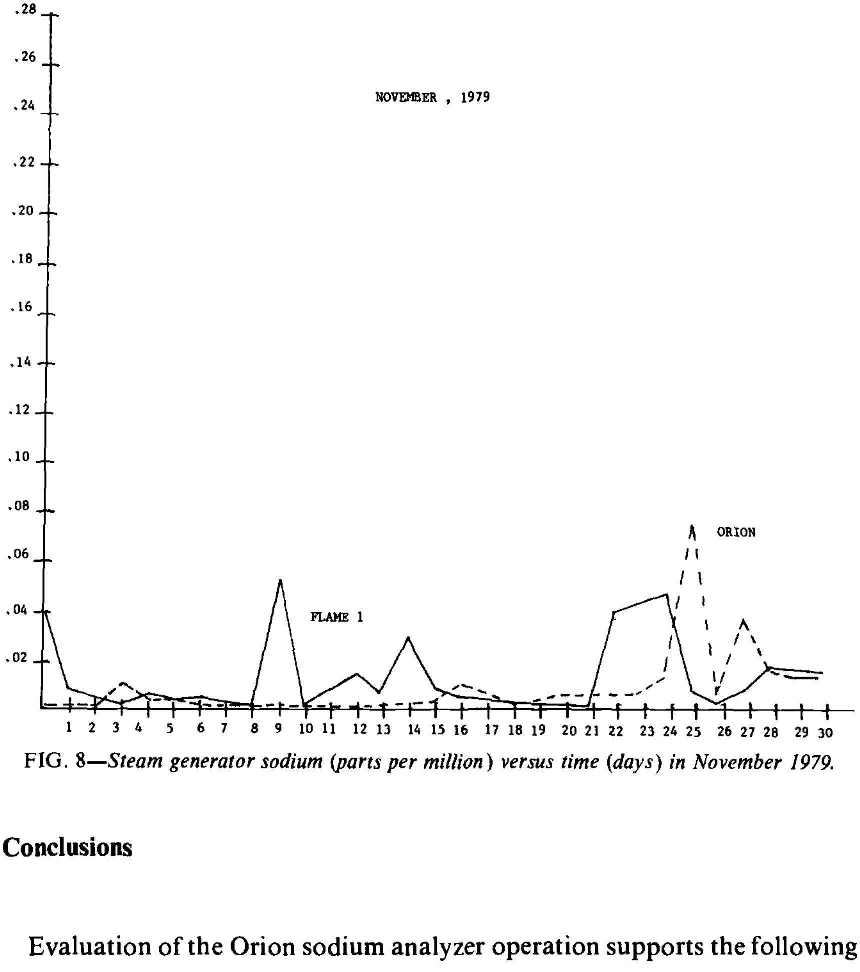

FIG. 8—*Steam generator sodium (parts per million) versus time (days) in November 1979.*

Conclusions

Evaluation of the Orion sodium analyzer operation supports the following statements:

1. Fluctuations in instrument flow or pressure, or both, result in significant perturbations in the observed sodium concentrations, which are not necessarily indicative of changes in the actual system sodium concentrations.
2. Response to an actual change in the system sodium level which approaches or exceeds the calibration range of the instrument results in significantly diminished accuracy. As a result of the observations explained in Points 1 and 2, significant maintenance input is required to maintain analyzer operation.

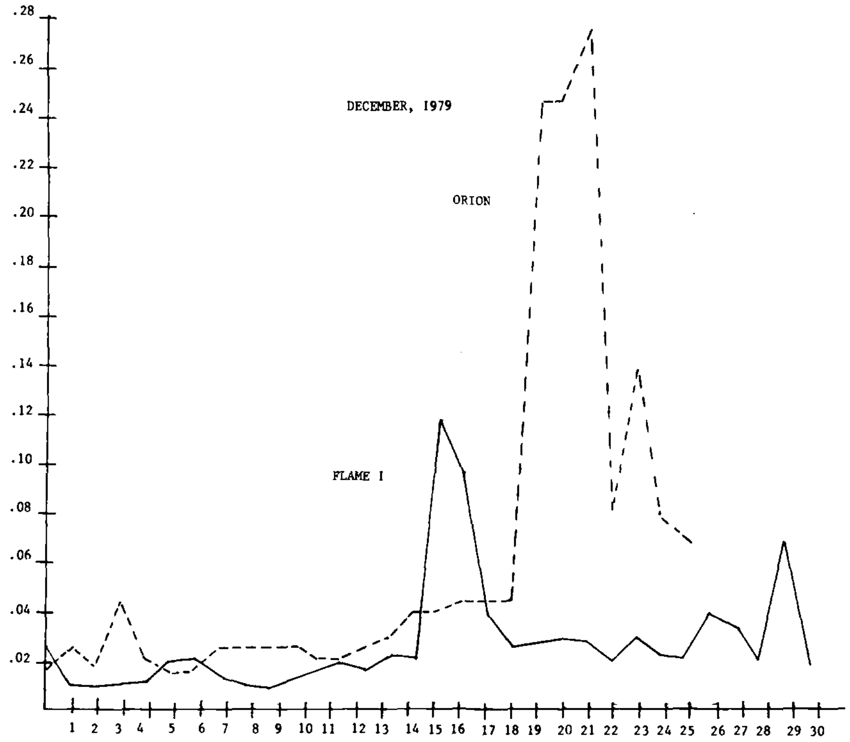

FIG. 9—*Steam generator sodium (parts per million) versus time (days) in December 1979.*

3. During those periods of time when instrument flow or pressure fluctuations, or both, are prevented, and system sodium levels are maintained within the established calibration range, the sodium concentration observed through the Orion analyzer is representative of real trends.

In conclusion, application of the continuous Orion specific-ion electrode analyzers should be restricted to systems characterized by low solids content to mitigate flow and pressure perturbations.

In addition, the instruments do not seem compatible to application in systems that periodically exhibit large variances in sodium level and where information on absolute concentrations versus relative trends is desired.

However, in those plant applications where flow and pressure perturbations can be avoided and where large sodium level variances are absent (or the diminished accuracy can be tolerated), the Orion analyzers produce data consistent with other methodologies with minimal maintenance input.

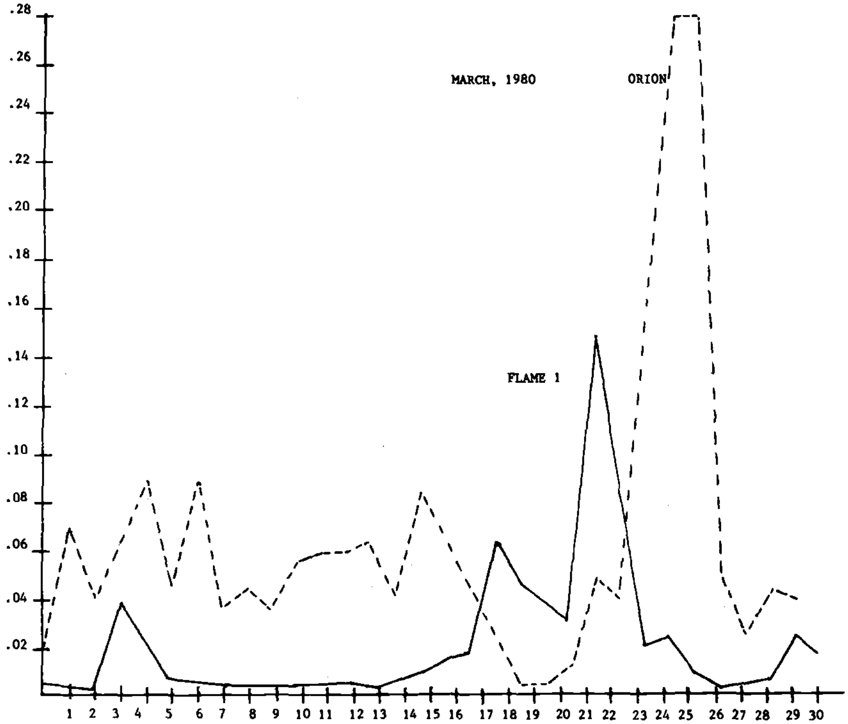

FIG. 10—*Steam generator sodium (parts per million) versus time (days) in March 1980.*

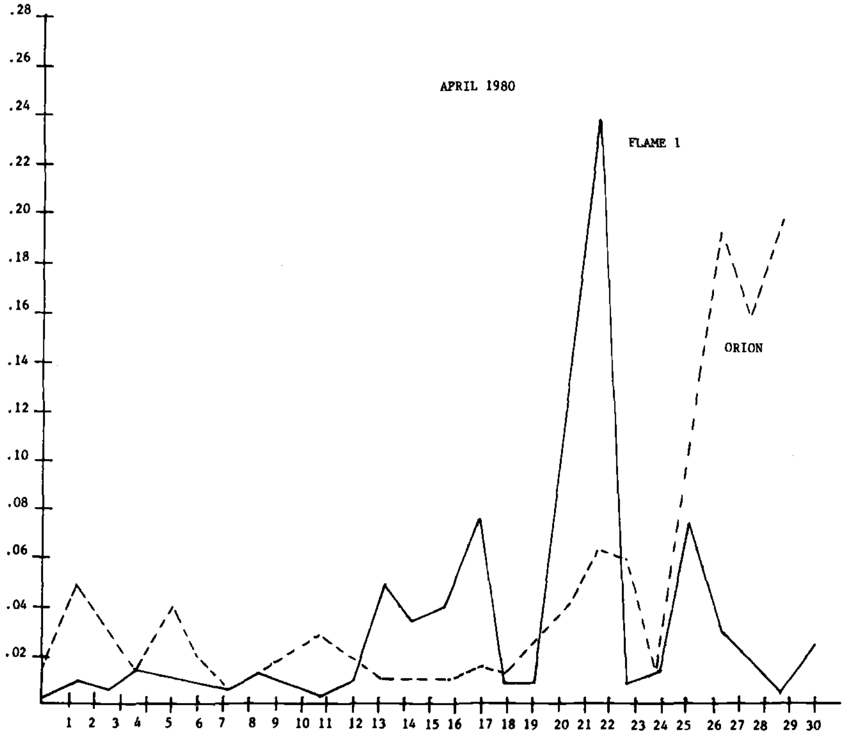

FIG. 11—*Steam generator sodium (parts per million) versus time (days) in April 1980.*

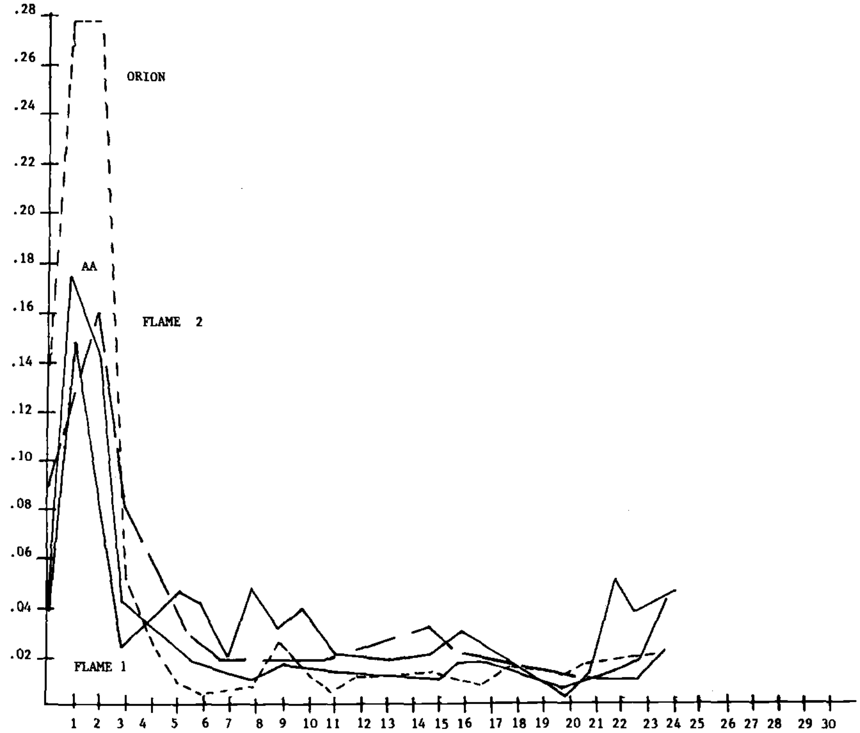

FIG. 12—*Steam generator sodium (parts per million) versus time (days), Test No. 1.*

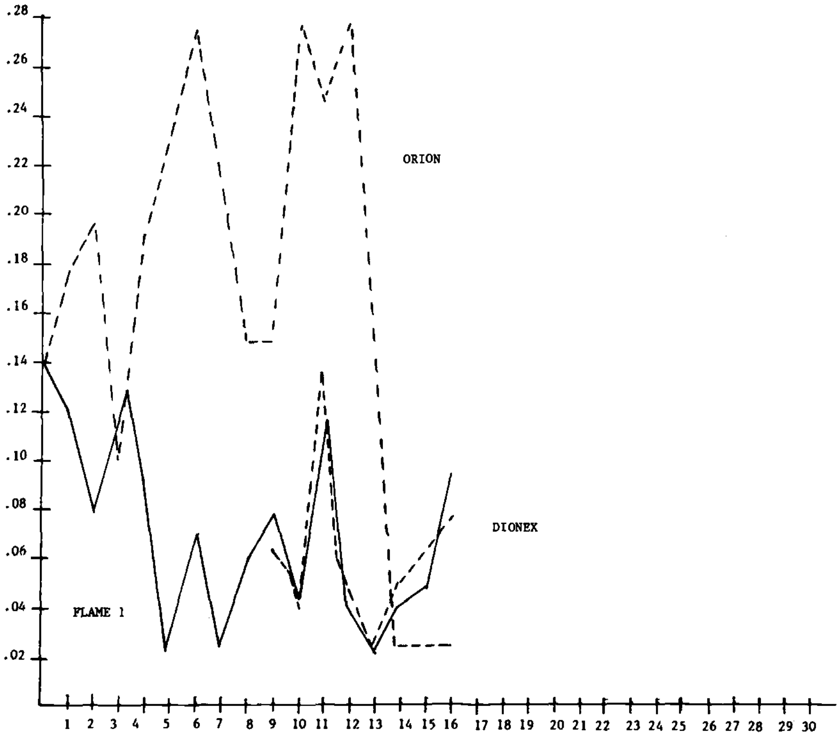

FIG. 13—*Steam generator sodium (parts per million) versus time (days), Test No. 2.*

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Use of On-Line Atomic Absorption in a Power Plant Environment

REFERENCE: Skriba, M. C., Gockley, G. B., and Battaglia, J. A., "**Use of On-Line Atomic Absorption in a Power Plant Environment,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 156–166.

ABSTRACT: Westinghouse has been conducting a program to upgrade the purity of primary-loop cooling water in pressurized water reactor (PWR) nuclear power plants, and a method was needed to measure cationic impurities such as calcium, magnesium, and aluminum in the 0 to 10-ppb range. After examination of alternative methods, a Perkin-Elmer Model 5000 flameless atomic absorption (AA) unit with an AS-40 autosampler was selected and tested on line in a nonlaboratory, auxiliary building area of an operating nuclear power plant.

Electrical isolation, dust and dirt protection, supplemental system cooling, and sample preconditioning all had to be provided to enable what is essentially a laboratory instrument to function in the more hostile plant environment. Some problems arose in the electronics of the spectrophotometer portion of the instrument, such as loss of preprogram instruction, multiple false readings, and loss of averaging functions. These problems were not of major proportions, however, and the system was able to track contamination levels through plant shutdown for refueling and consistently monitor impurities in the sub-parts-per-billion range. It has been shown that with the new automated flameless AA systems, high-quality analyses can be obtained on line and without the need of a highly trained spectroscopist as an operator.

KEY WORDS: analysis, composition, calcium, magnesium, aluminum, nuclear, power plants, atomic, absorption, primary, coolants, water, on line, water quality, instrumentation

The Westinghouse Electric Corporation has an ongoing program to upgrade the cooling water chemistry in the primary loops of their pressurized water reactors. This upgrading program is expected to have benefits in the areas of reducing such things as system corrosion, core–coolant interactions, and core deposits so that improved system operation can be obtained. Of particular interest in these studies are the calcium, aluminum, and magnesium ions since they appear to be the most active species in this problem area.

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Measurement of these ions at the very low concentration levels of interest (below 10 μg/litre or ppb) is a difficult problem from both the coolant and equipment requirement standpoints. The coolant (*a*) is radioactive, therefore small samples are preferred to reduce contamination, (*b*) may contain as much as 2 mg/litre lithium, (*c*) may contain as much as 2000 mg/litre boron in the form of boric acid, and (*d*) contains dissolved gases such as hydrogen. On the other hand, the equipment should (*a*) work on line in a continuous (or semicontinuous) mode to reduce sample contamination and provide real-time information, (*b*) require minimal operator attention and service, (*c*) provide a permanent record of the analyses, (*d*) analyze for calcium, magnesium, and aluminum in the parts-per-billion to sub-parts-per-billion range with reasonable accuracy, and (*e*) be reasonable in cost, have good field service available, and have readily available parts and supplies.

An initial scoping study was done to select the best method of analysis, and after testing many options, flameless atomic absorption (AA) was chosen for the initial prototype plant work. The unit purchased for this program was a Perkin-Elmer Model 5000, with an HGA-500 graphite furnace, and a Model AS-40 autosampler for sampling and injection. The features of being on line and having multielement capability, automatic operation, sensitivity, service availability, and microprocessor control all combined to make this a logical unit, at least for the initial, wider scope studies.

The major advantage the Perkin-Elmer unit had at the time of purchase was that the company had available a proven on-line sampling system which was operating in Europe. The unit also can analyze for up to six elements sequentially without operator assistance since it can be preprogrammed using magnetic cards.

Adaptations for Plant Installation

The Perkin-Elmer AA, however, is essentially a laboratory unit, and several adaptations were necessary to allow operation in the auxiliary building of the power plant; these are shown schematically in Fig. 1. One of our objectives was to show that analytical techniques were available for routine analyses of the low levels of contaminants we were specifying and that the analyses could be done in an operating power plant. The changes that were necessary fell into two categories: sample preconditioning and unit isolation. The valve train and ion-exchange column were to precondition the sample so that it could be injected into the furnace, and the Plexiglas cover, chiller, and step-down transformer were used to provide a more benign environment for the unit. The system as installed in the plant is shown in Fig. 2.

The valve train, shown schematically in Fig. 3, is of all stainless steel construction. Its purpose is to remove relatively large suspended solids, meter the flow, and protect the downstream components from overpressure.

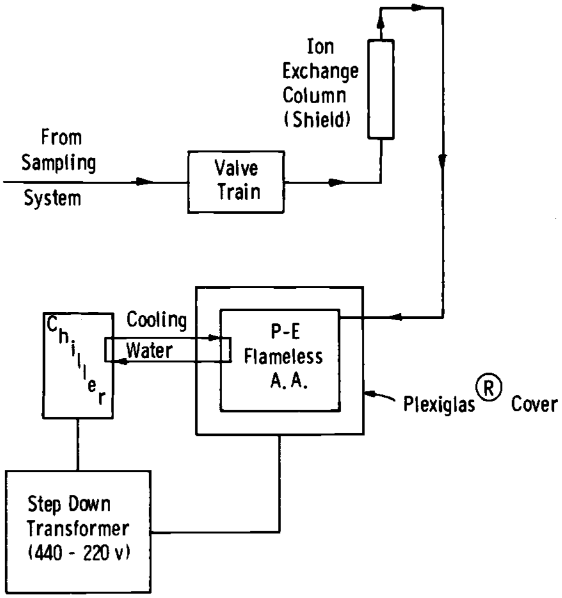

FIG. 1—*Adaptations needed to put an AA unit on line in plant.*

The first valve is a pressure-reducing valve to take the system pressure from a maximum of 1.55×10^6 kg/m^2 (2200 psi) and provide constant head supply to the on-line filter, which removes suspended solids, and the micrometering valve, which provides precise control of the sample flow rate. This portion of the valve train is protected by a pressure-relief valve which opens to the drain. After the metering valve, the sample flows to the ion-exchange cartridge which has a design pressure limit of 3.52×10^3 kg/m^2 (5 psig). Therefore, this portion of the valve train is protected by a pressure-relief valve similar to the first one. The installed valve train is shown in Fig. 4, and it functioned very well. Only occasional monitoring was necessary with some minor adjustments when the reactor coolant system exhibited wide variations in pressure.

Initial testing of the AA in the plant showed that the analyses were subject to interference from boric acid and that signal suppression was a function of the boric acid concentration. Figure 5 shows the magnitude of that effect. Since we were trying to analyze below 10 ppb, this signal suppression was unacceptable, and at levels of 500 ppm boron (which could be reached in plant operations) had a signal so low as to be unreadable. In addition, the boric acid gradually attacked the graphite furnace so that it deteriorated more rapidly than was desirable.

There was some evidence that using a technique of temperature ramp and holding a furnace soak at an intermediate temperature would allow the volatile boric acid to be driven off. The furnace could then be run up to analysis

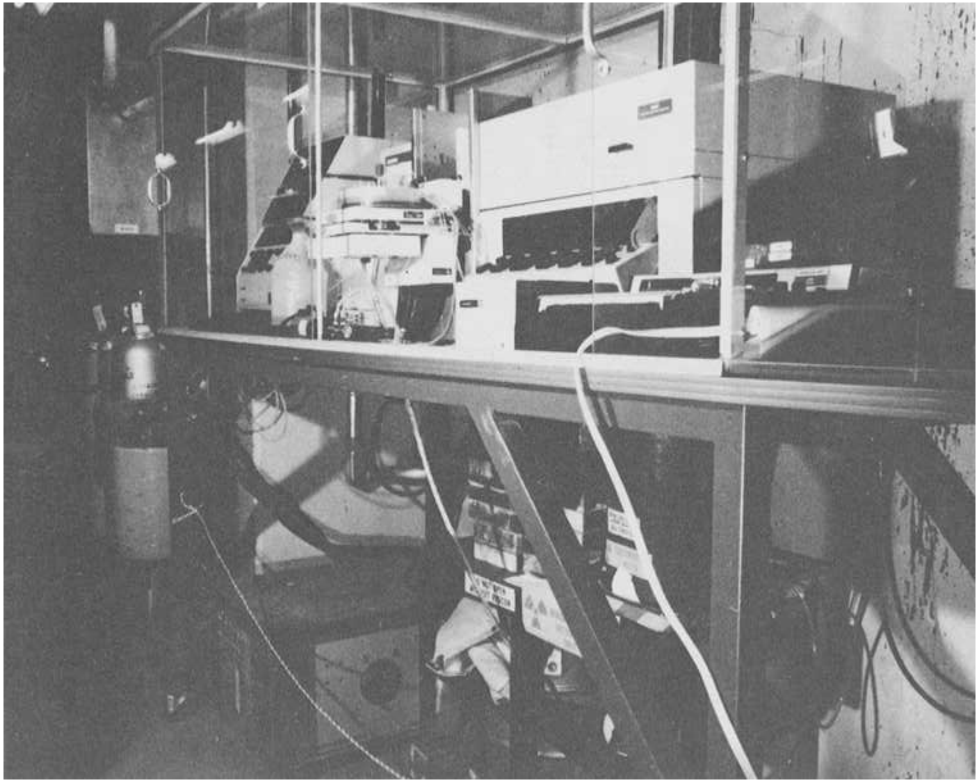

FIG. 2—*Perkin-Elmer AA unit installed in a power plant.*

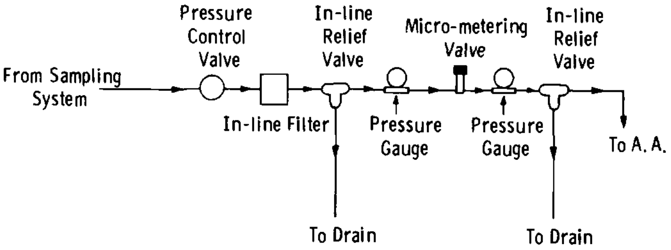

FIG. 3—*Valve train schematic drawing.*

temperature and the analysis done without preconditioning the sample. This was developmental, however, and previous work had shown that the boric acid could be stripped out using an anion resin without affecting the cation concentrations. A clear, inert, sealed plastic cartridge was used and filled with 2.41×10^{-3} m^3 (0.085 ft^3) of strong-base, nuclear-grade, anion resin in the hydroxide form. This cartridge could be changed out easily as it was connected with hose nipples. During the testing period, the boric acid concentration in the cartridge effluent was monitored by grab samples taken at the beginning of each shift. In 8 months of intermittent analyses, only two cartridges were used in the program. One broke through after ~600 h of operation at low boron concentration; the other is still in service.

In flameless atomic absorption analysis it has been generally accepted that the development and use of automatic sampling systems improves the precision of this method. Additionally, the autosampling systems reduce contamination and carry-over between samples by an effective flushing step. The system installed in the power plant consisted of a Perkin-Elmer AS-40 autosampler with an AS-2 on-stream component, capable of handling one to six streams.

The AS-40 portion of the system is operated by two small piston pumps (a sample pump and a flushing pump) mounted underneath the sample tray. The pumps are connected to a sample arm which rotates between the sample tray and the furnace port in the following manner:

1. The capillary tip of the sample arm is positioned in an overflowing cup of rinse water while in the rest position to constantly clean the tip.
2. The flushing pump cycles to rinse the capillary tip internally and externally. This fills the sample arm with flush (or blank solution).
3. The sampling arm is positioned directly above the overflowing cup and a 25-μl air bubble is drawn into the arm to separate the sample and the flushing liquid.
4. The sampling arm then indexes to the programmed sample cup on the sample tray. In the case of the AS-2 on-line system, the sample tray is equipped with eight constant overflowing cups, which are filled by blank and

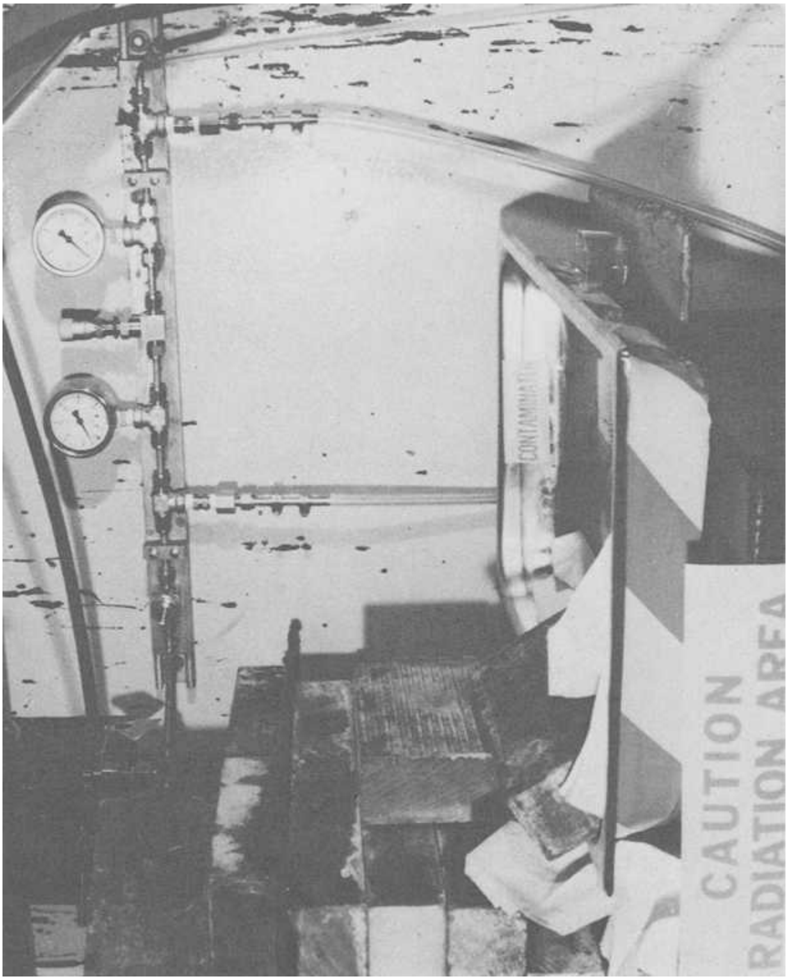

FIG. 4—*Valve train as installed in the power plant.*

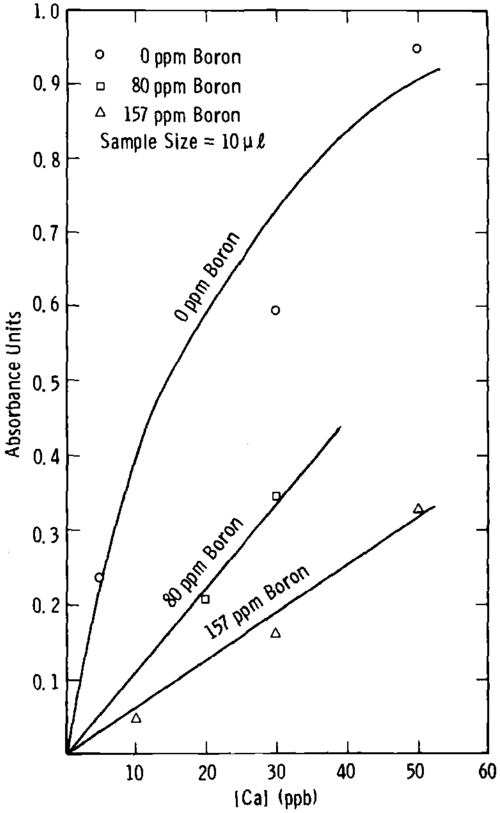

FIG. 5—*Effect of boron concentration on absorbance signal for calcium in the P-E 5000 flameless AA.*

standard solutions and the six on line streams. The blank and standard solutions are delivered to the sample tray by two small piston pumps. The six on line streams must be supplied in a constantly flowing stream with a 5 to 10-ml/min flow minimum. The trays are covered by a circular trough to limit evaporation and contamination. The sample arm is lowered into the programmed sample cup and the preselected sample volume is drawn into the arm.

5. The sample arm then swings over to the furnace, positioning the sample arm in the introduction hole in the graphite tube.
6. The liquid is dispensed into the tube by the pump.
7. The sample arm returns to the rest position in the overflowing cup.
8. The furnace program then begins. The tray will rotate to the next assigned position and the sequence begins again.

The sampling and furnace sequences are programmed into the instrument, by keyboard or magnetic cards, for operator-free working of the instrument.

The AA unit itself requires a cooling water flow to the optics and furnace holder. In the laboratory, this is normally provided by tap water, but in the restricted area of the power plant any water used must be treated as radioactive waste, so water use is carefully controlled. To provide the cooling necessary, a small portable chiller was used and the cooling water recirculated. As the heat demand is low, this chiller can be very small and the 5000-Btu/h system we used was more than adequate for the job.

During shakedown testing in the laboratory, prior to installation in the plant, it was found that electrical-line noise affected the electronics. To solve the problem, an isolation transformer was used. In the power plant, only 440 V was available, and the use of a 440 to 220-V stepdown transformer accomplished the same thing. But, if a 220 V supply is available in other plant installations, an isolation transformer is recommended.

Since the AA was mounted on a large wheel-equipped table, there was some concern over vibration transmission to the instrument and consequent drift of the optics. The wheeled table assembly was used to facilitate the transfer of the system from the laboratory assembly area at the Westinghouse Research and Development Center to the plant process area at the nuclear power plant. Provisions were made to mount the AA on vibration isolation pads, but it was found that these were not necessary since the unit was very stable.

One of the obvious concerns for the plant installation was protection from dust and dirt. Examination of the way the AA worked indicated that it had some built-in protection against airborne contamination because it was on line; therefore, the sample was protected. Also, there is a gas sweep through the furnace so that it will not aspirate contaminants like a flame AA, and the sample is handled by closed pump systems to reduce manual contamination. When we saw the sacks of cement stacked next to the installation area, however, this caused us some concern since we were trying to do parts-per-billion level analyses for calcium. The AA was, therefore, covered by a simple clear plastic box cover with sliding front doors. The box was kept closed all the time except when manual operations were needed.

Experience showed that the simple design was more than adequate for the job. Even when construction activities involving drilling of concrete were conducted in the same area, there was no noticeable effect on the instrument. Provisions had been made to ventilate the box and provide filtered makeup air, but it was never needed.

The box had one side benefit. The system was installed in a high-traffic area, and the control panels have many interesting buttons, lights, switches, and so on. Locking the front doors of the box kept curious people from interfering with the operation.

Operational Experience

The instrument functioned very well in the plant environment. Particularly useful was the ability to automatically change sample sizes, dilutions, furnace conditions, and sequencing with minor changes at the control panels. Ease of furnace change out, automatic data logging, and internal data processing was also very helpful. The on-line and autosampler portions of the system gave us virtually no problems. What problems did occur were in the electronics of the spectrophotometer itself.

The problems we had in operation were the following:

1. Periodic loss of memory of the wavelength-controlling motor. The energy would go to zero, so the absorbance readings would also be zero. Reprogramming the 5000 allowed us to circumvent the problem when it occurred, but the cause has never been found and the problem recurs.
2. The 5000 would occasionally start reading absorbances without a command from the 500 control unit. This would result in printouts through the heat-up and cool-down cycle, which would not allow the averaging of values to be done. The only solution found has been to shut the instrument down and restart it after 30 min to 1 h. This is also not always successful.
3. The most difficult problem has been an occasional tendency for the unit to invent its own programs. When it is programmed and started, rather than repeating the first program as specified, it will assign its own wavelengths, energy levels, and so on and begin analysis. Reprogramming usually solves the problem, but it still occasionally recurs.

Since the unit was installed in an operating area, service access to it was limited.

Impurity Analyses

The system performed far better from an analytical standpoint than we had expected. Initially, impurity levels were expected to be in the 10 to 50-ppb range, and we were to track the system cleanup as the impurities were removed. The analytical system was finally debugged and activated just before the plant was shut down for refueling, so a unique opportunity existed to track primary-loop chemistry from normal operation through cold shutdown. Analyses were run around the clock for a period of 5 days, and the results of the calcium analyses are shown in Fig. 6.

The primary-loop water was cleaner than earlier testing had indicated. Figure 6 shows that for the majority of the time calcium was below 1 ppb. These results are statistically valid, and, in addition, we can see peaks that have data points tracking up and down the curve, so our data are real. It should be noted that each data point shown is the average of three consecutive analyses. Also, for each point a furnace background, blank, and stand-

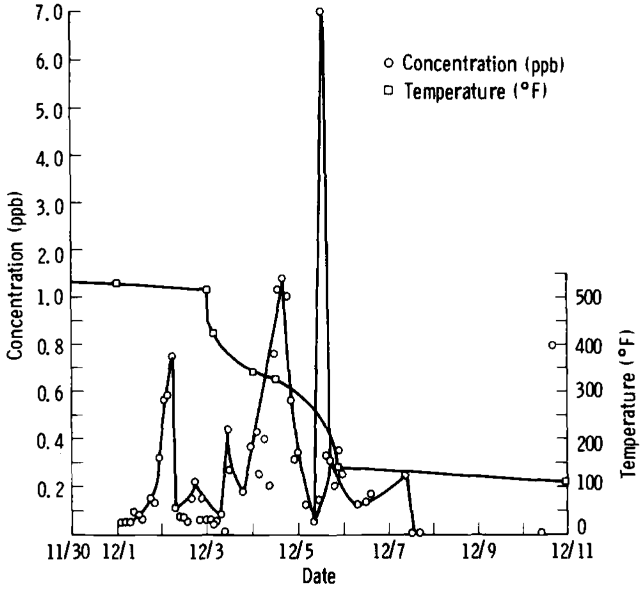

FIG. 6—*Shutdown monitoring of calcium concentration.*

ard were run to maintain a check on calibration. Statistical tests were applied to these data (as well as data collected for magnesium and aluminum) to verify that the analyses are significantly greater than zero. Some points have been checked through careful grab sampling and analysis by another laboratory, and the results are in good agreement.

Conclusions

Although flameless AA is a highly sensitive method of low-level analysis, it has been shown that with proper installation it is possible to conduct on-line analysis in a plant environment and without a trained spectroscopist. On-line analysis is an effective way to track trace materials in a sample stream with little danger of sample contamination.

If multielement capability is needed in a plant for trace levels of impurities, an installation of this type should be considered.

Acknowledgments

J. M. Otte, a laboratory technician in our group, must certainly be acknowledged for his large contributions in conducting the plant tests. Without his dedication and perserverance, the program would not have been nearly the success it was.

M. B. Theodore, C. L. Page, and Z. L. Kardos, all analysts at Westinghouse, deserve our heartfelt thanks for their assistance and guidance in the use of flameless methods and analytical techniques.

Last, but certainly not least, we would like to thank the Perkin-Elmer service staff for their close cooperation and support. One of the reasons we selected their instrument was the ready availability of service, and they have justified our choice by their excellent response.

S. A. Fisher[1]

Zero: The Unreachable Goal

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ABSTRACT: A review of the progress that has been made in improving the quality of high-purity water during the 40 plus years of existence of ASTM Committee D-19 on Water shows that the steps downward in impurity levels are impressive but the goal of zero impurities is still a long way off. We have reached the limits of the use of electrical conductivity as the sole monitor of further improvement in industrial water quality. If still lower impurity levels are sought, their precise nature must be elucidated, and they must be monitored as specific entities.

KEY WORDS: high-purity industrial water, water specifications, water quality, electrical conductivity of water, industrial water monitoring, power plants, instrumentation.

One of the advantages of age is that it provides perspective. Looking at where we have been and what we have accomplished over a span of years helps us to evaluate where we are. What I plan to address in this paper is what has been achieved during the lifetime of ASTM Committee D-19 on Water in extending our analytical capabilities toward zero impurities.

Many are involved in the development of complex instruments which are probing what are now considered the lower concentration levels of impurities in water. Others are concerned with the use of these instruments as safeguards for monitoring the purity of water produced. My purpose is to put our feet back on the ground in relation to reaching and measuring the ultimate dream—zero concentration. In doing so, I will share some of my concerns for the reality of numbers that are being reported. Further, I plan to take a look at the numerical requirements being set forth for water purity from a different and perhaps even startling viewpoint.

So, in brief, I will focus on three approaches to zero:

1. How much progress have we made in the production of pure water over the 40 plus years of ASTM Committee D-19 on Water's existence?
2. How close are we to zero now?
3. What general problems do we face in going beyond our present level?

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How Much Has the Purity of Reagent Water Increased in 40 Years?

It is interesting to consider philosophically that our ability to measure small quantities of impurities in water is linked directly to our ability to produce large quantities of water of sufficient purity that the measurement of sodium, chloride, and the like at low levels is a matter of commercial interest. I must point out, of course, that my remarks here are directed only toward high-purity water for industrial uses and do not include measurements advocated for hazard assessment in natural waters or waste streams.

The changes that have occurred in the ASTM Specifications for Reagent Water (D-1193) during the life of ASTM Committee D-19 directly parallel the development of our capabilities for producing ultrapure water on a commercial scale. Table 1 [*1–3*][2] shows the downward progression in the levels of impurities permitted in the highest grade reagent water during the lifetime of this committee. Current thinking at the task-group level goes even further. A proposed specification for electronics-grade reagent water recently balloted goes far beyond what we now have. In it, limits in the microgram-per-litre level are set for copper, sodium, zinc, and total silica. It should be made clear that this work is still at the development stage. Some of the proposed values are indeed below those of current proven analytical capabilities. Until that capability is fully developed, we cannot answer the question of whether we are able to make water of the desired quality in commercial quantities.

How Close Are We to Zero?

The goal both in the production of water for power generation, with which we are primarily concerned here, and in the electronics industry is to produce

TABLE 1—*Comparison of reagent water specifications over the years of ASTM Committee D-19, on water's existence.*

	Year		
	1951[a]	1966	1979
Reagent water type	referee	referee	type IA
Total matter, maximum, mg/litre	1	0.1	0.1
Electrical conductivity, maximum, μmho/cm at approximately 2.98 K (25°C)	1.5	0.1	0.06
Permanganate consumption, maximum, meq/litre in 60 min	0.006	0.004	0.004
Soluble silica, maximum[b]			
Total bacteria, maximum per millilitres			0

[a] See Refs *1*, *2*, and *3* for specifications for 1951, 1966, and 1979, respectively.

[b] Not detectable.

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

water with zero impurities. During the lifetime of this committee, as we see in Table 1, we have progressed from a discussion of methodology for impurities at the parts-per-million or milligrams-per-litre level, going through the parts-per-billion or micrograms-per-litre range, and are now concerned in some area with measurement capabilities at the parts-per-trillion or nanograms-per-litre level. The figure of 10^{-6} g per litre or 10^{-9} g per litre is an impressive one, and progress of this sort has been hailed by specifications writers in the industry. But just how far have we progressed on the road toward zero atoms per litre?

If you recall your basic general chemistry, the number of atoms in a gram atomic weight of any material is a fixed value known as Avogadro's number. In preparing this paper I went back and surveyed the progress that we have made in our certainty of the value of this number of atoms. As it happens, the first edition of Lange's *Handbook of Chemistry* was published in 1934, the year ASTM Committee D-19 was founded. Values for Avogadro's number at that time, at the time that I began my professional career, and those given in one of the latest editions of Lange's Handbook are shown in Table 2 [*4–6*]. It is interesting to contemplate the fact that the reliability of this fundamental constant has progressed at almost precisely the same rate as our ability to measure a common impurity such as sodium in water.

What Avogadro's constant tells us is that 23 g of sodium contain 6.02217×10^{23} sodium atoms. It is, therefore, instructive to look at our improved ability to produce and measure "low"-sodium water in terms of the number of sodium atoms that remain. This I have done in Table 3. We still have a long way to go to reach zero.

It is also, perhaps, instructive to consider reagent water specifications in terms of the actual possible number of residual ions that could remain in it.

TABLE 2—*Values for Avogadro's number from Lange's* Handbook of Chemistry.

Edition (Ref)	Year	Avogadro's Number
1 [4]	1934	$6.064 \pm 0.006 \times 10^{23}$
4 [5]	1941	$6.0227 \pm 0.0014 \times 10^{23}$
11 [6]	1973	$6.02217 \pm 0.00004 \times 10^{23}$

TABLE 3—*Sodium concentrations in atoms per litre.*

Concentration	Atoms per Litre
1 g/litre	2 619 500 000 000 000 000 000
1 mg/litre (1 ppm)	2 619 500 000 000 000 000
10 μg/litre (10 ppb)	26 195 000 000 000 000
1 μg/litre (1 ppb)	2 619 500 000 000 000
0.01 μg/litre (0.01 ppb)	26 195 000 000 000

One of the problems in doing this is that, for practical purposes, we rely almost entirely on a single parameter, electrical conductivity, for routine monitoring of the purity of the water produced in industrial quantities. True, reagent water specifications carry a limitation on total matter, but the determination of this is so arduous and frought with possibility for error that it is seldom, if ever, done on a routine basis.

But setting limits in terms of electrical conductivity carries with it great uncertainty since conductivity is a function of what ion or ions are present to conduct. It is well known, of course, that a strong electrolyte such as sodium hydroxide will, in general, produce a higher conductivity at a given molar concentration than a weak electrolyte such as ammonium hydroxide. At concentrations that are usually used to demonstrate this, this rule of thumb indeed holds.

In high-purity water, however, some quite surprising things happen. First of all, when we start talking of water in the range of a Type I reagent water with a conductivity of 0.06 μmho/cm, most of the current is carried by the H^+ and OH^- formed in the dissociation of water itself. At 25°C, a water with a zero concentration of impurities still has a conductivity of 0.0548 μmho/cm due to the hydrogen and hydroxide ions from the water itself. When we start adding hypothetical impurities to this very pure water, some very surprising things happen. Table 4 contains our best estimates of the amounts of different impurities that could be present in water that meets the conductivity specifications for Types I, II, and IV reagent waters.

Perhaps the most startling value is the high concentration of sodium hydroxide that could be present in a water with an electrical conductivity of 0.06 μmho/cm. The reason for this lies in the very large difference in the equivalent conductance of the sodium and hydrogen ions. When sodium hydroxide is added to pure water, in very small concentrations, the hydroxide ions react with the hydrogen ions of the water, shifting the water equilibrium. The net effect is the replacement of hydrogen ions with an equivalent conductance of 350 with sodium ions that have an equivalent conductance of

TABLE 4—*Amounts of various impurities possible in reagent water.*

	Reagent Water Type		
Impurities	I	II and III	IV
Electrical conductivity, maximum, μmho/cm	0.06	1.0	5.0
Possible impurities, ppm			
Carbon dioxide	0.001	0.7	16
Ammonia	?	0.08	0.9
Sodium hydroxide	0.0045	0.16	0.8
Hydrochloric acid	0.001	0.09	0.42
Sodium chloride	0.0023	0.42	2.3

only 50.9. Hence, water containing parts per billion of sodium hydroxide, and no other impurities, of course, should have an electrical conductivity less than that of pure water. We calculate a minimum at 0.8 ppb of 0.0546 μmho/cm, whereas the calculated value for pure water itself is 0.05483 μmho/cm.

Since these entities also have different gram atomic weights, the number of atoms in a milligram or microgram per litre also varies with the nature of the impurity. Table 5 gives the postulated number of atoms of various impurities that could be present in Type I and in Type II or Type III reagent water which meets the electrical conductivity specification. Pure water indeed looks less pure in these terms.

The Problems We Face

These numbers tell us one additional story. We have reached the levels in concentration where electrical conductivity alone is not a sufficiently reliable indication of water purity. We are now working in a range where the nature of the impurities, as shown in Table 4, makes a profound difference in the electrical conductivity measured. More serious is the fact that we have also reached the range at which the calibration of the cell-meter combination constitutes an as yet unsolved technical problem. And even more serious is the recalibration of instruments that are in service.

To split the hair that we are now contemplating in the range of 0.1 μmho/cm and below, we should be able to calibrate the instruments used in that range. Even if we extend our thinking to 1 μmho/cm we are talking about calibration solutions with a concentration of 0.4 mg/litre and less of sodium chloride. Start with a solution in the range where weighing is feasible and reliable and make serial dilutions, you may suggest. Where do you get

TABLE 5—*Possible atoms per litre in reagent water.*

	Reagent Water Type	
Impurities	I	II
Electrical conductivity, maximum, μmho/cm	0.06	1.0
Impurity		
Carbon dioxide	13 600 000 000 000 000	9 580 000 000 000 000 000
Ammonia		283 000 000 000 000 000
Sodium hydroxide as sodium	49 400 000 000 000 000	1 750 000 000 000 000 000
Hydrochloric acid as chloride	16 500 000 000 000 000	1 480 000 000 000 000 000
Sodium chloride		
chloride	23 600 000 000 000 000	4 320 000 000 000 000 000
sodium	23 600 000 000 000 000	4 320 000 000 000 000 000

the absolutely pure water to make those serial dilutions, and how do you determine that it is absolutely pure? Further, how do you work in an in-plant monitoring system to exclude carbon dioxide? Is it even possible to isolate the cell from the system that it is measuring in such a fashion that a calibration solution could be pumped through it? Remember, it is not just the cell that must be calibrated in modern conductivity systems but the combination of that cell and its meter. Put a series of cells and meters in the same line (we know of one system that has 17), and you will find that there is more variation from meter to meter than in the differences produced by the impurities we are discussing.

This means, of course, that we must look for specific impurities in the water if we wish to go beyond the present limits or even produce water at the present limits with a high degree of certainty. The trend has been in that direction in recent years. However, first we must agree upon what impurities we will look for. More and more systems are augmenting their electrical conductivity monitoring systems with silica and sodium monitors. This reflects the fact that the deposits and corrosion in the steam generators have made us aware that these two impurities are sources of problems in industrial water used for power generation. In the future, we will undoubtedly see more in-line monitoring systems for additional water impurities such as sulfate, chloride, and carbon dioxide. But before we go forward with them, it behooves us to take a look at how reliable the systems now in existence are.

Let us consider the problems in continuous monitoring of silica as an illustration. Silica monitors are probably the most common instrumentation presently supporting electrical conductivity monitors in power plants. First of all, much time has been spent arguing the question of specifically what the molybdenum-blue reaction, which is the basis of these monitors, actually measures. I do not believe there is currently any doubt that this method does not measure total silica. Few analytical chemists these days have the classical training that would have led them to read the extensive work of Hildebrand and Lundell of the National Bureau of Standards [7]. Had they done so, their appreciation of the complexity of the problems of putting silica into solution for analysis would be enhanced.

Let us assume, just for the purpose of discussion, that the ASTM Tests for Silica in Water and Waste Water [D 859-68 (1974)] on which the monitoring methods are based, does measure all of the silica in the water. And let us further assume that the precision that has been determined for the laboratory method holds for the method as run in monitoring equipment. The ASTM test states that the single-operator precision $S_o = 0.005x + 0.07$, where x is the concentration of silica in parts per billion. Now if we consider the true value in a water to be 10 ppb, this precision means that in two out of three cases the analyst will get a number between 9.25 and 10.75 ppb. The third value may be outside of this range. Or, to put it another way, the variation at 10 ppb is ±7.5 percent. If we move down to the 1 ppb value, which incidentally was considered by the writers of the silica test to be below the limit of detection in a 10-cm cell, our variation grows to ±70.5 percent, with a confidence level of only 65 percent.

Now, of course, these instruments also have to be standardized. Theoretically, we require a zero-silica water to set the zero on the instrument itself. Lacking this—and how would we know we had it if we did—all of the measurements become 1 ppb ± 70.5 percent plus some unknown factor, y, which is the amount of silica in the water that was used as a zero point in the instrument calibration.

Considering all of these problems, what reality can there be in a specification for silica at the 0.1 ppb level? How many of the measurements that we have seen published in recent years in the parts-per-billion level are in actuality 1 or 2 ppb above the base level of the best water that the plant is able to produce. Many times when I have gone into operating plants where standard silica solutions are supplied to the stations for routine calibration of the monitoring instruments, I have found that the condensate being monitored was used as the dilution water. Such monitoring does indicate when things are not going as well as they usually do, but it gives no indication of the real concentration in the condensate being returned to the system.

Comments pertaining to silica analysis apply equally to the analysis of sodium and other entities at low levels. We have, unfortunately, a chicken-and-egg situation in which the limits of our capability of measuring at these levels control the certainty with which we are able to prepare standards to calibrate the instruments used. Type I reagent water, as we have seen, is not good enough for this purpose. If we are to go to still lower levels than we now measure, reagent waters for specific purposes with special purification techniques to remove the specific impurities will be required.

Conclusions

As we have seen, we are still a long way from zero. As high as the standards are for our present reagent water, its purity still cannot be monitored with sufficient precision to guarantee us a source of water for the preparation of standards in the region where we now seek to measure impurities in industrial water. It is quite clear that if we are to go further in our requirements for water purity on a large scale, the electrical conductivity measurements must be augmented by the measurement of specific impurities. Hand in hand with this, however, will go the need for the preparation of special grades of reagent water to be used for specific analytical procedures. Without this additional development, putting down numbers in the parts-per-billion and less range as limits for water purity will remain a meaningless activity.

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Resistivity of Very Pure Water and Its Maximum Value

REFERENCE: Light, T. S. and Sawyer, P. B., "**Resistivity of Very Pure Water and Its Maximum Value,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 175–184.

ABSTRACT: Theoretical calculations have been made for the resistivity (and its reciprocal, the conductivity) of pure water in the vicinity of the neutral point at 25°C. A surprising result is that the maximum resistivity is not found at pH 6.998, which corresponds to absolute water, but at pH 7.039, which corresponds to water with approximately 0.8 μg/litre, (parts per billion) of sodium hydroxide added. The resistivities corresponding to these two points are 18.18 and 18.28 M$\Omega \cdot$cm respectively. Although the effect is slight, it will be of interest to users of high-purity water since resistivity is widely used as a criterion for water purity. The temperature coefficient of resistivity is also evaluated.

KEY WORDS: resistivity, power plants, conductivity, water, temperature coefficient, instrumentation, water quality

Resistivity, or its reciprocal, conductivity, is widely used as a criterion for the purity of water. Very pure water, for purposes of this paper, may be defined as water with a resistivity approaching that calculated for theoretically pure water; impurities present would be in the micrograms-per-kilogram (parts-per-billion) range. In recent years, this quality of water has become increasingly important in several advanced technology fields. In the power industry [*1*],[3] the susceptibility of steam turbines and their blades to costly corrosion damage makes the detection of composition impurities in water a necessity. The demands for pure water in the water coolant circuits of nuclear reactors are very stringent [*2*]. The production of solid-state devices requires extraordinary control of impurities and entails final washes of surfaces with very pure water [*3*]. In ultratrace analysis for heavy metals and other chemicals, the use of very pure water is required [*4*].

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

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The measurement of resistivity of water is considered to be a useful, simple, and reliable method for determining the presence of ionic impurities. ASTM Standards deal with the conductivity and resistivity of water and standard specifications for reagent water [ASTM Tests for Electrical Conductivity and Resistivity of Water (D 1125-77) and ASTM Specification for Reagent Water, (D 1193-77)]. It has been believed that the maximum resistivity of water, at a given temperature, will correspond to the maximum purity in the water. However, it is the purpose of this paper to point out that this maximum resistivity does not coincide with pure water but is displaced slightly on the alkaline side. Values for the resistivity of pure water over moderate temperature ranges have been given by Iverson [*5*] and Otten [*6*]. The present paper recalculates these values over the range of 0 to 100°C based on primary data and further predicts the maximum resistivities that might be expected in slightly impure alkaline water. The temperature coefficient of water resistivity is discussed.

Theoretical

The ionization or dissociation constant of water, K_w, at any given temperature, is expressed by the equation

$$[H^+]\,[OH^-] = K_w \tag{1}$$

where the brackets, [ ], symbolize the activities of the ions. In the very dilute solutions being considered in this paper, activity is taken to be synonomous with concentration, expressed either in molarity or molality units.

From Eq 1, two other useful notations may be derived; pK_w is defined as

$$pK_w = -\log K_w \tag{1a}$$

and the definition of a neutral solution, that is, one in which the $[H^+] = [OH^-]$, is

$$[H^+]_{neut} = (K_w)^{1/2} \tag{1b}$$

from which it follows

$$\mathrm{pH}_{neut} = -\log[H^+]_{neut} = (1/2)(pK_w) \tag{1c}$$

Resistivity readings are generally used to characterize high-purity water, but the data from which resistivity may be computed are expressed in terms of conductivity. The resistivity, or specific resistance, ρ, is expressed in units of ohm centimetres. Its reciprocal, conductivity (or specific conductance), κ, has long been expressed in the units mho per centimetre. In SI units, where the unit of conductance has been changed from the mho to the siemens (S), conductivity becomes siemens per centimetre. Both resistivity and conductivity are functions of the temperature, T. The relationship between resistivity and conductivity is defined as

$$\rho_T = \frac{1}{\kappa_T} \qquad (2)$$

The conductivity of pure water may be calculated from the limiting equivalent conductances of its hydrogen and hydroxide ions at temperature T, λ_T°, which have the units 10^6 S·cm^2·equivalent^{-1}

$$\kappa_T = 10^{-3}\,[\lambda_T^{\circ H^+}\,[H^+] + \lambda_T^{\circ OH^-}\,[OH^-]] \text{ pure water} \qquad (3)$$

The values of the constants K_w, $\lambda_{25°}^{\circ H^+}$, and $\lambda_{25°}^{\circ OH^-}$ at the reference temperature of 25°C have been studied by Harned and Owen [*7*]. Other values have been reported in the literature [*5,6,8,9*]. However, the values of Harned and Owen represent a critical compilation of numerous studies and apparently are the most accurate. Table 1 summarizes these values along with the resistivity and conductivity calculated from Eqs 2 and 3 and compares them with the Iverson [*5*] and Otten [*6*] results.

For water which is made slightly impure by the addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH), Eq 3 may be expanded to

$$\kappa_T = 10^{-3}\,[\lambda_T^{\circ H^+}\,[H^+] + \lambda_T^{\circ OH^-}\,[OH^-] + \lambda_T^{\circ Cl^-}\,[Cl^-]] \qquad (3a)$$

for acid (HCl) solutions and to

$$\kappa_T = 10^{-3}\,[\lambda_T^{\circ H^+}\,[H^+] + \lambda_T^{\circ OH^-}\,[OH^-] + \lambda_T^{\circ Na^+}\,[Na^+]] \qquad (3b)$$

for alkaline (NaOH) solutions.

Inspection of Eqs 3, 3*a*, and 3*b* yields an interesting observation. The conductivity of water would be expected to increase upon addition of some typical impurity. However, if the impurity is the hydroxide ion, with the associated cation, then initially the increased conductivity due to the hydroxide ion and cation is less than the loss due to the hydrogen ion. This observation can also be determined from Table 1 because the acid hydrogen ion is nearly twice as mobile as the hydroxyl ion and seven times as mobile as the sodium

TABLE 1—*Literature values of certain physical chemical constants at 25°C, calculated values of pure water conductivity and resistivity, and comparison with some literature values.*

Parameter	Value	Reference
pK_w	13.9965	[*7*]
$pH_{neut} = ½\, pK_w$	6.998	calculated, Eq 1*c*
$\lambda^{\circ H^+}$ 25°	349.8 10^6 S·cm^2·equivalent	[*7*]
$\lambda^{\circ OH^-}$ 25°	197.8 10^6 S·cm^2·equivalent	[*7*]
$\kappa_{25°}$ pure water	0.0550 μS/cm	calculated Eq 3
$\rho_{25°}$ pure water	18.18 MΩ·cm	calculated Eq 2
$\rho_{25°}$ pure water	18.24 MΩ·cm	[*5,6*]

ion. Therefore, if a small amount of sodium hydroxide is added to pure water, the net conductance decreases (that is, the resistivity increases). On continued addition of sodium hydroxide, the conductance will decrease to a minimum level and then increase.

This conductivity minimum, which occurs on the alkaline side, can be predicted quantitatively by differentiating Eq *3b* with respect to hydroxide ion concentration and setting it equal to zero to find the minimum

$$\frac{d\kappa_T}{d[\mathrm{OH}^-]} = 0 \text{ for minimum conductivity} \tag{4}$$

and combining this with Eq 1 and the charge conservation equation

$$[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{OH}^-] \tag{5}$$

gives the equation for calculating the hydroxide ion concentration at the conductivity minimum, $[\mathrm{OH}^-]_{\min}$

$$[\mathrm{OH}^-]_{\min} = \left\{\frac{\lambda_T{}^{\circ\mathrm{H}^+} - \lambda_T{}^{\circ\mathrm{Na}^+}}{\lambda_T{}^{\circ\mathrm{OH}^-} + \lambda_T{}^{\circ\mathrm{Na}^+}} K_{w_T}\right\}^{1/2} \tag{6}$$

Knowledge of the hydroxide ion concentration at the conductivity minimum allows calculation of the conductivity minimum and resistivity maximum.

In order to perform these calculations, it is necessary to have numerical values for the water ionization constant and the ionic equivalent conductances over the range of 0 to 100°C. Again using the compilation given by Harned and Owen [*7*], Table 2 [*10,11*] lists the data selected for this paper.

The values for the water dissociation constant, K_w, have been critically examined since the work of Harned and Owen [*7*], by Iverson [*5*], by Clever [*8*], and by Marshall and Franck [*9*]. Table 3 compares some of these literature values for K_w. The minor differences suggest that resistivity and conductivity values for pure water may be calculated to four significant figures at 25°C, but reliability decreases to two significant figures as the temperature approaches 100°C. Although values for K_w are reported as high as 1000°C and 10^9Pa (10 000 bars) [*9*], the lack of data for equivalent conductance seriously limits the ability to predict water resistivity above 100°C. The best data for the limiting equivalent conductance of OH^- appears to be available only up to 55°C [*5*] and the Table 2 data have been extrapolated to 100°C.

Resistivity of Pure Water

Using the data of Table 2 and Eq 3, the resistivity of pure water may be calculated over the range of 0 to 100°C. Table 4 presents the properties of pure water—its pH, conductivity, and resistivity—and compares the resistivity with the data of Iverson [*5*] and of Otten [*6*]. The present calculations of resistivity are based on a critical selection from the available data and agree

TABLE 2—*Values of equivalent conductance and water ionization constants used in calculations of resistivity of very pure and slightly impure water.*

Temperature, °C	$\lambda^{\circ H^+}$[a]	$\lambda^{\circ OH^-}$[a]	$\lambda^{\circ Na^+}$[a]	$\lambda^{\circ Cl^-}$[a]	K_w, × 10^{14}	pK_w
0	224.2	127.8	25.99		0.1139	14.9435
5	250.0	141.8	30.30		0.1846	14.7338
10	275.5	156.2	34.88		0.2920	14.5346
15	300.7	170.3	39.72		0.4505	14.3463
20	325.5	184.4	44.81		0.6809	14.1669
25	349.8	197.8	50.20[b]	76.39[b]	1.008	13.9965
30	373.7	211.6	55.72		1.469	13.8330
35	396.9	224.5	61.53		2.089	13.6801
40	419.5	237.2	67.55		2.919	13.5348
45	441.4	249.5	73.78		4.018	13.3960
50	462.6	261.4	80.21		5.474	13.2617
55	483.0	272.9	86.83		7.297	13.1369
60	502.5	284.2	93.64		9.614	13.0171
65	521.1	295.4	100.6		12.51	12.9027
70	538.7	306.1	107.8		16.04	12.7948
75	555.3	316.7	115.1		20.31	12.6924
80	570.8	326.7	122.5		25.41	12.5950
85	585.1	336.7	130.1		31.43	12.5027
90	598.3	346.1	137.8		38.46	12.4150
95	610.1	355.5	145.7		46.58	12.3318
100	620.7	364.9	153.7		55.86	12.2529

[a] 10^6 S·cm²/equivalent.

[b] Refs 10 and 11.

well with the other calculated values to within the expected reliability of the numbers. It is of interest to note in Table 4 the great effect of temperature. At the reference temperature of 25°C, the pH of 6.998 and resistivity of 18.18 MΩ·cm are fairly well identified constants. However, it should be noted that over the temperature range of 0 to 100°C, the pH of pure water varies from 7.5 to 6.1, whereas the resistivity may be as high as 84 MΩ·cm and as low as 1.4 MΩ·cm.

TABLE 3—*Values of water ionization constant,* pK$_w$, *from different sources.*

Temperature, °C	Harned and Owen [7]	Iverson [5]	Clever [8]	Marshall and Franck [9]
0	14.9435		14.950	14.938
25	13.9965	13.99654	13.998	13.995
50	13.2617	13.26154	13.262	13.275
75	12.6924	...	12.70	12.712
100	12.2529	...	12.27	12.265

TABLE 4—*Theoretical conductivity, resistivity, and pH of pure water as a function of temperature.*

Temperature, °C	pH	Conductivity, μS/cm	Resistivity, MΩ·cm	Iverson [5] Resistivity, MΩ·cm	Otten [6] Resistivity, MΩ·cm
0	7.472	0.0119	84.18		86.00
5	7.367	0.0168	59.40	58.91	59.99
10	7.267	0.0233	42.86		43.31
15	7.173	0.0316	31.63	31.77	31.87
20	7.084	0.0421	23.77		23.92
25	6.998	0.0550	18.18	18.24	18.24
30	6.917	0.0709	14.10		14.00
35	6.840	0.0898	11.13	11.20	11.08
40	6.767	0.112	8.91		8.82
45	6.698	0.139	7.22	7.29	7.11
50	6.631	0.169	5.90		5.77
55	6.568	0.204	4.90	4.97	4.75
60	6.509	0.244	4.10		3.97
65	6.451	0.289	3.46		3.32
70	6.397	0.338	2.96		2.89
75	6.346	0.393	2.55		2.45
80	6.298	0.452	2.21		2.14
85	6.251	0.517	1.94		1.87
90	6.208	0.586	1.71		1.66
95	6.166	0.659	1.52		1.45
100	6.127	0.737	1.36		1.27

Maximum Resistivity of Water

Using Eq 6 to calculate the hydroxide ion concentration at which minimum conductivity occurs and substituting in the preceding equations, the maximum resistivity of a water solution may be calculated. Table 5 summarizes the results over the temperature range of 0 to 65°C. Calculations at higher temperatures are not feasible because of the lack of sufficiently accurate data for equivalent conductance of the hydroxide ion. At the reference temperature of 25°C, it can be noted that the resistivity has shifted from 18.18 for pure water of pH 6.998 to 18.28 MΩ · cm for water made alkaline to pH 7.039 by addition of 0.76 ug/kg (parts per billion) of sodium hydroxide. Figure 1 shows the relationship between resistivity and pH at the reference temperature of 25°C. For other temperatures, the shift is of similar small magnitude but significantly measurable by modern pH meters and resistivity monitors.

Temperature Coefficient

This value is of interest to users of resistivity measuring equipment, since instrument readings are usually normalized to 25°C. The parameter is ex-

TABLE 5—*Maximum resistivity and associated parameters of water as a function of temperature.*

			Corresponding	
Temperature, °C	Minimum Conductivity, μS/cm	Maximum Resistivity, MΩ·cm	pH	Concentration of NaOH, μg/litre
0	0.0118	84.9	7.53	0.86
5	0.0167	59.9	7.42	0.42
10	0.0232	43.2	7.32	0.50
15	0.0314	31.8	7.22	0.58
20	0.0419	23.9	7.13	0.67
25	0.0547	18.28	7.039	0.76
30	0.0707	14.2	6.95	0.84
35	0.0895	11.2	6.87	0.92
40	0.112	8.94	6.80	0.98
45	0.138	7.24	6.73	1.03
50	0.169	5.91	6.66	1.06
55	0.204	4.90	6.59	1.04
60	0.244	4.10	6.53	0.98
65	0.289	3.46	6.46	0.85

pressed as a proportional temperature coefficient, α_T, in units of percent change per degree Celsius

$$\alpha_T = \frac{(d\rho/dT)_T}{\rho_T} \times 100 \tag{7}$$

Over small increments the temperature coefficient can be determined by a linear approximation. For example, between 20 and 30°C

$$\alpha_{25} = \frac{\rho_{30} - \rho_{20}}{10\rho_{25}} \times 100 = 5.32 \text{ percent/°C} \tag{8}$$

A better fit to the overall resistivity curve can be obtained from the formula commonly used in thermistor technology

$$\rho_T = ke^{\beta/T} \tag{9}$$

where

ρ_T = resistivity at absolute temperature, T,
k = proportionality constant in units of MΩ·cm,
e = 2.71828,
β = constant related to slope in temperature units, Kelvin, and
T = absolute temperature, Kelvin.

Equation 9 has the advantage that it can be readily differentiated to give the temperature coefficient

$$\alpha_T = -(\beta/T^2) \times 100 \text{ percent} \tag{10}$$

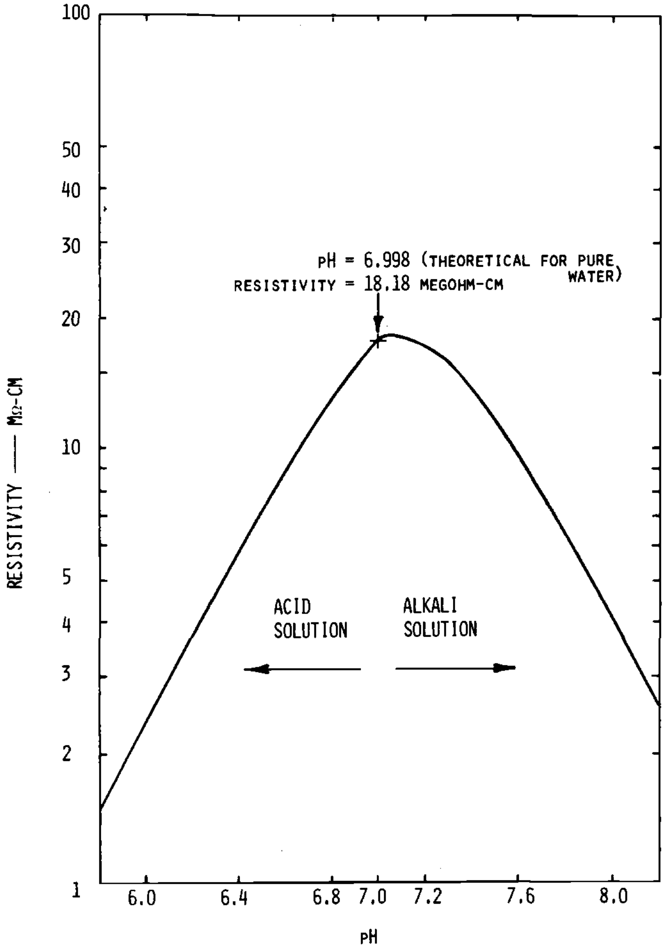

FIG. 1—*Variation of resistivity of water with pH around 7.0. (Additions of very small amounts of HCl and NaOH are made at 25°C.)*

and a true slope can be obtained at any desired point. Table 6 gives the values of the temperature coefficient, α_T, calculated from Eq 10 and the data in Table 5. Thus, a better value than $\alpha_{25} = -5.32$ percent per degree Celsius from the linear approximation of Eq 8 is $\alpha_{25} = -5.22$ percent per degree Celsius from Eq 10 using the values for the constants $k = 3.164 \times 10^{-6}$ $M\Omega \cdot cm$ and $\beta = 4641$ K, both derived over the range of 20 to 30°C. Because of the nonlinearity of the resistivity curve, as shown in Fig. 2, any use of the temperature coefficient values of Table 6 is subject to increasing errors for wider excursions of temperature, that is, each value of α_T is useful over a limited temperature interval.

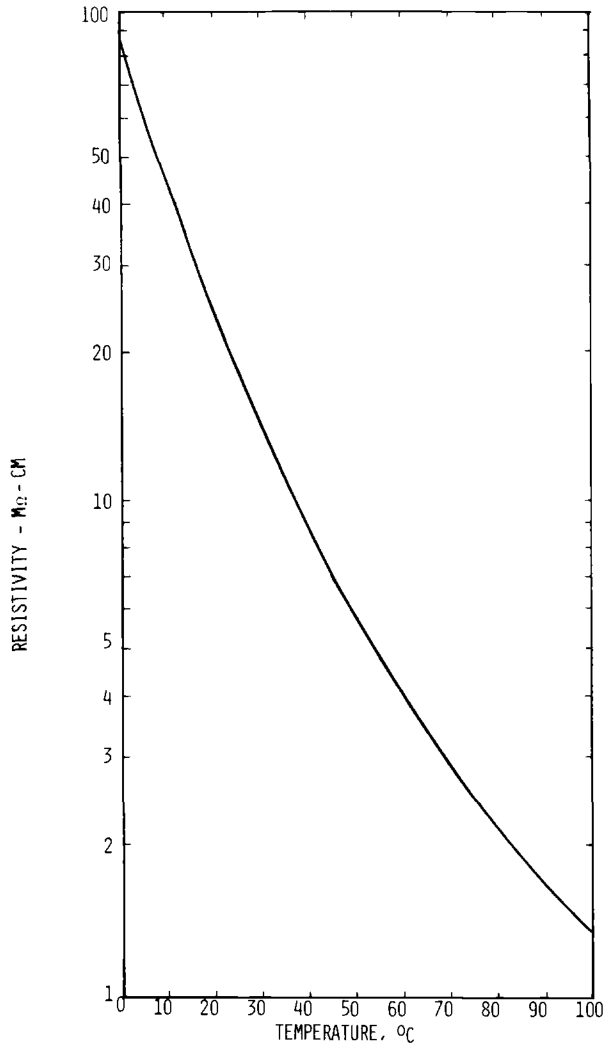

FIG. 2—*Resistivity of absolute water versus temperature.*

Conclusions

The measurement of the resistivity of very pure water remains as the simplest and most reliable method of determining its overall purity. A minor error in interpreting the purity of water may be made if the maximum resistivity is interpreted to coincide with maximum purity. The maximum resistivity actually occurs in the slightly alkaline region. The more likely source of error in interpreting water purity lies in the large temperature coefficient of resistivity. Measurements must be either carefully temperature compensated or made at a reference temperature.

TABLE 6—*Temperature coefficient of resistivity of pure water.*

Temperature, °C	α_T, % change per °C
0	−7.10
5	−6.75
10	−6.30
15	−5.89
20	−5.53
25	−5.22
30	−4.91
35	−4.59
40	−4.33
45	−4.12
50	−3.88
55	−3.64
60	−3.48
65	−3.26
70	−3.05
75	−2.92
80	−2.73
85	−2.56
90	−2.44
95	−2.29
100	−2.19

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Continuous Conductivity Monitoring of Anions in High-Purity Water

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REFERENCE: Lane, R. W., Sollo, F. W., and Neff, C. H., "**Continuous Conductivity Monitoring of Anions in High-Purity Water,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 185–195.

ABSTRACT: This paper describes the continuous and accurate monitoring of electrical conductivity of anions in feedwater and turbine condensate by two new instruments, a Feedwater Analyzer and a Condensate Reboiler. As has been pointed out, the advantages of this testing technique are that carbon dioxide and ammonia interferences are eliminated, the conductivity is measured at constant temperature, and increased sensitivity to anions is attained by measuring the conductivity of anions in the acidic and more conductive form. Design changes in this equipment have made possible more accurate conductivity measurement in the range of 0.01 to 0.1 S/cm at atmospheric boiling water temperature. This results in increased sensitivity of measurement, so that 1 to 5 ppb of $Cl^- + SO_4^=$ can be determined.

An advantage is shown in that low levels of 0.01 to 0.05 mg/litre of carbon dioxide (CO_2) have a lower conductivity at atmospheric boiling temperature than at room temperature (25°C). More accurate cation conductivity results may therefore be expected by measurement at atmospheric boiling water temperature than by degassing with nitrogen.

By including pH measurements along with conductivity and temperature measurements at room temperature, it is shown that ammonia and carbon dioxide of this two-component system may be calculated. Calculated ammonia and carbon dioxide results are shown not to be appreciably affected by the presence of 10 ppb chloride or more. The presence of 100 ppb total organic carbon (TOC) (as acetic acid) in steam condensate is also shown to have a negligible effect on the calculated ammonia and carbon dioxide results above 3 to 4 μS/cm.

KEY WORDS: feedwater analysis, condensate analysis, newly designed instruments, improved cation conductivity accuracy, ammonia, carbon dioxide, pH, conductivity, temperature, power plants, instrumentation, water quality

Steam purity of <5 μg/litre (ppb) chloride, sulfate, and sodium is being specified for steam to be used in large utility turbines. These limits have largely been based on (1) the finding of turbine deposits composed of these

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constituents and others [*1*][2] and (2) the occurrences of stress-corrosion cracking and corrosion fatigue of turbine blades and parts, which is apparently caused by these deposits and concentrations of these impurities. Since emphasis has therefore been placed on the continuous monitoring of steam impurities, this presentation will deal mainly with instruments [*2,3*] that have been developed for accurate and reliable measurement of the anions (Cl^- plus $SO_4^=$) by electrical conductivity.

Sampling and analysis of feedwater before it reaches the boiler offers the advantage of not requiring additional heat to attain analysis at atmospheric boiling water temperature. Operating the Feedwater Analyzer[3] (Fig. 1) at this temperature eliminates the interferences of amines, carbon dioxide, and

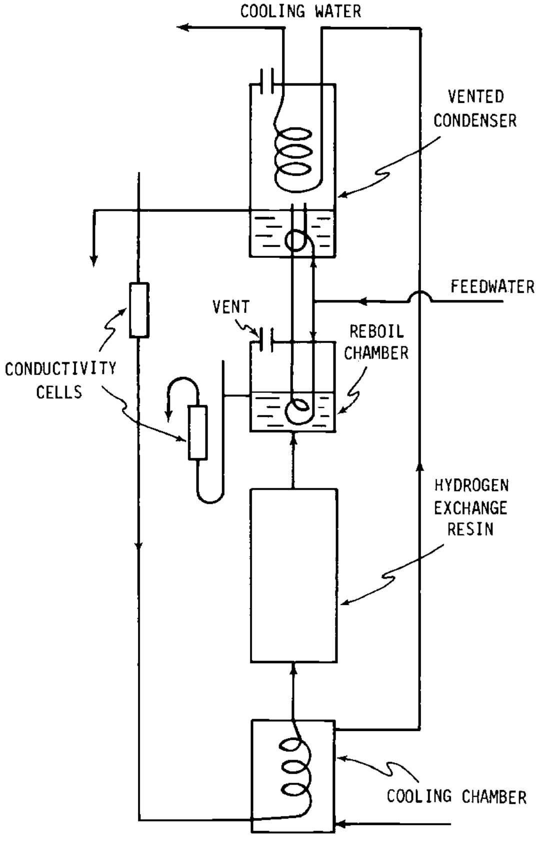

FIG. 1—*Feedwater Analyzer.*

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

[3] Instrument manufactured by Beckman Instruments, Inc., Cedar Grove Operation, Cedar Grove, N. J. 07009.

temperature variation in the determination of electrical conductivity, which is a measure of ionic contaminants. By analyzing the feedwater, evidence of the steam purity produced by once-through boilers can be more simply attained. There is no place to sample saturated steam from these boilers, and sampling the superheated steam effluent requires a complex sampling method in which moisture is introduced into a specially designed sampling nozzle. This technique [4] is necessary to prevent impurities in the superheated steam from depositing in the sampling line as the steam cools. This causes inaccurate and low results, which are not indicative of the purity of the steam being produced.

The Condensate-Reboiler Analyzer[3] (Fig. 2), however, may probably be used more effectively to analyze cooled feedwater, condensate from the condenser, and condensate polisher effluent, samples of which are now often piped to the central laboratory. This analyzer may prove easier to install and maintain since a high-temperature-pressurized system six or eight floors up, required for the Feedwater Analyzer, has the disadvantages of being located in an area where its maintenance may not receive adequate attention and of requiring long sampling lines which may prove impractical. Other alternatives, however, are being considered in order to improve the usefulness of this instrument.

The Feedwater Analyzer, which has previously been described [1,2], is similar in design to the former Steam Purity Analyzer [5] with the exception

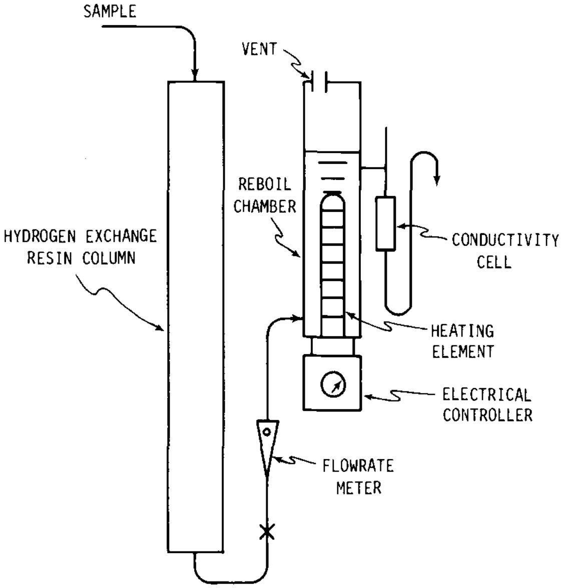

FIG. 2—*Electric Reboiler-Feedwater Analyzer.*

that feedwater rather than steam is tested, and feedwater is used to provide the heat for reboiling.

In the Condensate-Reboiler Analyzer, the cooled sample passes first over a conductivity cell to obtain the specific conductivity, and then through a magnetic-type flow cell, which has been installed to shut off the electric heater in case of flow stoppage. The flow next passes through a hydrogen exchanger to remove amines, a thermometer, and another conductivity cell. This cell serves to warn the user that a fresh charge of resin is required when the two cells read similarly. The water then passes through an electric heater, to heat the water to atmospheric boiling temperature, and finally through another conductivity cell.

From the recorded conductivity value of this cell at 98.5°C the chloride concentration in the range of 1 to 20 μg/litre may be calculated from the following equation

$$\mu\text{g/litre Cl}^- = 105.1 - 84.8°\text{C} + 351.6 \log°\text{C} \qquad (1)$$

The following data show the relationship between micrograms per litre of Cl^- and conductivity in microsiemens per centimetre, assuming sulfate and acetate are not present in significant quantities.

μg Cl^-/litre	μS/cm	μg Cl^-/litre	μS/cm
0.00	0.77	12	0.89
1	0.78	13	0.91
2	0.79	14	0.92
3	0.80	15	0.93
4	0.81	16	0.94
5	0.82	17	0.96
6	0.83	18	0.97
7	0.84	19	0.98
8	0.85	20	1.00
9	0.86	21	1.01
10	0.87	22	1.02
11	0.88	23	1.04

Proof of the accurate measurement of anion conductivity in the low Cl^- range is shown in Fig. 3, which discloses good agreement between the theoretical Cl^- and the Cl^- ion applied as Sodium Chloride (NaCl) to the Condensate-Reboiler influent. Similar good agreement with both Cl^- and $SO_4^=$ was shown in tests conducted in the Feedwater Analyzer in previous publications [*2,3*]. It should also be noted in Fig. 3 that there is good agreement between the theoretical and actual measurement of conductivity of pure water when no contaminants were being added.

Although other more complicated methods may measure the individual anions, as Cl^- or $SO_4^=$, it should be recognized that a continuous and simpler

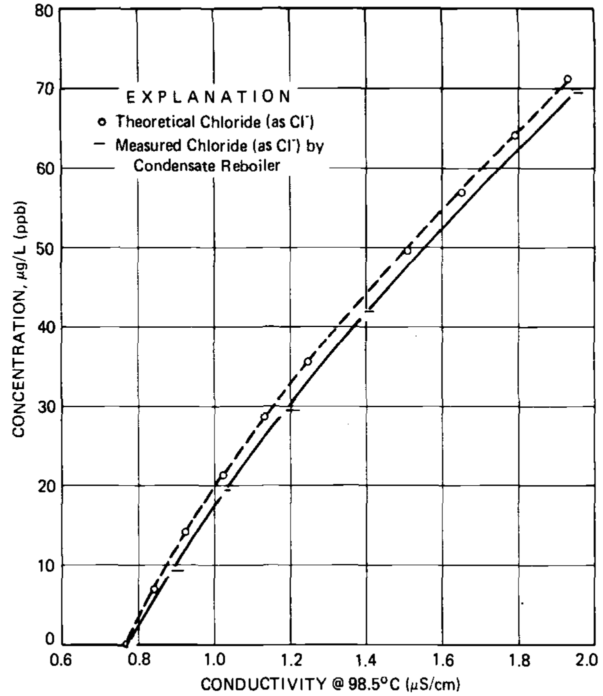

FIG. 3—*Conductivity of chloride ion (in acid form).*

technique of measuring the total anions yields the information desired. ***Are ionic contaminants entering the system and to what extent?*** These contaminants may be from a cooling water leak into the condenser, from improper operation or malfunction of a condensate polisher or deionizer, from the addition of impure or improper chemical treatment, or from other sources. Whether the ionic contaminant is chloride, sulfate, or some other anion may be of little consequence, however, the monitoring provided by continuous measurement provides the information to show the need for corrective action if necessary.

The cation conductivity technique has proven to be a valuable tool to detect ionic contaminants; however, carbon dioxide and variations in temperature, flow rate, and quantity of resin [*6*] can cause high blank values, which reduce the sensitivity to the measurement of low levels of $Cl^- + SO_4^=$ ions. Carbon dioxide removal by bubbling nitrogen [*7*] through the hydrogen exchanger effluent has been used relatively successfully, but the carbon dioxide removal is not complete (∝95 percent) and the nitrogen cost is high. Referring to Fig. 4, it will be noted that as little as 0.01 to 0.05 mg/litre carbon dioxide will provide a difference of 0.09 to 0.2 µS/cm in conductivity at 25°C. Referring to Fig. 5, it will be noted that 0.05 mg/litre of carbon dioxide, if

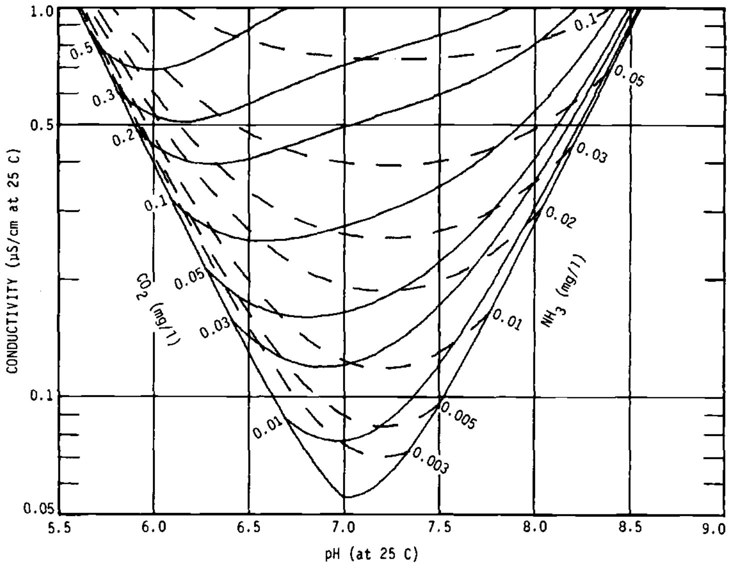

FIG. 4—*Conductivity and pH relationship of ammonia and carbon dioxide at 25°C (0.05 to 1.0 µS/cm).*

present, at boiling water temperature will provide a conductivity increase of less than 0.08 µS/cm, and it is unlikely that even these low quantities of carbon dioxide will be present at boiling water temperature. The theoretical and standardization curves shown in Fig. 3 verify that the conductivity of pure water was being obtained in the Condensate-Reboiler effluent.

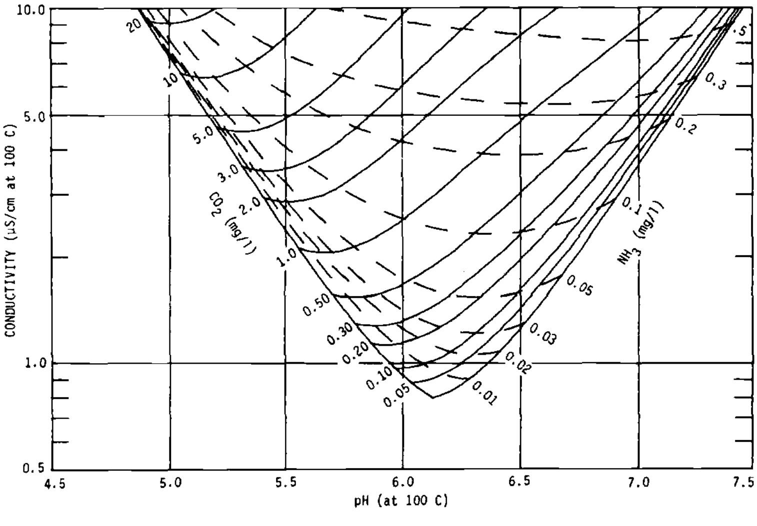

FIG. 5—*Conductivity and pH relationship of ammonia and carbon dioxide at 100°C.*

Examples of the Condensate-Reboiler application in plant operation are now presented. In one plant a brief increase in conductivity from 0.77 μS/cm (pure water at atmospheric boiling) to 1.03 μS/cm [equivalent to ∝22 ppb (μg/litre) Cl^-] was observed when a condensate polisher was put into service without adequate rinsing to the hot well. At another time, a similar increase in conductivity was observed when ammonia treatment containing impurities was introduced into the system. Although obtaining results in absolute values is preferred, deviations from a norm may be equally informative in providing monitoring information, which is indicative of satisfactory operation or the need for corrective action.

A recent investigation has shown that carbon dioxide may be obtained by calculation of the difference in conductivity between the inlet and outlet of the Condensate-Reboiler.

In a pure water system, as maintained in these plants, it is important to know all the constituents and their concentration in order to control corrosion and reduce the quantity of corrosion products, which may collect in various critical areas of the system. Ammonia concentrations of ∝1 mg/litre (ppm) are maintained to keep the pH at about 9.0 to inhibit corrosion. If carbon dioxide or air inleakage is derived from (1) leakage at the low-pressure end of the turbine, (2) raw water leakage into the condenser tubing, or (3) inleakage at pumps, this will reduce the pH, require increased ammonia addition, increase the conductivity (corrosion potential) in the system, re-

TABLE 1—*Carbon dioxide and ammonia in pure water at 25°C as related to pH and conductivity.*[a]

pH	8.80		8.90		9.00	
Conductivity	CO_2	NH_3	CO_2	NH_3	CO_2	NH_3
7.0	1.89	1.17	1.72	1.19	1.50	1.22
7.2	1.97	1.21	1.79	1.23	1.57	1.26
7.4	2.04	1.25	1.86	1.28	1.64	1.30
7.6	2.11	1.28	1.93	1.32	1.71	1.35
7.8	2.18	1.32	2.00	1.36	1.78	1.39
8.0	2.25	1.36	2.07	1.40	1.85	1.44
8.2	2.33	1.40	2.14	1.44	1.92	1.48
8.4	2.40	1.44	2.21	1.48	1.99	1.53
8.6	2.47	1.48	2.28	1.52	2.06	1.57
8.8	2.54	1.52	2.36	1.56	2.13	1.62
9.0	2.61	1.56	2.43	1.61	2.20	1.66
9.2	2.69	1.59	2.50	1.65	2.27	1.71
9.4	2.76	1.63	2.57	1.69	2.34	1.75
9.6	2.83	1.67	2.64	1.73	2.41	1.79
9.8	2.90	1.71	2.71	1.77	2.48	1.84

[a] Conductivity is expressed in microsiemens per centimetre and concentrations in milligrams per litre.

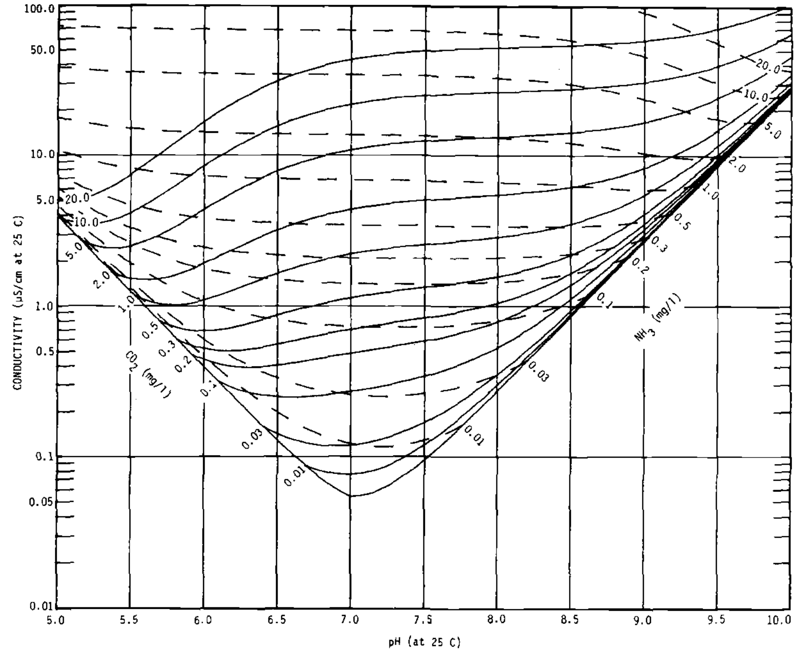

FIG. 6—*Conductivity and pH relationship of ammonia and carbon dioxide at 25°C (0.01 to 100 µS/cm).*

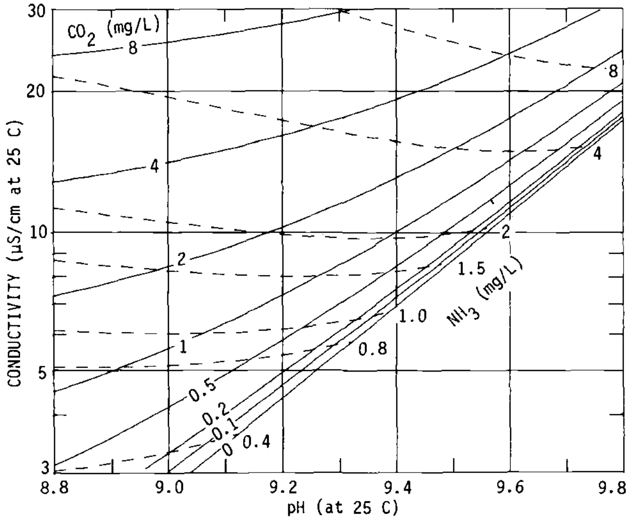

FIG. 7—*Ammonia and carbon dioxide relationship at 25°C (expanded scale).*

duce anion resin capacity, and increase the possibility of greater sodium leakage from the condensate polishing resins.

In addition to providing continuous analysis of chloride plus sulfate contaminants at low levels of 1 to 20 μg/litre, ammonia and carbon dioxide may also be determined with this equipment with the addition of pH measurement. This is accomplished by determining the specific conductivity, pH, and temperature of the sample at the entrance to the analyzer and then referring to Figs. 6 and 7 (Fig. 7 has been prepared on an expanded scale) or, preferably, referring to Table 1 (taken from a computer tabulation). Use of the computer table provides more exact results.

Let's assume that analyses of the turbine condenser condensate disclosed the following results:

Case I—From Table 1.

		CO_2	NH_3
Specific conductivity	8.0	2.07	1.40
pH	8.9		
Temperature	25°C		

Considering the condensate reboiler conductivity was 0.91 and calculating the Cl^- concentration from Eq 1, 13.5 ppb Cl^- is present, equivalent to 0.048 μS/cm (as NaCl) at 25°C.

Case II—From Table 1.

		CO_2	NH_3
Specific conductivity	9.6	2.41	1.79
pH	9.0		
Temperature	25°C		

Considering the condensate reboiler conductivity was 0.84 and calculating the Cl^- concentration from Eq 1, 7.2 ppb Cl^- is present, equivalent to 0.026 μS/cm (as NaCl) at 25°C.

Table 1 shows that this small change in conductivity due to the presence of a few parts per billion of Cl^- or $SO_4^=$ does not appreciably affect the CO_2 and ammonia (NH_3) shown to be present in Fig. 7 and Table 1.

It was brought to our attention that as much as 100 ppb total organic carbon (TOC) (as acetic acid) might also be present in the system, perhaps from resin breakdown or from contaminated raw water inleakage in the condenser. Accordingly, Fig. 8 and Table 2 were prepared,[4] and, in considering

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[4] Constants were taken from Robinson and Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1959; and *Handbook of Chemistry and Physics*, 52nd ed., R. C. Weast Chemical Rubber Co., Cleveland, Ohio, 1971–1972.

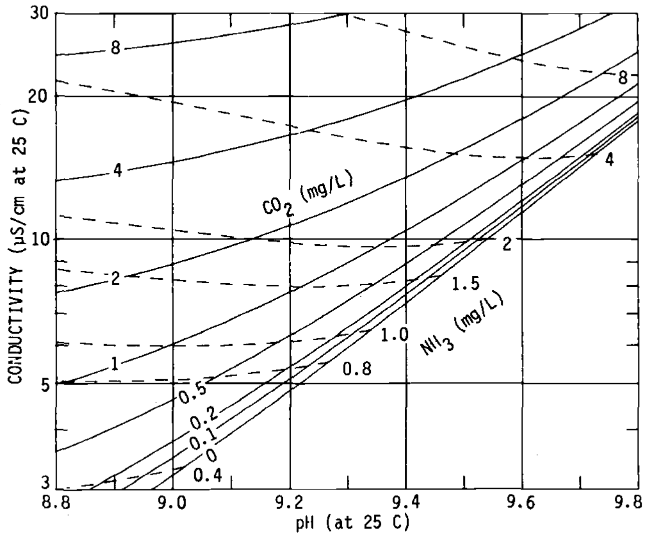

FIG. 8—*Ammonia and carbon dioxide relationship at 25°C with 100* µg/litre TOC added (*as acetic acid*) (*expanded scale*).

TABLE 2—*Carbon dioxide and ammonia in pure water at 25°C as related to pH and conductivity.*[a]

pH	8.80		8.90		9.00	
Conductivity	CO_2	NH_3	CO_2	NH_3	CO_2	NH_3
7.0	1.83	1.14	1.65	1.16	1.44	1.18
7.2	1.91	1.17	1.73	1.20	1.51	1.22
7.4	1.98	1.21	1.80	1.24	1.58	1.27
7.6	2.05	1.25	1.87	1.28	1.65	1.31
7.8	2.12	1.29	1.94	1.32	1.72	1.36
8.0	2.19	1.33	2.01	1.36	1.79	1.40
8.2	2.26	1.37	2.08	1.41	1.86	1.44
8.4	2.34	1.41	2.15	1.45	1.93	1.49
8.6	2.41	1.45	2.22	1.49	2.00	1.53
8.8	2.48	1.48	2.30	1.53	2.07	1.58
9.0	2.55	1.52	2.37	1.57	2.14	1.62
9.2	2.62	1.56	2.44	1.61	2.21	1.67
9.4	2.70	1.60	2.51	1.65	2.28	1.71
9.6	2.77	1.64	2.58	1.69	2.35	1.76
9.8	2.84	1.68	2.65	1.74	2.42	1.80

[a] Conductivity is expressed in microsiemens per centimetre and concentrations in milligrams per litre. Total acetic acid = 0.1 mg/litre (as C).

Cases I and II again, it will be noted that 100 ppb TOC (as acetic acid) has a negligible effect on the CO_2 and NH_3 previously shown to be present.

	Case I		Case II	
	CO_2	NH_3	CO_2	NH_3
No TOC	2.07	1.40	2.41	1.79
100 ppb TOC (acetic acid)	2.01	1.36	2.35	1.76

Summary

Continuous in-line methods of monitoring high-purity water for low, 1 to 20 μg/litre Cl^- by electrical conductivity and the advantages of the described technique of measurement at atmospheric boiling water temperature have been presented. In addition, a means for obtaining gaseous contaminant levels by this same technique has been suggested. Techniques for determining ammonia and carbon dioxide from pH, conductivity, and temperature measurements at condenser water temperature are shown, and examples are presented which show that low levels of chloride, sulfate, and acetate do not appreciably affect these calculated results.

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Description and Evaluation of a Continuous Sample Water Evaporator

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ABSTRACT: Current power industry requirements place increasing emphasis on water and steam purity. Many of the contaminants present in plant systems exist at levels below the detection limits of available analytical methods. Evaporation of large volumes of water in a controlled environment provides a means of increasing the concentration of contaminants to a level that can be readily analyzed by current methodology. Since the continuous sample evaporator described in ASTM Tests for Particulate and Dissolved Matter in Water (D 1888–78) is no longer marketed, an improved version of the evaporator was designed, fabricated, and tested for low-level contaminant recovery.

The new instrument is capable of evaporating solutions from sample bottles or a sample line at rates approaching 500 cm^3/h. The samples are concentrated in precleaned platinum dishes. A detailed description of the new evaporators and their operation is discussed.

Performance tests were conducted on both laboratory and field samples to define the limitations of the evaporation process for trace chemical analysis. These analyses included calcium, magnesium, iron, copper, potassium, sodium, chromium, nickel, manganese, zinc, lead, aluminum, silica, sulfate, chloride, phosphate, and nitrate. The laboratory studies showed that the evaporators were capable of chemical species recovery generally within ±20 percent of the absolute amount of synthetic species added. Evaporation and analyses of field samples obtained from operating power plants compared favorably with other concentrating techniques for most species. However, there are certain contaminants which cannot be determined accurately with current evaporation techniques and may require analysis by other available methods.

KEY WORDS: evaporation, trace contaminants, concentrating mechanism, high-purity water analysis, sample concentration, sample analysis, water quality, instrumentation, power plants

In the early 1950s, Babcock & Wilcox (B & W) manufactured a continuous sample water evaporator. The instrument was used to determine total solids concentration in feedwater samples at evaporation rates of $\simeq 150$ cm^3/h. The platinum evaporating dish and heater were positioned under a

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bell jar with filtered air circulation through the jar occurring by means of natural convection [ASTM Tests for Particulate and Dissolved Matter in Water (D 1888–78)]. A thermocap relay monitored the water level in the dish and operated a value which automatically allowed water additions upon system demand.

In the mid-1970s, industry began placing more emphasis on steam purity, deposition of contaminants in turbines, transport of contaminants through secondary systems, and other problems related to high-purity water systems. Many times the contaminants of interest were present in concentrations below the detection limits of the available analytical chemistry procedures. Collection and evaporation of large-volume samples provided a means of increasing the contaminant concentration to a level greater than the detection limit of the analytical chemistry procedure. Babcock & Wilcox initiated a program to improve the design and build several modern evaporators for internal use.

This paper describes the design of the updated evaporator and the recovery and field comparison tests conducted to evaluate the performance of the instrument.

Equipment

Evaporator Description

The newly designed water evaporator combines the capabilities of the first-generation evaporator with recent electronic technology. Other design features specified for the new evaporators were a controlled environment for sample evaporation, automatic safeguards to protect the sample, a means to measure the volume of water evaporated, a portable instrument with easy access to the evaporation dish, and variable heat input.

The instrument (Fig. 1) consists of a water delivery and monitoring system; a heated, forced-air system; an evaporation chamber; and appropriate controls and alarms to regulate the evaporation process and prevent loss or contamination of the sample. The water evaporator is represented schematically in Fig. 2.

During the evaporation process, a platinum dish sits on an adjustable platform inside a stainless steel evaporation chamber. The platform supports the dish directly beneath a Monel ring heater suspended in the chamber. A stainless steel inlet tube is used for sample addition to the platinum dish. The water level in the dish is controlled by a capacitance-type platinum probe. In the event of a failure in the capacitance system, a separate platinum wire electrode is used as a high water level alarm.

The water delivery and monitoring system transfers the water sample from the source or sample container to the platinum dish. Water flows from the supply to a calibrated tube and then into the dish. Two diaphragm valves

FIG. 1—*Continuous sample water evaporator.*

and a water level control probe interact to accomplish water volume measurement and delivery to the dish. A counter monitors the number of cycles completed by the water delivery system and allows a calculation of the total volume of water evaporated.

Heat input to the process is provided by a radiant ring heater, an air heater, and a mantle heater. Each heater has variable control to allow adjustment of heat input to prevent boiling of the sample. The radiant heater

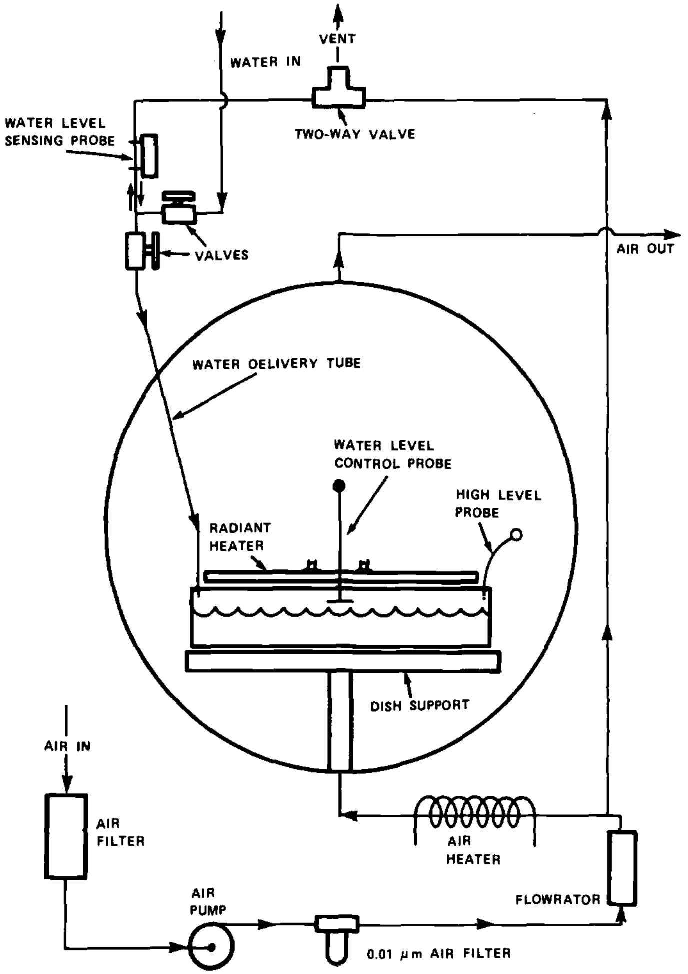

FIG. 2—*Schematic drawing of a continuous sample water evaporator.*

and air heater represent the primary heat sources, with the mantle heater being used mainly during heat up. The heated, forced-air system provides a continuous flow of hot air through the chamber to remove moisture. The air is filtered through a 0.01-μm filter to minimize sample contamination.

Alarm systems in the instrument protect the sample from loss or contamination in case of high water level, loss of air flow, high dish temperature, or no water delivery to the dish. These alarm systems allow continuous, automatic operation of the evaporators. Activation of any alarm causes the complete shutdown of the instrument.

This new instrument is capable of automatically sampling water from a large container or sampling line and evaporating the water in a platinum dish at a rate of 450 to 500 cm^3/h in a protected environment. The entire instrument (with the exceptions of the air pump and filter) is contained in a cabinet 66 cm (26 in.) wide, 41 cm (16 in.) deep, and 66 cm (26 in.) high. The instrument is portable and requires a 220-V power supply and a supply of filtered, compressed air.

Sample Container Preparation

Large-volume (19-litre) polyethylene sample containers were used for the laboratory and field tests. These containers have been used in many other programs by B & W for handling, sampling, and storing high-purity water. No problems related to contamination have been observed while using these containers and the following cleaning procedure.

Prior to use, the polyethylene sample containers were thoroughly rinsed using reagent water equivalent to ASTM Specifications for Reagent Water, (D 1193–77), Type I. Each container was then filled with a 10 percent by volume acid solution [either hydrochloric (HCl) or nitric acid (HNO_3)] prepared from reagent-grade acid and reagent water. The sample containers were soaked with the acid solution for 1 week. After soaking, the bottles were rinsed thoroughly with reagent water.

Evaporator Dish Preparation

Platinum dishes were first rinsed thoroughly with reagent water. Each dish was then soaked in a hot (near boiling) solution of $\simeq$25 percent by volume HCl for 2 to 4 h. Following the hot hydrochloric acid soaking, the dishes were either soaked in a solution of $\simeq$25 percent by volume HNO_3 for $\simeq$2 h and then rinsed thoroughly with reagent water or just rinsed thoroughly with reagent water.

Sample Solution Preparation

For each laboratory test, two large-volume (19-litre) containers were filled with reagent water. One container was kept separate and evaporated as the blank water sample. A known concentration of chemical species was then added to the second sample container, and this sample was evaporated as the synthetically contaminated test solution. The theoretical contaminant concentration in this solution was calculated based on the chemical analysis of the stock solution. The contaminant concentrations added ranged from 2 ppb to 400 ppb, with most concentrations being about 20 ppb. The containers were capped and stored under ambient conditions until the evaporation step. The maximum storage time for these samples was 1 week.

For the field comparison tests, the sample containers were taken to a nuclear power plant and used to collect water samples from various points in the secondary system. The samples were capped, returned to the laboratory, and stored under ambient conditions until the evaporation step. The storage time for the samples was approximately 1 week.

Test Procedures

Evaporator Performance Tests

Before embarking on a program to modify the evaporator design and modernize the first-generation evaporators, a series of laboratory tests was conducted to identify parameters important in the evaporation process. Tests were conducted on a mock-up of the evaporator system, which included capabilities to investigate various dish and heater sizes, water volumes, mantle heat versus radiant heat, water temperature, and heater distance from the water surface. The evaporation rate was measured against these various parameters.

Sample Evaporation

The blank water and the synthetically contaminated water samples were concentrated in the laboratory using the continuous sample water evaporators. Table 1 identifies the recovery test conditions for each test.

At the conclusion of each sample evaporation, the concentrate remaining in the platinum dish was reduced to 100 cm^3 on a steam bath and treated as follows:

1. For Tests A, B, and C, a 10 cm^3 aliquot was removed from the platinum dish for chloride analysis.
2. A rinse solution containing 10 cm^3 of concentrated reagent-grade hydrochloric acid was used to rinse the sample container walls. This ensured the pickup of trace amounts of contaminants that may have plated out on the walls of the sample container.
3. The rinse solution was added to the concentrate remaining in the platinum dish.
4. The dish was placed on a steam bath to aid in dissolving the contaminants in the concentrate.
5. The dissolved contaminants were transferred to a precleaned polyethylene bottle, and the volume was adjusted to 0.18 litres for Tests A, B, and C, and to 0.2 litres for Tests D and E and all the field tests.
6. The sample was then ready for chemical analysis.

TABLE 1—*Recovery test conditions.*

Test	Evaporator Style[a]	Cleaning Procedure		NH_3,[c] ppm	Diameter Dish Size, cm	Evaporator Rate	
		Sample Container[b]	Platinum Dish			cm^3/h	$cm^3/cm^2/h$
A	1	HNO_3 + reagent H_2O	HNO_3 + reagent H_2O	0	8.25	123 to 129	2.3 to 2.4
B	1	HNO_3 + reagent H_2O	HNO_3 + reagent H_2O	0	8.25	129 to 130	2.4
C	2	HNO_3 + reagent H_2O	HNO_3 + reagent H_2O	0	8.25	23 to 28	0.4 to 0.5
D	2	HCl + reagent H_2O	HCl + reagent H_2O[d]	0.5	14.0	436 to 482	2.8 to 3.1
E	2	HCl + reagent H_2O	HCl + reagent H_2O[d]	0.5	14.0	163 to 400	1 to 2.6[e]

[a] Style 1—first generation (evaporator style in ASTM D 1888-78); Style 2—second generation.

[b] Ten percent by volume acid soak followed by reagent water rinse.

[c] The effect of ammonia was investigated since it may be present in field samples for pH control.

[d] Hot (near boiling) 25 percent by volume HCl acid soak for 2 to 4 h.

[e] Evaporator shutdowns resulted in a lower overall rate. When in continuous operation, the rate was 430 to 480 cm^3/h (2.8 to 3.0 $cm^3/cm^2/h$).

Sample Analysis for Evaporator Concentrates

The following analytical methods were used:

1. Calcium, magnesium, sodium, lead, iron, nickel, copper, chromium, aluminum, manganese, potassium, and zinc were determined by atomic absorption spectrophotometry using procedures outlined in the ASTM Test for Metals in Water and Wastewater by Atomic Absorption Spectrophotometry [D 2576–70 (1976)].
2. Soluble silica was measured using the ASTM Test for Opacity of Paper [D 589–65 (1970)], Method B.
3. A modification of the ASTM Tests for Sulfate Ion in Water and Wastewater [D516–68 (1974)] was used to determine the total sulfur species as sulfate. The modification was essentially a sensitization, using a larger light path (longer cell) for lower detection capability. In addition, all sulfur species present in the sample were oxidized with bromine water and measured as sulfate.
4. Chloride analyses were performed according to the ASTM Tests for Chloride Ion in Water and Wastewater [D 512–67 1974)], Method C.

Additional Sample Analyses for Comparison Tests

The additional analyses conducted on field samples included ion chromatography [*1*][2] and sample concentration on cation membranes and cation plus anion resins columns [*2*]. Following contaminant elution from the ion-exchange resin [*2*], the procedures used in the analysis of the evaporator concentrates were followed. For the 1-litre grab samples, sodium and potassium were analyzed using the ASTM Tests for Sodium and Potassium in Water and Water-Formed Deposits by Flame Photometry [D 1428–64 (1977)], Method 3; chloride was analyzed by selective ion electrode, and sulfate and silica by the same methods as used on the evaporator concentrates.

Experimental Results

Evaporator Performance Tests

Data from the mock-up tests were useful in identifying important parameters. Overhead radiant heat provided a higher evaporation rate than mantle heat at a constant water temperature. Combining radiant and mantle heat further improved the evaporation rate in the mock-up.

Evaluation of the dish size showed that increasing dish size and heater size resulted in an increase in the volume of water evaporated. However, increas-

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

ing the dish size while maintaining a constant heater size did not result in a higher evaporation rate. Decreasing the distance between the heater and the water surface also resulted in an improved evaporation rate.

Based on these test results, the second-generation evaporators were designed to include mantle heating capabilities, a large dish size and appropriately sized heater, and adjustments to provide the capability of placing the heater very close to the water surface. Water volume did not prove to be a significant parameter except during start-up, and water temperature was a factor to the extent that it was important to maintain the temperature below 100°C.

The performance test results for second-generation evaporator showed that the instrument could evaporate 430 to 480 cm^3/h (see Table 1). However, the evaporation rate per unit area remained essentially unchanged from the rate determined for the first-generation evaporators.

Laboratory Recovery Tests

The results of the recovery tests are shown in Tables 2 and 3. Recovery Tests A and B were conducted using the first-generation evaporators with evaporation rates of $\simeq 2.4$ cm^3/cm^2/h. The recovery percentages generally ranged between 80 and 120 percent for these tests. Recovery problems were observed for sodium, aluminum, silica, sulfate, and chloride. Recovery Test C was conducted using a 5-μm filtered hot (150°C) air supply without an overhead heater. This test was conducted to evaluate the effect of a low evaporation rate ($\simeq 0.$ cm^3/cm^2/h) on contaminant recovery. Contaminant recoveries for this test generally ranged between 80 and 106 percent and were observed to be consistently lower than Recovery Tests A and B. Again, difficulties were experienced with the recovery of sodium, aluminum, silica, sulfate, and chloride. Since chloride analysis required special handling techniques and the analytical results were not reproducible, this analysis was discontinued on further evaporator concentrates.

Tests D and E were conducted to evaluate recovery with the newly developed evaporators with high radiant heat input. The evaporation rates during these tests were between 2.8 and 3.1 cm^3/cm^2/h. During these tests ammonia was added to the solution to determine if this volatile component affected recovery of other species of interest. No attempt was made to determine the recovery of ammonia or any ammonia salts or acids. Contaminant recoveries generally ranged between 80 and 120 percent and were observed to fluctuate more than in Tests A, B, and C. Problems were observed for sodium, aluminum, iron, and phosphate. The variations observed for these contaminants in the blank water suggested that poor recovery percentages may have resulted from blank or synthetic sample contamination.

TABLE 2—*Results of recovery tests A, B, and C.*[a]

Element	Blank Concentration, ppb			Contaminant Concentration Added, ppb,	Total Contaminant Concentration, ppb			Contaminant Concentration Recovered, ppb			Percent Recovery		
	Test A	Test B	Test C	Tests A, B, C	Test A	Test B	Test C	Test A	Test B	Test C	Test A	Test B	Test C
Ca	0.1	0.1	0.1	19.9	20.0	20.0	20.0	17.8	16.2	15.9	89	81	80
Mg	0.2	0.1	0.1	2.0	2.2	2.1	2.1	2.6	2.5	2.1	118	119	100
Fe	0.3	0.7	2.0	19.9	20.2	20.9	21.9	20.0	18.3	19.6	99	88	89
Cu	0.1	0.2	0.7	19.9	20.0	20.1	20.6	17.6	18.3	16.6	88	91	81
K	0.2	0.3	24.2	5.0	5.2	5.3	29.2	5.9	6.6	4.0	113	106	14[c]
Na	0.7	1.5	2.8	3.0[b]	3.7	4.5	5.3	4.7	3.4	2.2	127	76	42[c]
Cr	<0.1	0.1	0.1	19.9	19.9	20.0	20.0	16.8	17.3	17.1	84	87	86
Ni	0.2	0.2	1.0	19.9	20.1	20.1	20.9	18.6	19.1	17.4	93	95	83
Mn	0.1	0.9	0.6	10.0	10.1	10.9	10.6	9.0	9.4	8.7	89	86	82
Zn	0.2	0.2	0.4	2.0	2.2	2.2	2.4	2.3	2.0	2.0	104	91	83
Pb	<0.1	<0.1	<0.1	49.8	49.8	49.8	49.8	41.2	44.6	43.3	83	90	87
Al	<0.1	<0.1	0.5	2.0	2.0	2.0	2.5	3.0	1.5	4.0	150	75	160
SiO_2	11.5	4.3	12.4	0.5	12.0	4.8	12.9	4.2	1.7	17.6	35	35	136
SO_4	3.9	5.6	101.8	54.8	58.7	60.4	156.6	30.3	33.9	70.7	52	56	45
Cl	1.2	1.4	1.7	3.0	4.2	4.4	4.7	5.3	3.3	3.6	126	75	77

[a] Concentration factors:
Test A—blank, 112.9; synthetic, 112.0.
Test B—blank, 110.3; synthetic, 110.5.
Test C—blank, 108.5; synthetic, 112.1.

[b] Test C contaminant concentration added was 2.5 ppb.

[c] Blank water sample contamination.

TABLE 3—*Results of recovery tests D and E.*[a]

Element	Blank Concentration, ppb		Contaminant Concentration Added, ppb	Total Contaminant Concentration Added, ppb		Concentration Recovered, ppb		Percent Recovery	
	Test D	Test E	Tests D and E	Test D	Test E	Test D	Test E	Test D	Test E
Ca	0.3	0.3	19.0	19.3	19.3	16.2	15.2	84	79
Mg	<0.1	0.8	2.5	<2.6	3.3	2.6	4.0	100	121
Fe	0.9	2.8	16.8	17.7	19.6	14.1	7.6	80	39[b]
Cu	0.9	0.3	19.6	20.5	19.9	15.4	17.2	75	86
K	0.1	0.9	15.4	15.5	16.3	13.7	16.4	88	101
Na	0.2	1.9	8.7	8.9	10.6	8.4	11.4	94	108
Cr	0.9	1.4	20.1	21.0	21.5	12.0	15.7	57	73
Ni	1.3	0.9	18.5	19.8	19.4	19.3	18.0	97	93
Mn	0.3	1.2	9.7	10.0	10.9	11.0	9.2	110	84
Zn	1.0	4.3	2.2	3.2	6.5	1.8	2.5	56	38
Pb	0.1	<0.1	34.0	34.1	34.1	36.3	40.7	106	119
Al	0.1	1.0	0.8	0.9	1.8	3.5	1.5	388	83
SiO_2	2.3	2.0	0.9	3.2	2.9	1.1	2.7	34	93
SO_4	9.6	14.2	54.0	63.6	68.0	74.9	68.3	118	100
PO_4	0.1	1.0	4.0	<4.1	5.0	8.0	8.1	195	162
NO_3	17.1	11.4	353.0	370.1	364.4	254.7	277.8	69	76
F	<0.5	0.5	1.7	<2.2	2.2	1.2	2.0	55	91

[a] Both blank and synthetic solutions contained 0.5 ppm NH_3. Concentration factors:
Test D—blank, 104.9; synthetic, 101.4.
Test E—blank, 105.9; synthetic, 100.3.

[b] Blank water contamination or operator error suspected.

Field Comparison Tests

Test 1—The data obtained by the analyses for sodium, potassium, and soluble silica on 1-litre grab and evaporator concentrates are compared for samples obtained from the secondary system of a nuclear plant (Table 4).

Sodium, potassium, and silica were chosen for comparison because they can be determined in the low parts-per-billion range on a grab sample without concentration. The 1-litre and evaporator concentrate samples generally agreed regarding sodium and potassium values. The exception was the poor agreement of potassium values on Sample 6 and Sample 9. It is suspected that the high results on Sample 6 and 9 may be due to contamination. These results were checked by both flame photometry and atomic absorption and showed good agreement. This confirmed that the high results were not due to analytical error. The 1-litre and evaporator concentrate silica values generally agreed for the very low silica concentrations; but at high silica concentrations [$\geq$10 ppb silicon dioxide (SiO_2)], the evaporator concentrates gave low results. This appears to be due to the addition of acid to the evaporator concentrate to dissolve the residue. This procedure may change the form of silica so that it is not quantitatively measured by the method used.

Test 2—The second test involved the collection of samples from six different points in the secondary system of a nuclear plant by various techniques. In Table 5 evaporator concentrates are compared with the results of 1-litre grab, cation columns, and cation resin membranes. The samples were accumulated during different time intervals. The results agree reasonably well, although the evaporator concentrates tend to be slightly higher.

TABLE 4—*Results of field comparison Test 1.*

	ppb Na[a]		ppb K[b]		ppb SiO_2[c]	
Sample	1-litre	Evaporator Concentrate	1-litre	Evaporator Concentrate	1-litre	Evaporator Concentrate
1	1.0	1.4	1.0	0.3	1.0	0.5
2	3.0	5.4	1.0	2.4	1.0	0.3
3	2.0	3.9	1.0	1.1	1.0	0.2
4	6.0	8.8	1.0	0.9	5.0	4.3
5	1.0	3.5	1.0	1.0	1.0	0.2
6	9.0	7.9	5.3	1.1	1.0	0.5
7	85.0	78.9	1.0	0.6	67.0	9.8
8	70.0	67.6	1.0	1.3	50.0	10.4
9	6.5	8.3	1.0	10.2	5.0	0.9
10	15.5	15.0	1.0	0.8	10.0	3.3

[a] One-litre sodium values were obtained by flame photometry and evaporator concentrates by atomic absorption.

[b] One-litre potassium values were obtained by flame photometry and evaporator concentrates by atomic absorption.

[c] One-litre and evaporator concentrate SiO_2 values were obtained by colorimetric ASTM Tests for Silica in Water and Wastewater [D 859-68 (1974)], Method B.

TABLE 5—*Results of field comparison Test 2*

	Sodium Concentration, ppb			
Sample	1-litre[a]	Evaporator Concentrates[b]	Cation Column[c]	Cation Resin Membrane[d]
11	4.2	5.4	4.2	3.8
12	<1.0	1.8	0.2	0.5
13	<1.0	0.8	0.2	0.2
14	<1.0	1.4	0.2	0.3
15	<1.0	1.2	0.2	0.4
16	7.3	8.1	5.8	6.8

[a] Sampled in ~6 min.
[b] Sampled in 5 to 10 h.
[c] Sampled in ~7 days, Samples 12 and 13 exposed briefly to high temperature.
[d] Sampled in 5 to 8 h—similar to samples of Footnote *b*.

Test 3—This test involved samples taken during wet lay-up or draining of steam generators from several plants. This provided an opportunity to compare evaporator concentrates with direct analysis on samples for certain contaminants present at high concentrations. In addition to previous analytical methods used to determine contaminants, ion chromatography was used for a few 1-litre grab samples. Also, a low-sulfate method [*3*] was used for the 1-litre grab samples to provide an additional analysis for this species. The results are shown in Table 6.

Generally, the results for sulfate, sodium, potassium, and phosphate show fair to good agreement between 1-litre grab samples and evaporator concentrates. Silica values for the evaporator concentrates gave low results for the reason mentioned previously. Because of the importance of sulfur compounds in secondary systems of nuclear plants regarding deposition and corrosion in steam generators and turbines, we believe that further investigations of the methods for concentration and analysis are needed.

Test 4—The data on five samples from a nuclear plant, which were taken by different concentrating techniques and analyzed for several contaminants, are reported in Table 7. The evaporator concentrates compared favorably with the other techniques (cation membranes, cation plus anion columns, and 1-litre samples) for the various species measured. Note that the sulfate levels on evaporator concentrates are consistently higher than anion column results. Total sulfur, reported as sulfate, analysis was done by the modified ASTM D 516-68 (1974) method for *both* of these sample types. Sulfate contamination could have occurred by leaching from sample container walls, producing high-sulfate results for the evaporator concentrates. Conversely, the anion resin may not be accumulating all types of sulfur species present in the system, or perhaps all sulfur species were not regenerated from the anion resin column for measurement. The continuous sample evaporator cannot be used to concentrate volatiles such as ammonia. The cation resin

TABLE 6—*Results of field comparison Test 3.*

	Plant No. 1 Steam Generator A		Plant No. 2 Steam Generator B		Plant No. 3 Steam Generator A		Plant No. 3 Steam Generator B		Plant No. 4 Steam Generator A		Plant No. 4 Steam Generator B	
	1-litre[a]	EC[b]	1-litre	EC	1-litre	EC	1-litre	EC	1-litre	EC	1-litre	EC
Total sulfur as SO_4, ppb[c]	<200	69	<200	384	1190	830	1080	920	1 420	790	<200	230
Sulfur as SO_4, ppb[d]	41	. . .	385	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Sulfur as SO_4, ppb[e]	26	. . .	60	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Sodium, ppb	160	129	320	351	1070	1370	550	662	4 700	5510	1000	1210
Potassium, ppb	. . .	67	11	23	57	64	34	16	1 720	2020	380	318
Silica (SiO_2), ppb	590	. . .	1580	1224	2450	930	560	450	11 200	2780	3050	1720
Phosphate (PO_4), ppb[d]	11	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Phosphate (PO_4), ppb[f]	. . .	13	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

[a] One-litre grab sample.
[b] EC = evaporator concentrate.
[c] Modified ASTM Tests D 516-67 (1974), measure total sulfur, reported as sulfate.
[d] Ion chromatography, measures sulfate.
[e] CERL method, measures sulfate.
[f] ASTM Tests for Phosphorus in Water (D 515-78), Method B.

TABLE 7—*Results of field comparison Test 4.*

	Ca	Mg	Fe	Cu	K	Na	Cr	Ni	Mn	Zn	Pb	Al	SO_4	PO_4	NH_3
							Sample 1, ppb								
EC[a]	0.3	0.5	5.6	0.1	1.8	3.7	0.2	0.6	0.2	0.7	<0.1	0.3	16.5	<1	. . .
CM[b]	0.4	0.1	3.0	0.1	0.2	5.0	<0.1	0.6	0.2	0.6	0.5	<0.1	. . .	. . .	450
C/A[c]	<0.1	<0.1	8.0	<0.1	0.1	4.2	<0.1	0.7	0.3	<0.1	<0.1	<0.5	8.2	0.1	370
1-litre[d]	. . .	. . .	. . .	. . .	1.0	3.8	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
							Sample 2, ppb								
EC	0.8	0.8	4.0	1.1	0.8	1.7	0.8	0.6	0.3	1.1	0.3	<0.6	17.7	<2	. . .
CM	0.4	1.2	1.0	0.4	0.2	1.6	<0.1	0.1	0.1	<0.1	<0.1	<0.9	. . .	. . .	450
C/A	0.8	0.1	0.1	0.2	<0.1	1.2	<0.1	<0.1	0.1	<0.1	<0.1	<0.6	11.0	<0.1	400
1-litre	. . .	. . .	. . .	. . .	. . .	1.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
							Sample 3, ppb								
EC	0.1	0.1	1.5	0.1	0.2	0.8	0.1	0.4	0.2	0.2	0.2	0.9	<1	<1	. . .
CM	0.3	1.7	0.8	<0.1	0.2	1.5	<0.1	0.2	0.1	0.2	0.1	<0.8	. . .	. . .	7
C/A	0.3	<0.1	0.2	<0.1	<0.1	1.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.6	<0.1	<0.1	11
1-litre	. . .	. . .	. . .	. . .	. . .	3.0	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
							Sample 4, ppb								
EC	0.1	0.4	17.9	0.4	1.2	37.6	0.2	0.8	2.5	0.2	<0.1	0.9	17.0	<0.2	. . .
CM	0.1	1.2	29.0	<0.1	0.9	55.0	<0.1	0.7	0.7	<0.1	<0.1	1.2	. . .	. . .	103
C/A	<0.1	0.1	35.3	<0.1	0.9	54.1	0.2	0.8	1.1	<0.1	<0.1	<0.8	6.2	0.2	130
1-litre	. . .	. . .	. . .	. . .	1.0	43.5	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
							Sample 5, ppb								
EC	0.1	0.2	16	<1	0.7	31.6	0.2	1.2	1	0.1	<0.1	2	19	<2	. . .
CM	2.3	0.8	7	<0.1	0.9	44.4	<0.1	0.6	0.1	0.1	<0.1	1.3	. . .	. . .	102
C/A	<0.1	<0.1	37	<0.1	0.7	41.8	<0.1	1.3	<0.1	<0.1	<0.1	2.6	16.9	0.2	120
1-litre	. . .	. . .	. . .	. . .	1.0	32.5	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

[a] EC = evaporator concentrate.
[b] CM = cation membrane.
[c] C/A = cation plus anion column.
[d] One-litre grab sample, direct analysis.

column produced somewhat higher iron results in Samples 4 and 5 than the cation membrane and evaporator concentrates. Generally, the cation membrane and cation column produced similar results. Note that the anion columns and 1-litre grab samples agreed well regarding silica.

Conclusions

Continuous sample evaporators provide a means for conducting trace chemical analysis. Laboratory studies indicated that results obtained from samples concentrated in continuous sample evaporators were representative of contaminants present in the original solution. From the recovery tests conducted, it appears that for most species the results can be considered to be within ±20 percent of the absolute values. Isolated analyses conducted during the recovery test program varied from expected results. Some of these higher recovery percentages may have resulted from problems with conducting recovery tests rather than from problems with the evaporation process itself. Blank water contamination presents a considerable difficulty in conducting recovery tests using solutions containing trace levels of contaminants. Contamination with microgram quantities of an element causes misleading results.

As long as boiling of the sample does not occur, evaporation rate does not significantly affect the recovery of contaminants. Contaminant recovery percentages on tests conducted with evaporation rates of 0.4 to 0.5 $cm^3/cm^2/h$ did not significantly differ from those from tests conducted with rates of 2.4 to 4.1 $cm^3/cm^2/h$. Also, the presence of small quantities of ammonia up to 0.5 ppm did not affect recovery percentages.

Evaporation and analyses of field samples obtained from operating power plants compared favorably with other concentrating techniques for most species. However, there are certain contaminants (such as chloride, silica, sulfate, aluminum, volatiles) which cannot be accurately determined with current evaporation techniques and may require analysis by other available methods.

Because of the importance of sulfur compounds in the secondary system of nuclear plants regarding deposition and corrosion in steam generators and turbines, we believe that further investigation regarding the methods for concentration and analysis are needed. Also, sample containers may be a source of contamination or cause removal of chemicals by plate out and adsorption. The sample container material, the method of cleaning, and the time of storage of samples are parameters that deserve further study.

Acknowledgment

The efforts of many people at the Babcock & Wilcox Research Center were required to complete the design, fabrication, and testing of the continuous-sample water evaporator. Many thanks go to C. R. Turner for performing the evaporator performance tests and to N. V. Sangree, D. R. Setlak, and the Instruments Section for constructing the instrument. We also acknowledge J. M. Kibler, W. V. Scott, and G. T. Upperman, who made significant contributions to the completion of the laboratory recovery test and field comparison test portions of this program.

References

[*1*] Ion chromatograph-the American Society for Testing and Materials, Subcommittee D 19.05 on Inorganic Constituents in Water, is currently developing a standard practice document for operation of this type of instrument.

[*2*] Detailed procedures are specified in the 1978 and 1979 progress reports from Electric Power Research Institute, Palo Alto, Calif., Contract RP 1124-3.

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Guy Washinger[1] *and Peeter Kark*[1]

Determination of Trace Chlorine and Oxidants in Seawater by Differential Pulse Polarography

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REFERENCE: Washinger, Guy and Kark, Peeter, "**Determination of Trace Chlorine and Oxidants in Seawater by Differential Pulse Polarography,**" *Power Plant Instrumentation for Measurement of High-Purity Water Quality, ASTM STP 742,* R. W. Lane and Gerard Otten, Eds., American Society for Testing and Materials, 1981, pp. 213–226.

ABSTRACT: This paper describes a rapid and reliable technique for the determination of chlorine and other oxidants in power plant and industrial cooling waters, with particular emphasis on seawater systems. The analytical work is based upon the standard technique of chlorine and oxidant reduction by phenylarsine oxide. Excess phenylarsine oxide is detected quantitatively and nondestructively by differential pulse polarography and has a detection limit of less than 5 ppb chlorine equivalent.

The procedures described in this paper are shown to be applicable for the analysis of total residual chlorine. However, extension of the principle to other types of oxidant determination under different conditions of pH and catalyst should be straightfoward.

KEY WORDS: chlorine, trace chlorine, oxidants, trace oxidants, power plant effluent, effluent, water, cooling water, biological fouling, trace analysis, chloramines, power plants, instrumentation, water quality

Most power plants and industrial sites require large amounts of water to dissipate waste heat. Once-through-type cooling systems have the inherent need for the prevention of biological fouling. The most widely used and accepted method for the control of biological fouling is chlorination.

The U.S. Environmental Protection Agency has established guidelines for the discharge of free chlorine into receiving bodies. A maximum of 0.5 ppm and 0.2 ppm average for up to 2 h per day per cooling unit is permitted. However, state standards may be more restrictive than federal standards. Mattice and Zittel have indicated 20 ppb as a threshold toxicity level [*1*].[2]

The standard amperometric titration method [*2,3*] for the analysis of residual oxidants (chlorine) has a reliable detection limit of about 100 ppb.

The polarographic technique described herein is based upon and extends the work of Smart, Lowry, and Mancy, and includes applications to sea-

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[1] Applications chemists, Analytical Instrument Division, respectively, EG&G Princeton Applied Research Corp., Princeton, N.J. 08540.

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

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water-type samples and a standard addition technique which has the capability of "fixing" the oxidant level in the field for subsequent laboratory analysis [*4*].

Theory

Upon introduction of chlorine gas into water the reaction shown in Eq 1 proceeds rapidly and completely.

$$Cl_2(g) + H_2O \xrightarrow{\text{fast}} HOCl + H^+ + Cl^- \qquad (1)$$

The biocidal nature of pure chlorinated water comes from oxidative activity of hypochloride species. However, when chlorine is added to seawater, as opposed to fresh water, the oxidation of bromide (present at about 67 ppm) occurs as shown in the following reaction [*1*]. This reaction

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \qquad (2)$$

has been reported to reach 99 percent completion in less than 10 s and is even faster at lower pH. Hypobromide species are, themselves, strongly oxidizing species so that the following list of chlorinated and brominated species are likely to be found in chlorinated saline discharge waters.

bromamines
chloramines
chloroforms
bromoforms
halogenated organic compounds

Many of these species are oxidizers although they are weaker and slower reacting than hypohalides.

Chlorine and its oxidizing derivatives react with phenylarsine oxide (PAO) under a variety of conditions of pH and chemical catalysis. By judicious choice of the analytical conditions, investigators can determine separately certain derivatives based upon their relative oxidizing power (Table 1). Hypohalide reacts most readily followed by species such as monohalamines and dihalamines. Adding potassium iodide and lowering the pH activates slower

TABLE 1—*Experimental conditions and chlorine species determined.*

	pH	KI	Species Determined
Free available chlorine	6.5 to 7.5	none	$HOCl$, OCl^-
Free available chlorine + monochloramines	6.5 to 7.5	yes	$HOCl$, OCl^-, monochloramines
Combined chlorine	3.5 to 4.5	yes	OCl^-, monochloramines, dichloramines

reacting species, such as haloorganics. Following is the relative rates of reaction, with PAO, of several species for chlorine derivatives.

$$HOCl, OCl^- > \text{monochloramines} > \text{dichloramines}$$

The following reactions form the basis of standard methods of chlorine analysis whereby the quantitative oxidation of PAO is observed either directly or in the back titration of excess PAO.

$$Cl_2(g) + H_2O \xrightarrow{\text{fast}} HOCl + H^+ + Cl^-$$

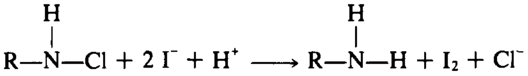
$$HOCl + H^+ + 2I^- \longrightarrow Cl^- + I_2 + H_2O$$

Analytical

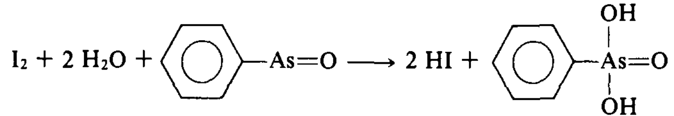
$$\underset{\text{(inactive)}}{I_2} + \underset{\text{(active)}}{PAO} \longrightarrow \underset{\text{(inactive)}}{PAOX} + \underset{\text{(inactive)}}{2I^-}$$

Examples of species which can be determined using PAO are shown in the following reactions

$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$
$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$
$$IO_3^- + 6H^+ + 5I^- \longrightarrow 3I_2 + 3H_2O$$
$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$
$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$



$$R\text{—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}Cl + 2\,I^- + H^+ \longrightarrow R\text{—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}H + I_2 + Cl^-$$



(PAO)

In general any species with a reduction potential more positive than I_2 (=0.535) can be determined using PAO.

Alternative methods for monitoring or determining chlorine include the use of galvanic sensors, ion-selective electrodes, or "polarographic membrane" electrodes. All of these methods involve the observation of very small changes in current or potential caused by continuous electrochemical reactions at the sensor. These observations may be subject to noise, drift, kinetic complications, or to a wide variety of chemical interferences, particularly at high instrumental sensitivities.

Differential pulse polarography is a reliable and sensitive method for the determination of phenylarsine oxide. Only unoxidized PAO is polarographically detected at the mercury electrode. The analytical signal is in the form of a well-defined peak whose height is proportional to PAO concentration and whose shape and position are qualitative indicators of PAO (see Fig. 1). Differential pulse polarography (DPP) is, thus, not subject to the type of noise and drift encountered with the use of amperometric or potentiometric electrodes and provides an output whose form can be interpreted to detect complications in the analysis. Since the dropping mercury electrode (DME) is continuously renewed, the sensitivity fluctuations associated with solid electrodes are not observed.

Since the polarographic behavior of PAO in fresh water has been thoroughly characterized by Lowry, Smart, and Mancy, this paper will focus on the use of PAO as an indicator of oxidant concentration in seawater.

Experimental

Instrumentation and Chemicals

Polarographic measurements were made using the following polarographic analyzers: Model 384, Model 174A, or Model 364. All systems used the Model 303 static mercury drop electrode system (SMDE) and are available from EG&G Princeton Applied Research Corp.

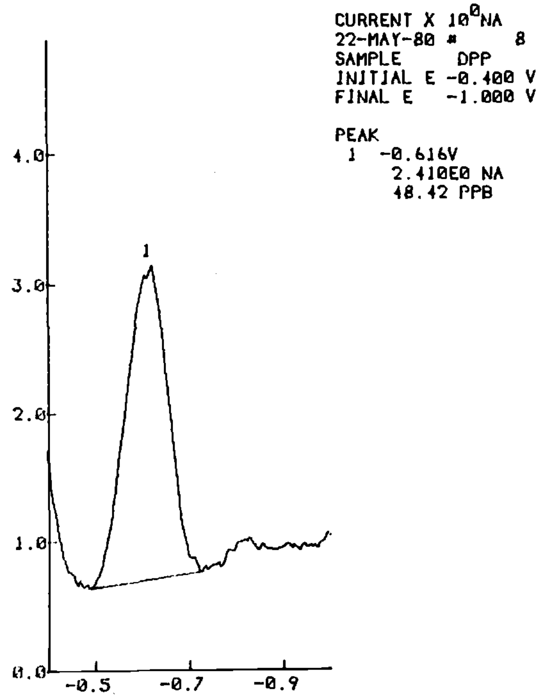


FIG. 1—*PAO in synthetic seawater* (*pH 3.5*).

Titrations were done using a radiometer Model ABU80 autoburette. The measurement system included platinum wire mesh working and counter electrodes and a saturated calomel reference electrode (SCE). A Model 174A polarographic analyzer provided potentiostatic control, and the current at the platinum electrode was output to a Houston Omniscribe strip chart recorder for end-point determination.

The chlorine source, laboratory grade, Fisher 4 to 6 percent sodium hypochlorite was standardized against certified Fisher 0.00564 *N* phenylarsine oxide solution. All other chemicals and reagents were reagent grade. Buffers and electrolytes were tested prior to their use to ensure that no chlorine equivalent was incorporated.

Data

The data presented in this section was obtained from a synthetic seawater electrolyte [3 percent sodium chloride NaCl]. Total combined chlorine determination was accomplished in synthetic seawater containing 5 mg/ml potassium iodide and buffered to pH 3.2 to 4.0 with acetate buffer (0.1 *M* final acetate concentration). The PAO peak used for the analysis in this system occurs at about -0.64 ± 0.025 V versus the silver-silver chloride reference electrode filled with saturated NaCl. At the lower end of the pH range the peak shifts to slightly more positive values whereas at the higher end of the pH range the peak shifts to slightly more negative values. The peak also shifts slightly negative with increasing concentration. Figure 1 shows the peak obtained for 48.42 ppb PAO in acetate electrolyte. The peak was quantitated using the method of standard additions and Fig. 2 shows a plot of the peak height versus concentration for the standards. The PAO concentration is equivalent to 20.46 ppb chlorine. A signal equivalent to three times the background noise is often used as an estimate of detection limits. In the case of Fig. 1, then, the detection limit would be about 5.4 ppb PAO, which is equivalent to 2.3 ppb chlorine.

Standard Addition Method

The following procedure was developed to determine the total chlorine equivalent in seawater samples. The analysis is performed in five steps. Note that the determination of free available chlorine can be accomplished using phosphate buffer (pH 6.7) in place of the acetate buffer described.

1. *Collection*—A 100-ml sample volume is a reasonable sample size. The container should be thoroughly cleaned and, ideally, made of dark glass to prevent the decomposition by light. A 100-ml volumetric flask wrapped in aluminum foil works well. The flask should have sufficient volume above the fiducial mark so that 1 ml of buffer, 0.5 ml of potassium iodide solution, and up to 1 ml of PAO fixing solution can be added conveniently.

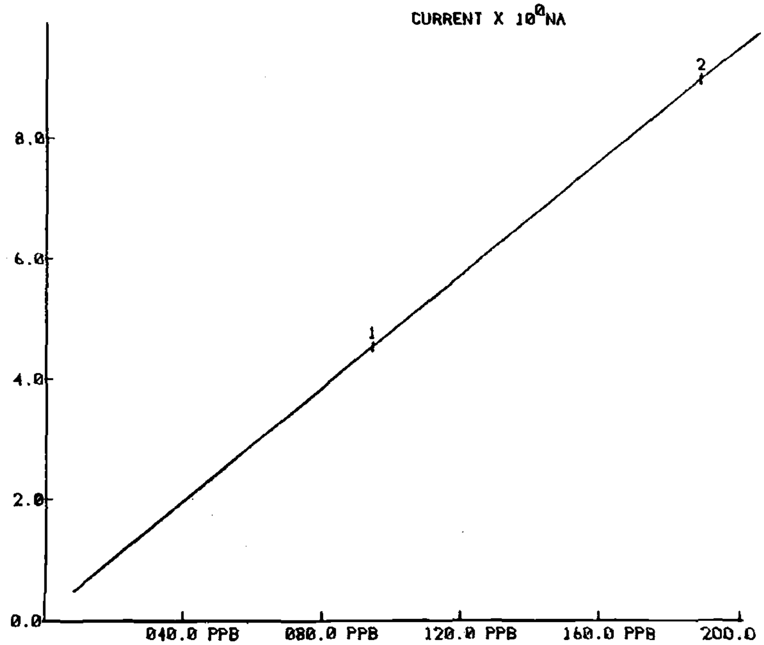


FIG. 2—*Standard addition calibration curve for PAO in synthetic seawater (pH 3.5).*

2. *Buffering and activation* of the sample is accomplished by adding 1 ml of 10 *M* acetate buffer (pH 3.5) and 0.5 ml of 100 mg/ml potassium iodide solution to the sample. The potassium iodide solution should be prepared fresh and kept out of the light.

3. *Immobilization (fixing)*—The chlorine equivalent is fixed by adding an accurately known excess of PAO standard solution to the buffered and activated sample. Standardized PAO solution can be obtained from a variety of laboratory supply companies. The amount of PAO to be added to each sample depends upon the amount of chlorine equivalent expected to be found. We have obtained good accuracy by adding PAO at roughly twice the chlorine equivalent. Table 2 shows some chlorine equivalents and appropriate PAO additions.

TABLE 2—*Appropriate immobilization additions using 0.00564* N *PAO solution.*

Expected Chlorine Equivalent, ppb	Fixing Volume, ml
1000	1.00
500	0.50
250	0.25
100	0.10
50	0.050
10	0.010

4. *Measurement*—Polarographic measurement of the amount of PAO left after adding excess PAO in step 3 was done using the instrumental parameters outlined in the following printout from the analyzer.

```
            MODEL 384 POLAROGRAPHIC ANALYZER
12-MAY-80                    SAMPLE  N. J. SEA WATER
DPP                          ANALYTE  PAO FOR CHLORINE EQUIVALENT
INITIAL E  -0.300 V
FINAL E    -1.200 V          SUPP. ELEC.  .1 M ACETATE (pH 3.5) + KI
PURGE  240 SECONDS
DROP TIME  1.0 SECONDS       SAMPLE PREP.  NONE
SCAN INCREMENT  4 MV         ______________________________
PULSE HEIGHT  0.050 V
REPLICATIONS  1              ______________________________

STANDARD ADDITION
BLANK SUBTRACTION:  NO
TANGENT FIT:  YES
PEAK LOCATION:  YES
DERIVATIVE:  NO

            10 11 12 13 14 15 16 17
OVERRIDE    N  Y  Y  Y  N  N  Y  N

PEAK      POT         STD 1        STD 2
  1     -0.640 V    86.14 PPB    172.3 PPB
```

Exactly 10.00 ml of the immobilized sample was placed in the sample cell under the Model 303 SMDE system. The sample was purged for 4 min and scanned in the DPP mode, usually from −0.40 V to −1.0 V versus silver-silver chloride (saturated NaCl). The peak used for the analysis occurs at about −0.64 V and is quantitated using the method of standard addition. Two standard spikes of PAO should be used to determine the amount of PAO in the sample cell. The appropriate amount of PAO used to spike the sample cell can often be approximated by taking one tenth of the amount of PAO used to immobilize the 100-ml sample in Step 3.

5. *Calculations*—Chlorine equivalent is usually reported in units of parts per million or parts per billion. The prestandardized phenylarsine oxide solution used in our experiments was certified at 0.00564 *N*. However, when using the Model 384 for the determination of the chlorine equivalent, it was convenient to express PAO concentration in units of ppm or ppb. The 0.00564 *N* PAO solution is equivalent to 473.8 ppm PAO.

The chlorine equivalent in the sample is given by

$$\text{Chlorine equivalent (ppm)} = \text{PAO (ppm)}_{\text{used}} \times \frac{35.5\ \text{g/equivalent}}{84.0\ \text{g/equivalent}} \times \frac{V_F(\text{sample})}{V_I(\text{sample})} \quad (3)$$

where PAO $(\text{ppm})_{\text{used}}$ is the amount of PAO which was consumed by the chlorine equivalent in the sample and is determined from the following relationship

$$\text{PAO}\ (\text{ppm})_{\text{used}} = \text{PAO}\ (\text{ppm})_{\text{original}} - \text{PAO}\ (\text{ppm})_{\text{found}} \qquad (4)$$

where PAO $(\text{ppm})_{\text{original}}$ is the concentration of PAO used in fixing the sample, including dilution to 101.5 ml; PAO $(\text{ppm})_{\text{found}}$ is the concentration of PAO left in the sample and determined by polarographic measurement in Step 4; V_I(sample) is equal to the volume of sample taken prior to buffering and activation; and V_F(sample) is equal to the volume of the sample after the addition of the buffering and activation reagents and the immobilization spike.

Comparison with Amperometric Titration

A preliminary comparison of the polarographic method described above with the amperometric titration method indicates that both methods agree well above 200 ppb chlorine, but at lower levels the error in the titration method increases rapidly (see Fig. 3).

Titrations were done using the radiometer system described under the Instrumentation and Chemicals section of this paper. The electrode potential was 0.0 V versus SCE. The data presented in Fig. 3 are the result of single pa-

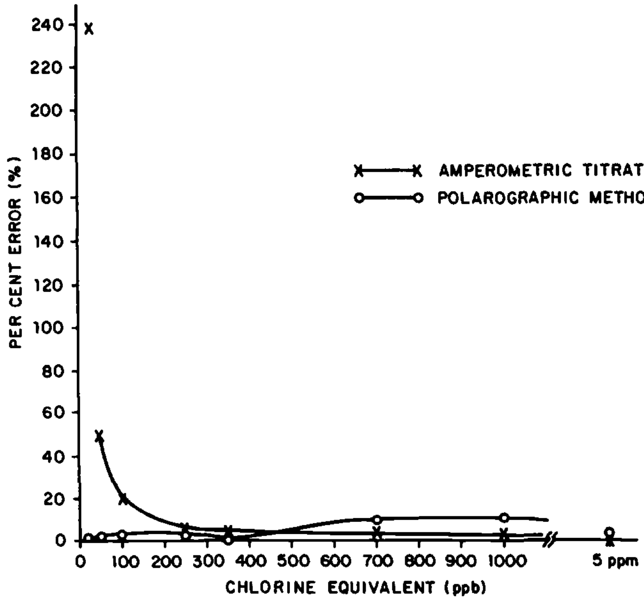


FIG. 3—*Error comparison for chlorine methods.*

rallel titration and polarographic runs against standards prepared from a 5-ppm sodium hypochlorite stock. The sodium hypochlorite stock was standardized using the amperometric titration method. Synthetic seawater electrolyte, described previously, was used for both methods. The errors observed at low levels in the titration method are unexplained, however, dilution of the 0.00564 *N* PAO titrant by 50 percent served only to decrease the clarity of the end-point break.

The addition of a small amount of acid to the cell just prior to running the polarogram has recently been shown to give PAO calibration curves which are more sensitive (0.6 nA/ppb versus 0.4 nA/ppb) and cover a slightly broader concentration range.

Results obtained from parallel analyses of synthetic seawater samples by the DPP method and the amperometric titration method are given in Table 3. Each sample was prepared by adding small volumes of a stock NaOCl solution to 1 litre of 3 percent NaCl solution. The volumetric flask containing the sample was covered with aluminum foil and the analyses were run, in triplicate, as quickly as possible.

Titrations were carried out with a commercially available amperometric chlorine titrator using the manufacturer's recommended procedure. The DPP analysis was carried out using the procedure described previously except that just prior to initiating the scan, 100 μl of 6 *M* HCL was added to the cell. The resulting pH is about 1 and the PAO peak occurs at about −0.4 V versus silver–silver chloride.

As the previous comparison indicates, Table 3 shows good agreement of the two methods at moderate to high chlorine levels, but at low levels (about 200 ppb) the amperometric titration lost accuracy and eventually sensitivity while the DPP method still gave good response at the 10 ppb level.

Seawater Samples

Seawater from just off the New Jersey shore along with Barnagat Bay water samples were obtained for analysis by the method described. Polarographic blanks were prepared by omitting Step 3 (immobilization) from the procedure. The polarographic data obtained for New Jersey seawater is shown on Figs. 4, 5, and 6. Calculation of the chlorine equivalent yields 24.09 ppb, Table 3. Similar curves were obtained for the bay water sample and resulted in a chlorine equivalent of 10.22 ppb.

The seawater sample was also analyzed under conditions where the less reactive oxidative species would not react. The results are also given on Table 4 and indicate that, of the 24.09 ppb total chlorine equivalent, about two thirds of the contribution is probably due to slower reacting species.

Reanalysis of a laboratory-spiked bay water sample for total chlorine 24 h after immobilization gave 99.2 percent of theoretical recovery at 79.9 ppb

TABLE 3—*Comparison of DPP method versus titration method of parallel analyses of synthetic seawater samples.*

Sample No.	Chlorine Sample Preparation, per litre		Titration Results, ppm	Titration Average, ppm	Polarographic Results, ppm	Polarographic Average, ppm	Comments
	Volume Added to 1 l	Stock Solution[a]					
1	100 μl	stock	3.25 3.01 2.09 2.93	2.82	4.01 3.49 3.81	3.77	outside recommended range for either technique
2	50 μl	stock	1.22 1.09 1.12	1.14	1.457 1.211 1.352	1.340	upper limit for either technique
3	25 μl	stock	0.64 0.60 0.60	0.61	0.638 0.564 0.485	0.562	good agreement
4	200 μl	10/100	0.54 0.50 0.45 0.42	0.48	0.616 0.551 0.459	0.542	good agreement

5	100 μl	10/100	0.25 0.26 0.20	0.24	0.279 0.255 0.270	0.268	good agreement
6	50 μl	10/100	0.15 0.17 0.17	0.16	0.125 0.135 0.109	0.123	titration starting to give high results; polarography still predictable
7	25 μl	10/100	0.11 0.10 0.13	0.11	0.0540 0.0574 0.0688	0.0601	titration gives high results; polarography predictable
8	10 μl	10/100	no response		0.0222 0.0182 0.0161	0.0188	no response from titration; polarography still has good sensitivity
9	5 μl	10/100	no response		0.0134 0.0171 0.0111	0.0138	no response from titration; polarography still has good sensitivity
10	blank	blank	no response		no response		

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[a] Chlorine source was NaOCl solution (nominally 25 000 ppm).

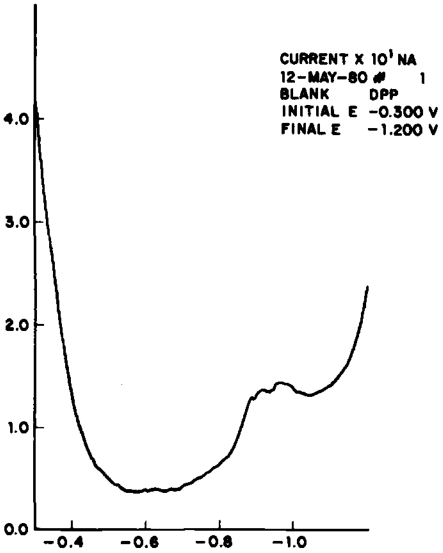

FIG. 4—*New Jersey seawater blank (pH 3.5).*

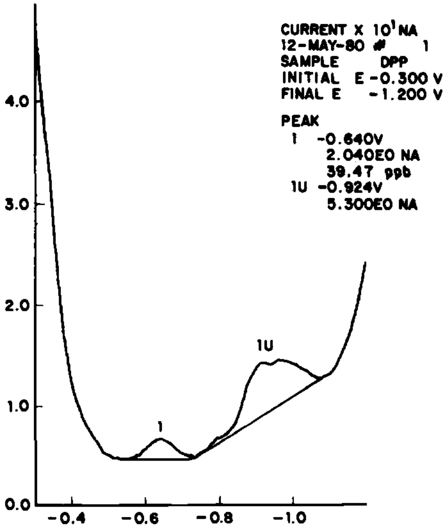

FIG. 5—*PAO in New Jersey seawater (pH 3.5).*

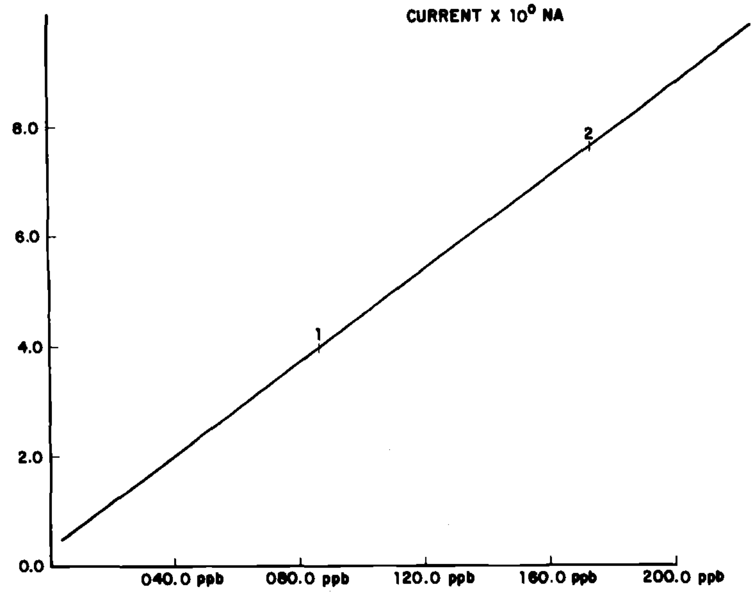

FIG. 6—*Standard addition calibration curve for PAO in New Jersey seawater (pH 3.5).*

chlorine and indicates that samples can be "fixed" in the field for later polarographic analysis with negligible change in the polarographic signal.

Discussion

The polarographic technique described in this paper has been shown to be a viable analytical technique for the determination of chlorine and oxidants at the trace level. It is reliable and the polarographic scan gives the analyst a qualitative indication of the performance of the analysis. The peak shape and position can be an indicator of possible interferences while the ability to observe (and subtract, if necessary) a sample blank is also helpful.

The method is based on the same chemistry as the standard titrimetric methods and agrees well with the amperometric technique. It has been shown to be accurate at chlorine equivalents from 100 ppb down to 5 ppb, where the amperometric technique is suspected to fail. The ability to "fix"

TABLE 4—*Seawater samples.*

Sample Source	pH	KI, mg/ml	Chlorine Equivalent, ppb	Comment
New Jersey seawater	3.5	5	24.09	total residual
New Jersey seawater	6.5	0	0.841	free available
New Jersey seawater	6.5	5	7.469	free available and slower reacting
Barnagat Bay Water	3.5	5	10.22	total residual

sample concentrations in the field for polarographic analysis, up to at least 24 h later, should prove convenient.

The standard addition technique developed minimizes matrix effects from samples of varying composition, however, a standard curve method may also be used when convenient.

Although this procedure was developed for total residual chlorine equivalent in seawater, analysts should find it useful for other matrices, including fresh water effluents and power plant cooling waters.

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[*2*] *Methods for Chemical Analysis of Water and Wastes,* Method 330.1, U.S. Environmental Protection Agency, Washington, D.C., March 1979.

[*3*] *1976 Annual Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1976, pp. 276–289.

[*4*] Smart, R. B., Lowry, J. H., and Mancy, K. H., *Environmental Science and Technology,* Vol. 13, 1979, p. 89.

Summary

Summary

The papers in this book have been arranged in the following order: (1) the panel discussion, (2) general guidelines and requirements for monitoring high-purity water, and (3) presentations of the newer techniques and applications of monitoring by ion chromatography, atomic absorption spectrometry, specific-ion electrodes, ion-exchange columns, electrical conductivity, a gravimetric technique, and differential pulse polarography. Particular attention has been directed toward the development of on-line instruments that provide continuous measurement by these techniques. The importance of proper sampling techniques, where to sample, sample bottle materials, the preparation of sample bottles, preservation of the samples, and the necessary care and handling of samples have also been emphasized.

J. K. Rice, the introductory session chairman, and the panelists, F. J. Pocock, O. Jonas, T. C. Hoppe, and J. Brown, have discussed the history of the measurement of the quality of high-purity water, the measurement methods now available for measuring the quality of higher-purity water, and the need for continuous on-line instrumentation to provide the chemical control needed in monitoring all volatile types of treatment in the modern high-pressure power plant. The meticulous care and the difficulties involved in measuring 1-ppb levels of impurities have been emphasized. The importance of measuring and minimizing the Cl^- and $SO_4^=$ ingress into the system and the need for monitoring the total organic carbon have been discussed. The need for continuous analyses plus grab sampling of condensate and steam, and the difficulties of sampling properly, choosing the points of sampling, investigating the transfer of corrosion products in the system, and assessing and developing correlation of the collected data have all been given attention. At Ontario Hydro (Toronto, Canada), concentrations of corrosion products were determined by analyzing samples collected on Millipore filters and cation resin–impregnated paper. It was also reported that valveless capillary samplers acted as both sampling probes and pressure reducers to provide unbiased samples of feedwater particulates.

Noll has pointed out that the chemical concentrations allowed in the steam–water cycle are dictated by the low levels specified for the turbine and that the specifications for boiler water, feedwater, condensate, and makeup water then fall in line in logical sequence. Measurements of pH, sodium, and cation conductivity, however, are considered essential. Noll also presented a chart showing the most sensitive monitoring scheme for monitoring cooling water inleakage. The choice of monitoring Na^+, silicon dioxide, or cation

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conductivity was observed to be dependent on the analysis of the cooling water.

Selby has emphasized the need for proper power plant organizational structure and educational requirements for plant chemists in order to attain reliable maintenance and calibration of water quality instrumentation. His data indicate that plants delegating the responsibility of operating and maintaining this instrumentation for water quality control to those responsible for plant chemistry functions had fewer problems with instrumentation and with chemical control.

Pensenstadler, Peterson, Bellows, and Hickam have reported on their 3-year program in six fossil fuel plants, in which thorough studies of the steam-turbine chemical environment and the determination of the source of corrodent species were conducted. This program included the development and application of a continuous on-line analyzer for determining Na^+, oxygen, pH, cation conductivity, and specific conductivity. The steam sample supplied to this analyzer was a cooled, continuously flowing sample taken from a well-designed sampling nozzle in the crossover piping between the intermediate and low-pressure turbines. This point of sampling was chosen because turbine deposits and turbine cracking have been generally observed in this area. In addition, a grab sampling program was simultaneously conducted as a total plant survey, in which samples were taken at multiple locations and submitted to ion chromatography analysis. Although the quality of steam from plants experiencing turbine attack was observed to be within the recommended ranges of Na^+ and cation conductivity most of the time, steam from plants not experiencing turbine attack was generally of higher purity and provided larger margins for error. At some plants high cation conductivity indicated appreciable air inleakage; however, it was observed that it is not known at this time whether such air inleakage is a factor in the general corrosion problem. It was reported that cation conductivity was a better indication of the likelihood of turbine corrosion than the Na^+ determination.

Willhite, Sawochka, and Pearl have demonstrated that cumulative sampling in cation and anion ion-exchange columns for periods of 6500 min provided indicative results for Na^+, Cl^-, and $SO_4^=$ from eleven sample points in nuclear plant studies. There was relatively good agreement between specific ion-electrode results for Na^+ and ion chromatography results for $SO_4^=$ during short-term studies. The sample collection system also included a Millipore 0.45-μm membrane for collecting filterable species before they reached the cation and anion resin columns.

Rawa has observed that there had previously been no accurate method for measuring trace concentrations of anionic constituents but that the new analytical technique of ion chromatography provides a means of identifying and quantifying the anions Cl^-, NO_3^-, $PO_4^{\equiv}$ and $SO_4^=$ at microgram-per-litre levels. The levels of detection are improved approximately a hundredfold by the concentrator column technique.

Girard and Glatz have reported that a nonsuppressed ion chromatography technique offers a new alternative method which avoids the need for a suppressor column and regeneration of said column. The sensitivity to Cl^-, NO_3^-, and $SO_4^=$ in this technique is nearly equal to that in the conventional technique.

Simpson, Robles, and Passell have reported the development of an on-line instrument employing ion chromatography for measuring anions and cations at microgram-per-litre levels in an electric generating plant. This development also includes an on-line sampling and calibration system.

Diggens has advised that while specific-ion electrode technology has been used successfully in laboratory measurement for many years, recent developments in which these electrodes are less complex and more reliable are proving that this measurement technique, particularly for sodium, is one of the most reliable and useful in the modern power plant. Other electrodes for Cl^-, chlorine, Ca^{++}, $SO_3^=$, and $S^=$ are reported to be accurate in the microgram-per-litre range.

Eherts has reported that he has not found the results obtained with Na^+ ion analyzers to agree well with the actual system concentration variance obtained by atomic absorption spectrometry or ion chromatography. His experience indicates that this measurement should be restricted to systems characterized by low solids content and that the nonrepresentative variations observed correlate with flow–pressure perturbations in the system.

Skriba, Gockley, and Battaglia have reported in their paper that the new and automated flameless atomic absorption technique is usable as an on-line instrument for the determination of calcium, magnesium, and aluminum in the 0 to 10-ppb range in an operating nuclear power plant.

Fisher has traced the progress that has been made in improving the quality of high-purity water over the past 40 years but admits that the goal of attaining zero impurities has not been attained. She has reported that present purity requirements, particularly those required for specific industries, have exceeded the monitoring ability of the electrical conductivity method, which means that this measurement must be augmented by the inclusion of measurements of specific impurities.

Light and Sawyer have reported that the maximum resistivity of pure water occurs at a pH of 7.039, not 6.998, which corresponds to approximately 0.8 μg/litre of sodium hydroxide. They consider the measurement of resistivity of very pure water to be the simplest and most reliable method of determining its overall purity. They have also pointed out that such measurements should be either carefully temperature compensated or made at the reference temperature.

Lane, Sollo, and Neff have reported on an in-line electric conductivity method for monitoring anions in power plant system waters. This method eliminates interference by amines by incorporating a hydrogen exchanger in the instrument flow and eliminates the effects of temperature variations and carbon dioxide by measuring conductivity at constant atmospheric boiling water temperature by means of an electric heater. Data show that 1 to 5 μg/litre of Cl^- + $SO_4^=$ can be determined by this technique. More accurate cation conductivity results can be obtained at atmospheric boiling temperature than at 25°C because possible trace amounts [0.01 to 0.05 mg/litre of carbon dioxide (CO_2)] present have a minimal conductivity at this higher temperature. It was also demonstrated that ammonia (NH_3) and CO_2 in a two-component system can be determined from a computer table when pH, conductivity, and temperature values are provided.

Elmiger, Mravich, and Stauffer have reported on a new continuous sample evaporator which has been developed for concentrating the contaminant present in plant systems to levels at which determinations can be made by modern analytical techniques. Chemical species recovery within ±20 percent of the absolute amount added was reported. Further research to investigate the methods of concentration, the effect of sample container materials, and so on are required.

Washinger and Kark have described a polarographic technique for determining chlorine and oxidants at trace levels. It is a method based on the same chemistry as the standard titrimetric methods and the results agree well with those of the amperometric technique. The polarographic technique has the advantage over the amperometric method of being accurate at chlorine equivalents ranging from 100 μg/litre down to 5 μg/litre, at which level the amperometric technique is suspected of failing. This method is reported also to be useful in seawater systems and in determining other types of oxidants.

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