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ERRATA

On page 7, Table A-1 should read as follows:

Table A-1—Example Calculations

Calculation to be Performed	Unit of Measure for All Ions	Calculation
Total sodium (Na) content in mg/L (Interferences: The elements that are not determined constitute an error in that these undetermined elements, such as potassium and lithium, are reported as sodium.)	mg/L	Na = 23 × {[(mg/L Cl)(35.453) + (mg/L SO_4)(48.0308) + (mg/L CO_3)(30.0047) + (mg/L HCO_3)(61.0173)] – [(mg/L Ca)(20.04) + (mg/L Mg)(12.156) + (mg/L Ba)(68.67) + (mg/L Fe)(27.9235)]}
Total dissolved solids	mg/L	TDS = Na + Ca + Mg + Ba + Fe + Cl + SO_4 + CO_3 + HCO_3
Resistivity = summation	mg/L × resistivity factor	R = Na + [(mg/L Ca)(0.95) + (mg/L Mg)(2.0) + (mg/L Cl) + (mg/L SO_4)(0.5) + (mg/L HCO_3)(0.27) + (mg/L CO_3)(1.26)]

Manual of Petroleum Measurement Standards Chapter 17—Marine Measurement

Section 3—Guidelines for Identification of the Source of Free Waters Associated With Marine Petroleum Cargo Movements

FIRST EDITION, APRIL 1992

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005

Manual of Petroleum Measurement Standards Chapter 17—Marine Measurement

Section 3—Guidelines for Identification of the Source of Free Waters Associated With Marine Petroleum Cargo Movements

Measurement Coordination Department

FIRST EDITION, APRIL 1992

American
Petroleum
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FOREWORD

This publication covers standard guidelines for identification of the source of free waters associated with marine petroleum cargo movements.

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Suggested revisions are invited and should be submitted to the director of the Measurement Coordination Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

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Chapter 17—Marine Measurement

SECTION 3—GUIDELINES FOR IDENTIFICATION OF THE SOURCE OF FREE WATERS ASSOCIATED WITH MARINE PETROLEUM CARGO MOVEMENTS

17.3.1 Introduction

17.3.1.1 The presence of free water is a factor in marine custody transfers of bulk petroleum, especially in the case of crude oil cargoes.

17.3.1.2 The source and type of water contamination encountered can be identified if proper sampling and testing procedures are followed.

17.3.1.3 Depending on the type of loading involved (i.e., shoreside-to-vessel, offshore buoy, or vessel-to-vessel) water contamination can involve produced formation waters, export-processing wash water, sea-line leakage, ballast water within the vessel, or ballast water from a lightering vessel.

17.3.1.4 In addition, the party receiving the cargo at discharge may also encounter waters that entered the vessel during its voyage.

17.3.1.5 This chapter outlines recommended water-sampling locations and testing procedures to determine the most probable source(s) of free water volumes that occur in custody transfer.

17.3.2 Scope and Field of Application

17.3.2.1 This chapter recommends the water samples and volumes to be taken, the containers to be used, the care and distribution of the samples, and the analytical procedures for use in identifying the probable source(s) of free water associated with marine petroleum cargoes. This procedure should be considered when significant amounts of free water are detected.

17.3.2.2 This chapter includes the following:

a. Basic sampling and on-site testing procedure.
b. Basic analytical procedures.
c. Appendix A—Interpretation and Presentation of Results.
d. Appendix B—Comprehensive Investigative Program.
e. Examples of analysis and report forms.
f. The notice that final results should be understood to apply on the specific voyage under consideration.

17.3.3 Referenced Publications

API
  Manual of Petroleum Measurement Standards (MPMS)
    Chapter 3—"Tank Gauging" (in press)

Note: Standard 2545, "Method of Gaging Petroleum and Petroleum Products," currently covers this subject.

    Chapter 8—"Sampling"
    Chapter 8.1, "Manual Sampling of Petroleum and Petroleum Products," First Edition, October 1989
    Chapter 8.2, "Automatic Sampling of Petroleum and Petroleum Products," First Edition, April 1983
    Chapter 17—"Marine Measurement"
    Chapter 17.1, "Guidelines for Marine Cargo Inspection," Second Edition, January 1986
    Chapter 17.2, "Measurement of Cargoes on Board Marine Vessels," First Edition, July 1990
  RP 45 *Analysis of Oilfield Waters* (Dallas: API, 1968)
ASTM
  The Annual Book of ASTM Standards, Section 11, Water and Environmental Technology
    Volume 11.01, Water
    Volume 11.02, Water
Elsevier Scientific Publishing Company
  Geochemistry of Oil Field Waters, Collins
National Association of Corrosion Engineers
  Introduction to Oilfield Water Technology, Ostroff
Prentice Hall, Inc.
  Oceans, Their Physics, Chemistry, and General Biology Series, Sverdrup, Johnson, & Fleming
CRC Press
  CRC Handbook of Marine Science, Smith
John Wiley & Sons
  The Sea, Volume 5, *Marine Chemistry,* Goldberg
Clearinghouse for Federal Scientific and Technical Information
  Pacific Ocean, Volume 3, *Chemistry of the Pacific Ocean,* Kort
Texas A&M University, Department of Oceanography
  Chemistry and Analysis of Trace Metals in Sea Water, Slowey
Academic Press
  Chemical Oceanography, Riley, Skirrow
American Association of Petroleum Geologists
  Fluids in Subsurface Environments, A Symposium, Young, Galley

17.3.4 Equipment

17.3.4.1 SAMPLING EQUIPMENT

Equipment for sampling free water is described in Chapters 8.1 and 8.2.

17.3.4.2 SAMPLING CONTAINERS

Sampling containers should be clean, one quart or one liter containers made of glass or high-density polyethylene.

17.3.4.3 IDENTIFICATION LABELS OR TAGS

Labels or tags should contain information listed in 17.3.6.6 and must be able to be securely affixed to sample containers. See Figure 1 for sample label.

17.3.4.4 IDENTIFICATION SEALS

Identification seals should be of the single use type with unique number codes.

17.3.4.5 ADDITIONAL EQUIPMENT

A portable pH meter is the preferred equipment for determination of pH of samples on site. The pH test papers may be used when water samples are clear enough to yield accurate readings.

17.3.5 Measurement and Sampling of Free Water

17.3.5.1 Measuring and sampling are done in accordance with the procedures and equipment outlined in Chapters 3, 8, 17.1, and 17.2.

17.3.5.2 Free water can be measured and sampled during cargo inspection or at any other time during the cargo movement.

17.3.6 Basic Sampling and On-Site Testing Procedure

17.3.6.1 Detection and measurement of free water are performed as described in 17.3.5.

17.3.6.2 A letter of protest may be issued to the appropriate parties for any free water found in cargo tanks prior to or after loading or prior to discharge per Chapter 17.1, "Guidelines."

17.3.6.3 The procedure for sampling the free water is described in 17.3.5.

17.3.6.3.1 Samples of free water should be taken when the free water level in any compartment is within the capabilities of the appropriate sampling equipment.

17.3.6.3.2 When the free water level in any compartment exceeds 1 foot (30 centimeters), additional spot samples shall be taken at a minimum of 1-foot increments. The first sample should be taken near the oil-water interface, each subsequent sample from the next increment downward, and the final sample from the bottom of the compartment. This procedure minimizes any disturbance of the free water.

17.3.6.3.3 Care should be exercised to obtain free water samples that are as free of petroleum as is practical.

17.3.6.4 Locations from which water samples are to be taken should include (if applicable) but are not limited to the following:

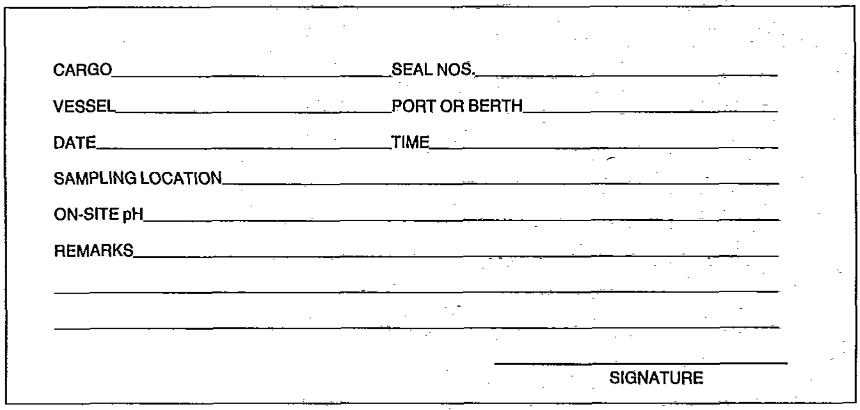
a. Water under cargo in shore storage tanks, either before loading or after discharge (including rainwater on roof, if any).
b. Water drawn off shore tanks from water drain.
c. Lightering vessels.
d. Seawater surrounding vessel at level of sea suctions.
e. Ballast or deballast lines.
f. Underwater load lines or connecting hoses after being displaced into cargo tanks.
g. Any other potential source of water entering cargo before or during loading or discharge.
h. Vessel compartments before loading, after loading, before discharge, and after discharge.
  1. Cargo tanks.
  2. Ballast tanks.
  3. Noncargo areas.
  4. Lines.
  5. Any area containing water.

17.3.6.5 Each sample should consist of a container as described in 17.3.4.2 filled to capacity with the water sample. Each sample shall be prepared in duplicate.

Note: Hydrocarbon sampling is predicated on a buildup of hydrostatic pressure, so the glass bottle is filled ⅞ full in order to avoid problems. However, in this system, any oxygen (air) introduced during sampling can result in reactions and changes in pH or in precipitates and other deleterious effects. Therefore, it is technically correct to fill the glass bottles to capacity. However, should shipping or handling procedures preclude this practice, then the consequences must be accepted. If high-density polyethylene bottles are used, they can be squeezed to exclude the air before they are sealed.

17.3.6.6 Identification labels or tags (17.3.4.3) should be completed and attached or applied to each sample. See Figure 1 for an example of an acceptable sample label or tag. Data that should be listed on the label are as follows:

a. Cargo identification.
b. Seal numbers (17.3.4.4).
c. Vessel name.
d. Port or berth.
e. Date and time of sampling.
f. Location (17.3.6.4).
g. Level of sampling, for example, 1 foot or center of water depth.
h. On-site pH reading.
i. Remarks.
j. Identity of sampling personnel.



CARGO____________________SEAL NOS.____________________

VESSEL____________________PORT OR BERTH____________________

DATE____________________TIME____________________

SAMPLING LOCATION____________________

ON-SITE pH____________________

REMARKS____________________

SIGNATURE

Figure 1—Example of Sample Label for Water Source Identification

17.3.6.7 Each water sample should be tested on site for pH as soon as practical after sampling. Temperature changes, oxidation as a result of entrained air during sampling, and release of entrained gases due to the pressure change may result in changes in pH.

Note: See Appendix A.4.5 for significance of on-site pH testing.

17.3.6.7.1 Sampling personnel should be trained in pH determinations. The manufacturer's instructions regarding use of testing equipment (medium) must be carefully followed for optimum test results.

17.3.6.7.2 The on-site pH result should be recorded on the sample identification tag immediately after testing.

17.3.6.8 The procedure for the distribution of samples is as follows.

17.3.6.8.1 After completion of on-site testing (17.3.6.7), appropriate seals (17.3.4.4) should be installed.

17.3.6.8.2 One set of samples should be retained at the point of origin for a minimum of 90 days from date of sampling or as agreed by requesting parties.

17.3.6.8.3 One set of samples will be delivered for independent testing as soon as possible after sampling.

17.3.6.8.4 A sample receipt must be completed and signed by each party receiving a sample. See the example of a Chain of Custody Record in Figure 2.

17.3.6.9 In addition to requirements outlined in 17.3.6.6, a report or letter summarizing the events of the voyage must accompany the samples. Minimum requirements for the report or letter are as follows:

a. The loading and discharge ports.
b. Dates and times of each event or occurrence.
c. Ports of call and lighterings.
d. Voyage routes, including seas crossed.
e. Any significant atmospheric or meteorological disturbance during voyage, loading, or discharge such as hurricanes, typhoons, or cyclones.
f. A complete list of all samples taken accompanied by the pertinent data as the identification labels or tags (17.3.6.6).
g. Heating records if cargo was heated.
h. Any other anomalies that could affect the cargo.

17.3.6.10 The procedure for the Report of Sampling is as follows.

17.3.6.10.1 A Report of Sampling will be issued to all interested parties.

17.3.6.10.2 The Report of Sampling should outline the source of each sample, date of sampling, method and equipment used, name of sampling party, seal identification, field pH test result, and distribution of samples.

17.3.6.10.3 The Report of Sampling should also specify any elements of this guideline that could not be followed.

17.3.7 Basic Analytical Procedures

17.3.7.1 Methods for performing analytical testing are referenced in API Recommended Practice 45.

17.3.7.2 Minimum tests to be performed for each sample submitted to the laboratory are listed in Table 1.

17.3.7.3 The procedure for the presentation of analytical data is as follows.

17.3.7.3.1 Results of all laboratory testing will be presented to interested parties in a report of analysis issued by the testing laboratory for each sample submitted, following instructions and format in Appendix A.2 and A.3. Any comments, including analytical anomalies, will be expressed on each report.

Method of Shipment: Shipped by: XYZ Express, ABC Inspection Co., Inc., City, Country

Received for Analytical Laboratories Date Time

LABORATORY NUMBER SAMPLE DESCRIPTION

Water Sample

Vessel____

[redacted] Vessel Tank ? Center on arrival at________________________________

Company Name________________________, City, Country, Date, Time 0000 hrs

Seal #________________.

Water Sample

Vessel____

[redacted] Vessel Tank ? Port on arrival at________________________________,

Company Name________________________, City, Country, Date, Time 0000 hrs

Seal #________________.

Water Sample

Vessel____

[redacted] Vessel Tank ? Starboard on arrival at________________________________,

Company Name________________________, City, Country, Date, Time 0000 hrs

Seal #________________.

Water Sample

[redacted] From______________________________Bay at Sea Suction Level on Date, Time 0000 hrs

Seal #________________.

Received by: Date Time Relinquished by: Date Time

Received by: Date Time Relinquished by: Date Time

Received by: Date Time Relinquished by: Date Time

Figure 2—Sample Receipt for Chain of Custody Record

17.3.7.3.2 Interpretation of data and conclusions will be based on the constraints in Appendix A.4. The summary report will be prepared by a trained or qualified person experienced in the identification of the sources of free waters associated with petroleum.

Note: The person(s) performing the interpretation should (a) be knowledgeable of the reactive chemistry and analytical problems associated with highly concentrated, saline solutions, (b) be familiar with the logistics of marine petroleum cargo movements, and (c) have at their disposal as complete a history of the samples (17.3.6.9 and 17.3.6.10) as can be supplied in order to weigh all the factors that enter this complex system.

Table 1—Minimum Test Requirements

Constituent	Symbol	Procedure
Specific gravity		Hydrometer
Resistivity		Meter
Chlorides	Cl	Silver nitrate titration
Sulfate	SO_4	Barium chloride
Carbonate	CO_3	Titration (alkalinity)
Bicarbonate	HCO_3	Titration (alkalinity)
Hydroxide	OH	Titration (alkalinity)
pH		pH Meter
Sodium + potassium	Na + K	Calculate, report as Na
Calcium	Ca	Titration
Magnesium	Mg	Titration
Iron	Fe	Titration
Barium	Ba	Precipitation

APPENDIX A—INTERPRETATION AND PRESENTATION OF RESULTS

A.1 General Statements

A.1.1 Comparisons of sample patterns and major-ion to minor-ion ratios provide identification of source waters.

A.1.2 In order to establish a uniform basis of comparison, each sample component in a series must be analyzed using the same test method.

A.1.3 The volume of sample should not be diluted or extended in order to perform a more extensive battery of tests. Destroying the natural buffering that exists in these samples changes the solution parameters or ion concentration, and large errors result.

A.2 Expression of Analytical Results

A.2.1 Milligrams per liter (mg/L) is the most common weight-to-volume relationship used to express concentration of dissolved components. Milligrams per liter can be converted to parts per million (ppm) using the expression ppm = (mg/L)/density (kg/L). However, within normal analytical precision and accuracy of these analyses, ppm = (mg/L)/(specific gravity).

A.2.2 Milliequivalents per liter (meq/L) is a weight-to-volume relationship obtained by dividing the weight of the component by its milliequivalent weight.

Note: See API Recommended Practice 45 for values to be used in this computation.

A.2.3 All data except pH, resistivity, and relative density shall be reported in milligrams per liter and milliequivalents per liter.

A.2.4 The dimensions of the pH, resistivity, and relative density will be defined by the methods of calculation presented in the analytical procedure (17.3.7).

A.2.5 Table A-1 contains examples of the calculations that are acceptable for determining total concentrations of specific ions or constituents.

A.3 Report Form

An example of a report form is depicted in Figure A-1.

A.3.1 A separate report should be made for each sample.

A.3.2 Data will be presented in tabular form as well as by *Stiff-Davis plot or other mineral patterns*. In the *Stiff-Davis plot* the positive ions are plotted to the left and the negative ions to the right of a vertical line that represents zero. The connected points provide a pattern.

A.3.3 Each sample is plotted using the standard coordinates of one scale unit representing 100 milliequivalents of sodium or chloride ions and 10 milliequivalents of the other ions.

A.3.4 All samples are replotted that have off-scale parameters on the first plot or that have insufficient definition. Atypical coordinates that are useful are one scale unit represents 1000 milliequivalents of sodium or chloride and 100 milli-equivalents of the other ions.

Note: See the example of the Comprehensive Report Form (Figure A-2) and the Delaware River plot (Figure A-3) in the standard coordinates and the Delaware River Enhanced plot (Figure A-4), where the coordinates have been changed to enhance the plot.

Table A-1—Example Calculations

Calculation to Be Performed	Unit of Measure for All Ions:	Calculation
Total sodium (Na) content	milliequivalents per liter= meq/L	Na=23 x {[(meq/L Cl) (35.453) + (meq/L SO_4) (48.0308) + (meq/L CO_3) (30.0047) + (meq/L HCO_3) (61.0173)] - [(meq/L Ca) (20.04) + (meq/L Mg) (12.156) + (meq/L Ba) (68.67) + (meq/L Fe) (27.9235)]}
Total dissolved solids (TDS)	mg/L	TDS = Na + Ca + Mg + Ba + Fe + Cl + SO_4 + CO_3 + HCO_3
Resistivity = summation	mg/L × resistivity factor	R = Na + [(mg/L Ca) (0.95) + (mg/L Mg) (2.0) + (mg/L Cl) + (mg/L SO_4) (0.5) + (mg/L HCO_3) (0.27)+ (mg/L CO_3) (1.26)]

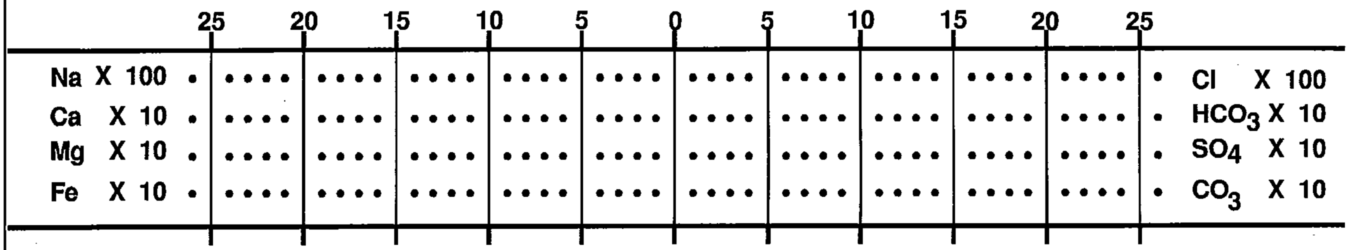
COMPANY NAME ______________________________

SAMPLE NAME (I.D.) ______________________________

DATE/TIME SAMPLED ______________________________

LABORATORY NUMBER ______________ **SEAL NUMBER** ______________

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY __________ pH __________ RESISTIVITY (ohm/cm) __________ @ __________

	meq/L	mq/L	ppm/wt
ANIONS			
Chloride			
Bicarbonate			
Sulfate			
Carbonate			
CATIONS			
Sodium + Potassium (Calc)			
Calcium			
Magnesium			
Iron			
Barium			

Magnesium/Calcium Ratio ______________

Total Dissolved Solids (calculated) ______________

Total Dissolved Solids (experimental) ______________

Figure A-1—Example of Basic Report Form for Coma Water Identification Analysis Data

A.4 Interpretation

Although some of these tests used individually are excellent indicators of the origin of a certain water, there is the possibility of pollution, contamination, or mishandling of samples. It is therefore recommended that several of the test parameters be used to establish a data base and that each water sample be examined on the basis of a battery of tests rather than one individual test.

A.4.1 SPECIFIC GRAVITY

Specific gravity must be used in calculating concentrations of components, and several samples in a series with essentially the same gravity should be from the same source.

Note: Immediate on-site determination of sampled water gravities can provide early indication that the waters being detected may or may not be of a shipborne source. A Specific Gravity Hydrometer in the range of 1.000 to 1.220 in 0.002 divisions is recommended for the on-site investigation of free water samples withdrawn from beneath cargoes of crude oil petroleum.

A.4.2 RESISTIVITY

Resistivity is a measure of total ion concentration. Several samples in a series with essentially the same resistivity should be from the same source.

A.4.3 CHLORIDES

Chlorides are present in seawater at some 19,000 to 21,000 ppm by weight and vary near shorelines due to freshwater discharge or to oceanic basins having high evaporation rates. However, chlorides are consistent in specific areas. Reservoir waters, salt dome, and formation waters have higher concentrations, but concentrations vary near the edges of the formation. Formations other than salt domes may have water fresher than seawater.

A.4.4 SULFATES

Sulfates in sea water have concentrations of about 2500 to 3000 ppm by weight, while in reservoir water, concentrations are considerably less, usually 1000 ppm by weight or less. See A.4.9 for applicable comments.

A.4.5 CARBONATE, BICARBONATE, HYDROXIDE, AND pH

Carbonate, bicarbonate, hydroxide, and pH must be evaluated concurrently, as a unit. The pH of seawater is very consistent but may vary due to changes in local conditions and handling. *The pH should be determined as soon as possible after the sample is taken because oxygen can be introduced due to aeration during sampling, samples can be subjected to temperature changes during shipment, and the water layer below a head of oil is under some pressure and therefore may contain entrained gases. These factors, coupled with the commingling of different sources of water, can result in reactions that change the pH after standing.* The pH is examined in conjunction with carbonates and bicarbonates to help indicate origin. Seawater, with a pH of 7.3, does not contain any carbonates and contains less than 100 ppm by weight of bicarbonates. On the other hand, reservoir water with a high pH contains hundreds of parts per million by weight of bicarbonates. The hydroxide (OH^{-}) content is useful because it is indicative of refinery process water such as spent caustic in the shore tanks.

A.4.6 SODIUM AND POTASSIUM

Sodium and potassium are present in seawater at a total concentration of 12,000 to 13,000 ppm by weight. These values vary near shorelines due to freshwater discharges or to basins that have high evaporation rates. However, the values are consistent in specific areas. Reservoir waters found in salt dome formations have higher concentrations, although concentrations vary near the edges of the formation. Formations other than salt domes may have considerably more fresh water than is found in the seas.

Note: The calculation technique is recommended, since determination of the individual components at these high concentrations is not practical in the average laboratory.

A.4.7 CALCIUM AND MAGNESIUM

Calcium (Ca^{-})and Magnesium (Mg^{-}) are 1300 and 400 ppm by weight, respectively. Much less magnesium is present in reservoir water, and calcium varies somewhat with geologic formations found in conjunction with the producing field.

A.4.8 IRON

Iron (Fe) is present due to corrosion of pipelines and tanks. The content is determined because it must be considered in the total-ion calculation.

A.4.9 BARIUM

Barium (Ba^{-})content is very low in all waters except formation water (brines). However, barium must be evaluated in conjunction with the sulfate ($SO_4^{=}$) concentration because barium cannot exist if sulfate ion is present. Barium reacts with the ion to form insoluble salts or precipitates.

A.4.10 MAGNESIUM TO CALCIUM RATIO

The magnesium to calcium (Mg/Ca) ratio is used in conjunction with milligram per liter amounts. In seawater the Mg/Ca ratio is consistent at essentially 3.0 milligrams per liter. Formation waters vary with formation conditions and handling, but their ratios are less than 2.0 and may even drop below 1.0 milligrams per liter.

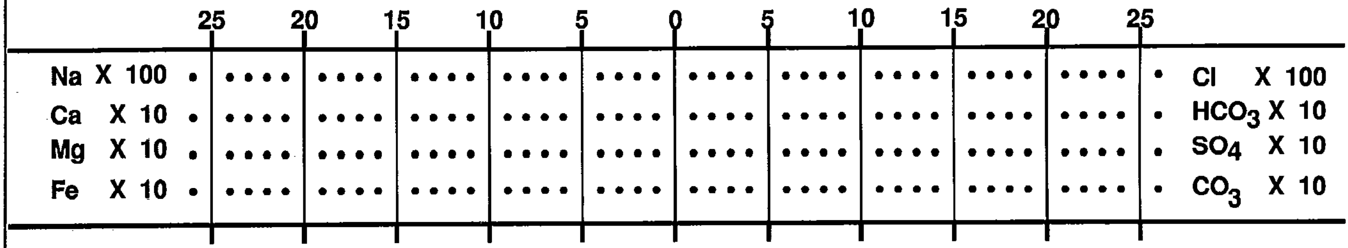
COMPANY NAME ____________________

SAMPLE NAME (I.D.) ____________________

DATE/TIME SAMPLED ____________________

LABORATORY NUMBER __________ **SEAL NUMBER** __________

MINERAL PATTERN MEQ/LITER COMPREHENSIVE REPORT FORM



SPECIFIC GRAVITY ________ pH ________ RESISTIVITY (ohm/cm) ________ @ ________

	meq/L	mq/L	ppm/wt
ANIONS			
Chloride	________	________	________
Bicarbonate	________	________	________
Sulfate	________	________	________
Carbonate	________	________	________
Hydroxide	________	________	________
Iodine	________	________	________
CATIONS			
Sodium + Potassium (Calc)	________	________	________
Calcium	________	________	________
Magnesium	________	________	________
Iron	________	________	________
Barium	________	________	________
Strontium	________	________	________
Silica	________	________	________

Magnesium/Calcium Ratio ________

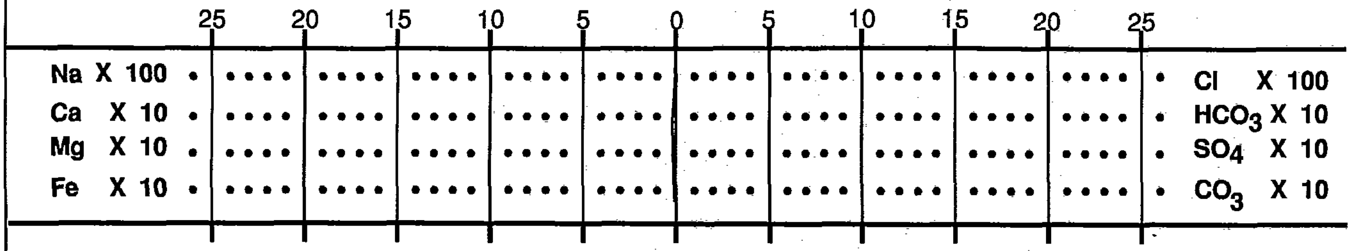
Total Dissolved Solids (calculated) ________

Total Dissolved Solids (experimental) ________

Figure A-2—Example of Comprehensive Report Form for Coma Water Identification Analysis Data

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	DELAWARE RIVER		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY	0.998	pH	7.3	RESISTIVITY (ohm/cm)	90	@	-0-

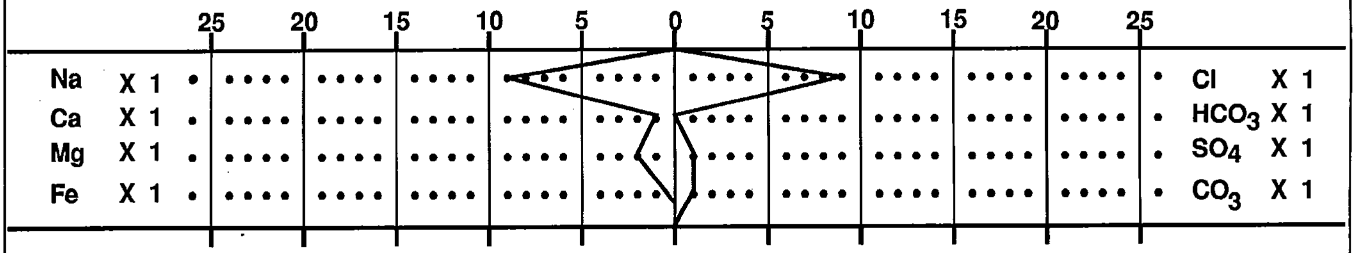
ANIONS	meq/L	mg/L	ppm/wt
Chloride	9	308	307
Bicarbonate	0	0	0
Sulfate	1	65	65
Carbonate	1	42	42
CATIONS			
Sodium + Potassium (Calc)	8.0	184	184
Calcium	1	24	24
Magnesium	2	27	27
Iron	0	0	0
Barium	0	0	0

Magnesium/Calcium Ratio	1.1
Total Dissolved Solids (calculated)	651
Total Dissolved Solids (experimental)	743

Figure A-3—Report Form for Coma Water Identification Analysis Data for Delaware River

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	DELAWARE RIVER - ENHANCED PLOT		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER ENHANCED PLOT



SPECIFIC GRAVITY 0.998 pH 7.3 RESISTIVITY (ohm/cm) 90 @ -0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	9	308	307
Bicarbonate	0	0	0
Sulfate	1	65	65
Carbonate	1	42	42
CATIONS			
Sodium + Potassium (Calc)	8.0	184	184
Calcium	1	24	24
Magnesium	2	27	27
Iron	0	0	0
Barium	0	0	0

Magnesium/Calcium Ratio	1.1
Total Dissolved Solids (calculated)	651
Total Dissolved Solids (experimental)	743

Figure A-4—Report Form for Coma Water Identification Analysis Data for Enhanced Plot of Delaware River

A.4.11 DILUTION EFFECTS

Dilution effects preclude using absolute values and promote the use of ratios and plots such as the Stiff-Davis plot. Large volumes of contaminated water may be badly layered and thus require very sophisticated sampling techniques in order to get representative samples of each of the several layers and thus determine the several sources.

A.4.12 APPROXIMATE VALUES

Approximate values of river, city, and formation waters are found in Table A-2. However, formation waters vary in composition such that any comparison must be site specific.

A.4.13 SEAWATER

Component Ranges of Seawater are found in Table A-3. Examples of specific seawater samples and actual analyses of seawater are listed in Tables A-4 and A-5.

A.4.14 REPORT FORMS

Examples of report forms and plots compiled from the data in the foregoing tables are shown in Figure A-5.

A.4.15 OTHER PARAMETERS

A number of other parameters and components have been found to be indicative of the source of waters found in cargoes. However, their determination requires more sophisticated analytical techniques than those listed in API Recommended Practice 45. Additional techniques are included in Appendix B.

Strontium is an example of one of these parameters. Its concentration is usually about 15 ppm by weight in seawater and at least twice that value in reservoir water, at times measuring several hundred milligrams per liter.

Total dissolved solids (TDS) is another example. TDS is usually reported as determined using a meter and by calculation. The calculation (summation) does yield a check for total ion content.

Table A-2—Approximate Values of Waters

Constituent (mg/L))	River Water	City Water	Brine(Formation)		
			A	B	C
Carbonate	0		0	0	0
Bicarbonate	219	120	159	281	12
Sulfate	40	2	157	42	0
Chloride	20	11	29,573	72,782	101,479
Calcium	59	1	881	2,727	9,226
Magnesium	10	1	498	655	1,791
Sodium + potassium	30	51	17,258	42,000	46,000
Iron, total	0.1	0.4	135	13	35
Barium				24	127
TDS	378.1	186.4	46,661	118,524	158,670
pH	7.7	7.6	6.5	6.5	5.0

Note: *Above examples are for illustrative purposes only.*

Table A-3—Component Ranges of Seawater

Component		Approximate Values
Sulfates	ppm wt.	2,000–3,500
	mg/L	2,050–3,600
Strontium	ppm wt.	6–14
	mg/L	6–14
Magnesium	ppm wt.	1,100–2,000
	mg/L	1,125–2,050
Calcium	ppm wt.	250–500
	mg/L	250–500
Magnesium/Calcium Ratio		3–6
Chlorides	ppm wt.	14,000–25,000
	mg/L	14,350–25,500
Sodium	ppm wt.	9,000–14,000
	mg/L	9,225–14,350
pH - Hydrogen ion $^+$		7–8
Carbonates	ppm wt.	0
	mg/L	0
Bicarbonates	ppm wt.	less than 140
	mg/L	less than 140
Specific Gravity	gm/cc	1.02–1.03
Total Dissolved Solids	ppm wt.	21,000–37,000
	mg/L	21,500–38,000

Note: Above examples are for illustrative purposes only.

Table A-4—Examples of Specific Seawater Samples

	Singapore SBM Seawater	Japan Keiypo Sea Berth	France SBM Sete	Yoshido Maru Seawater	Egypt Ain Sukhna Red Sea	Sidi Kerir Oct. 8, 1981 Seawater	Sidi Kerir Sept. 16, 1981 Seawater	Juaymah Sept. 29, 1980 Seawater
Chloride	17,700	18,700	21,300	21,300	24,300	22,500	22,500	22,500
Sulfate	2,130	2,550	2,550	2,870	3,250	3,100	3,220	3,080
Carbonate	0	0	0	0	0	0	0	0
Bicarbonate	44	65	75	63	76	78	76	80
Sodium	10,000	9,880	10,500	10,900	14,000	11,000	13,600	11,800
Potassium	281	181	245	188	300	260	191	
Calcium	384	383	250	456	330	424	482	405
Magnesium	1,190	1,180	1,080	1,300	2,000	1,590	1,500	1,380
Iron	<1	<1	<1	<1	<1	<1	<1	<1
Barium	1	<1	1	1	1	<1	1	1
Strontium	6	7	8	8	8	8	9	11
Specific gravity	1.0175	1.0283	1.0301	1.0270	1.0329	1.0304	1.0288	1.0312
Resistivity	15.0	14.8	14.0	13.6	12.0	13.0	12.0	12.6
pH	7.4	7.6	8.4	7.5	8.2	5.8	7.7	7.2
Mg/Ca ratio	3.1	3.1	4.1	2.9	6.1	3.1	3.4	3.4
TDS	0	0	0	0	0	0	0	0

Results are expressed in milligrams per liter (mg/L).

Note: Values contained in this table are presented for illustrative purposes only. These results reference a specific location at a specific point in time and shall not be used as a reference for typical water in a geographic area.

Table A-5—More Examples of Specific Seawater Samples

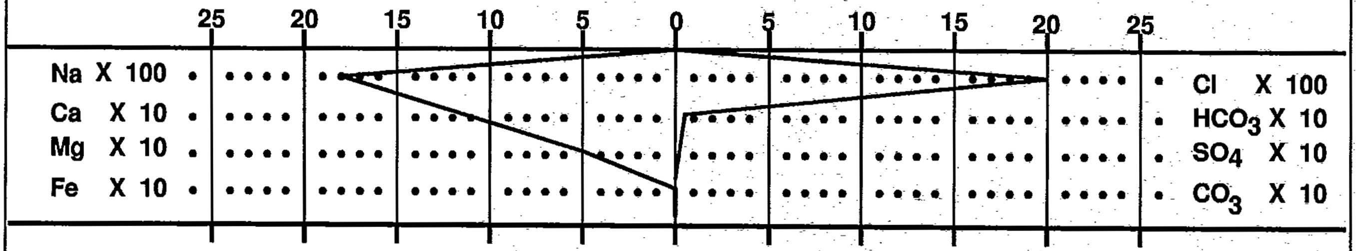
	Pascagoula Offshore			Singapore		Killre, Japan		Korea	
	Port	Lightering	Delaware River	June 14, 1984	June 15, 1984	June 23, 1984	June 24, 1984	June 20, 1984	June 22, 1984
Chloride	16,400	11,300	308	15,400	14,400	18,000	19,900	20,100	20,600
Sulfate	2,150	1,330	65	1,950	2,050	2,460	2,460	2,260	2,360
Carbonate	0	0	0	0	0	0	0	0	0
Bicarbonate	137	97	42	12	11	138	144	127	126
Sodium	10,300	6,560	193	9,030	9,030	11,000	11,100	10,200	9,860
Potassium	328	219	8.08	349	339	420	422	397	376
Calcium	358	238	24	356	356	441	444	410	398
Magnesium	1,120	741	27	1,190	1,180	1,280	1,280	1,190	1,170
Iron	0.489	0.662	0.035	0.096	0.115	0.080	0.099	0.090	0.116
Barium	0.251	0.237	0.027	0.052	0.057	0.049	0.055	0.062	0.087
Strontium	14	12	0.313	7	7	9	9	8	8
Specific gravity	1.026	1.016	0.998	1.017	1.018	1.017	1.013	1.016	1.012
Resistivity	128	155	90	110	110	110	110	110	110
pH	7.5	6.9	7.3	7.9	7.9	8.2	8.2	7.8	7.7
Mg/Ca ratio	3.12	3.11	1.16	3.34	3.32	2.91	2.89	2.90	2.94
TDS	29,600	21,200	743	29,400	29,100	37,300	36,200	34,700	32,700

Results expressed in milligrams per liter (mg/L).

Note: Values contained in this table are presented for illustrative purposes only. These results reference a specific location at a specific point in time and shall not be used as a reference for typical water in a geographic area.

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	BRINE "B"		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY	-0-	pH	6.5	RESISTIVITY (ohm/cm)	-0-	@	-0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	2,053	72,782	0*
Bicarbonate	5	281	0*
Sulfate	1	42	0*
Carbonate	0	0	0*
CATIONS			
Sodium + Potassium (Calc)	1,868	42,955	0*
Calcium	136	2,727	0*
Magnesium	54	655	0*
Iron	0.5	13	0*
Barium	0.3	24	0*

Magnesium/Calcium Ratio	0.2
Total Dissolved Solids (calculated)	119,479
Total Dissolved Solids (experimental)	118,524

*Cannot calculate ppm/wt without having specific gravity.

Figure A-5—More Examples of Report Forms for Coma Water Identification Analysis Data

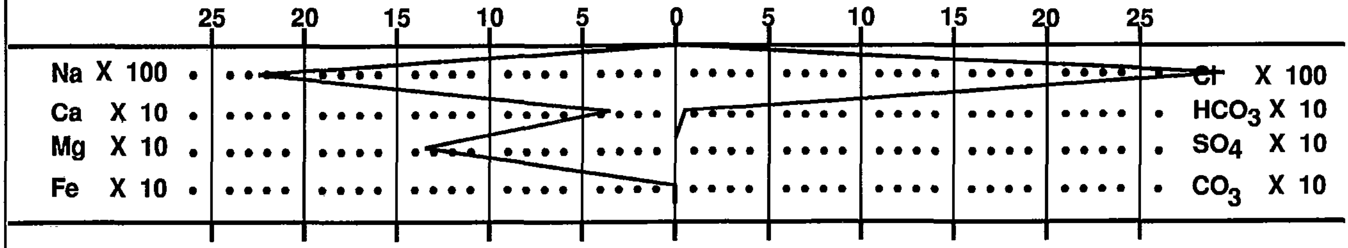
COMPANY NAME NO NAME

SAMPLE NAME (I.D.) BRINE “C”

DATE/TIME SAMPLED -0-

LABORATORY NUMBER -0- **SEAL NUMBER** -0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY -0- pH 5.0 RESISTIVITY (ohm/cm) -0- @ -0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	2,862	101,479	0*
Bicarbonate	0.2	12	0*
Sulfate	0	0	0*
Carbonate	0	0	0*
CATIONS			
Sodium + Potassium (Calc)	2,253	51,790	0*
Calcium	460	9,226	0*
Magnesium	147	1,791	0*
Iron	1	35	0*
Barium	2	127	0*

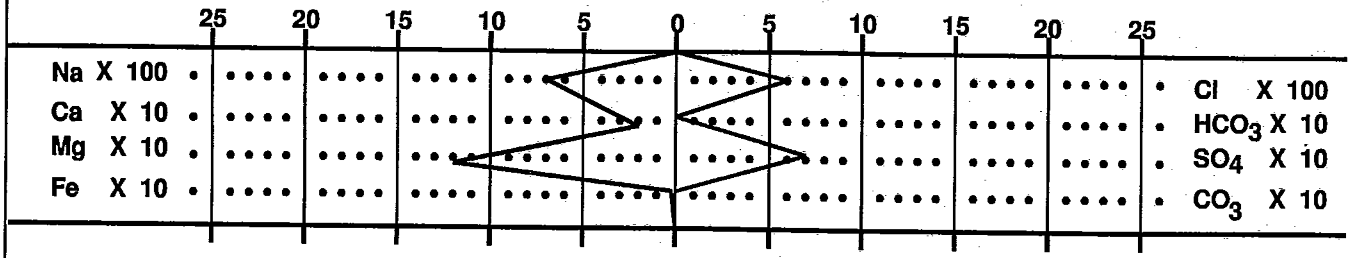
Magnesium/Calcium Ratio	0.2
Total Dissolved Solids (calculated)	164,460
Total Dissolved Solids (experimental)	158,670

*Cannot calculate ppm/wt without having specific gravity.

Figure A-5—Continued

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	JUAYMAH-SEAWATER		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY 1.0312 pH 7.2 RESISTIVITY (ohm/cm) 12.6 @ -0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	635	22,500	23,202
Bicarbonate	1	80	82
Sulfate	64	3,000	3,176
Carbonate	0	0	0
CATIONS			
Sodium + Potassium (Calc)	567	13,025	13,431
Calcium	20	405	418
Magnesium	114	1,380	1,423
Iron	0.03	1.0	1.0
Barium	0.01	1.0	1.0

Magnesium/Calcium Ratio	3.4
Total Dissolved Solids (calculated)	40,472
Total Dissolved Solids (experimental)	NOT RUN

Figure A-5—Continued

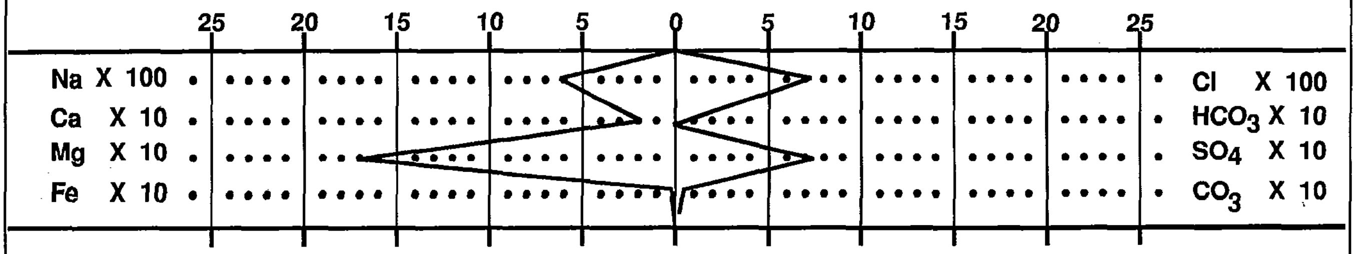
COMPANY NAME NO NAME

SAMPLE NAME (I.D.) EGYPT-AIN SUKHNA-RED SEA

DATE/TIME SAMPLED -0-

LABORATORY NUMBER -0- **SEAL NUMBER** -0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY 1.0329 pH 8.2 RESISTIVITY (ohm/cm) 12 @ -0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	685	24,300	25,099
Bicarbonate	1	76	79
Sulfate	68	3,250	3,357
Carbonate	0	0	0
CATIONS			
Sodium + Potassium (Calc)	574	13,185	13,619
Calcium	16	330	341
Magnesium	165	2,000	2,066
Iron	0.03	1.0	1.0
Barium	0.01	1.0	1.0

Magnesium/Calcium Ratio	6.1
Total Dissolved Solids (calculated)	43,143
Total Dissolved Solids (experimental)	NOT RUN

Figure A-5—Continued

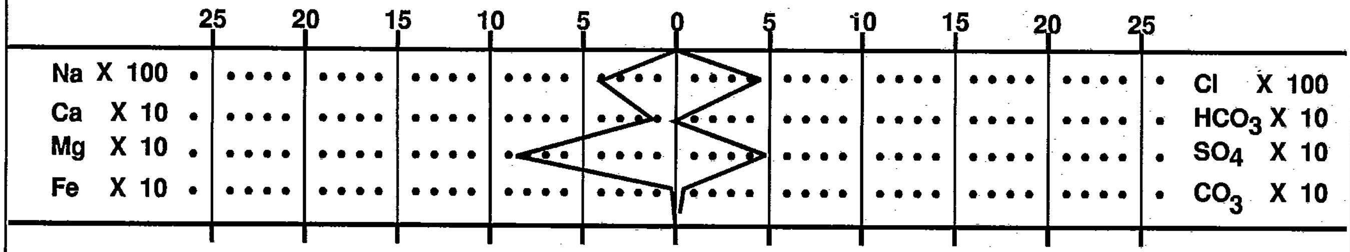
COMPANY NAME NO NAME

SAMPLE NAME (I.D.) PASCAGOULA-PORT

DATE/TIME SAMPLED -0-

LABORATORY NUMBER -0- **SEAL NUMBER** -0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY 1.026 pH 7.5 RESISTIVITY (ohm/cm) 128 @ -0-

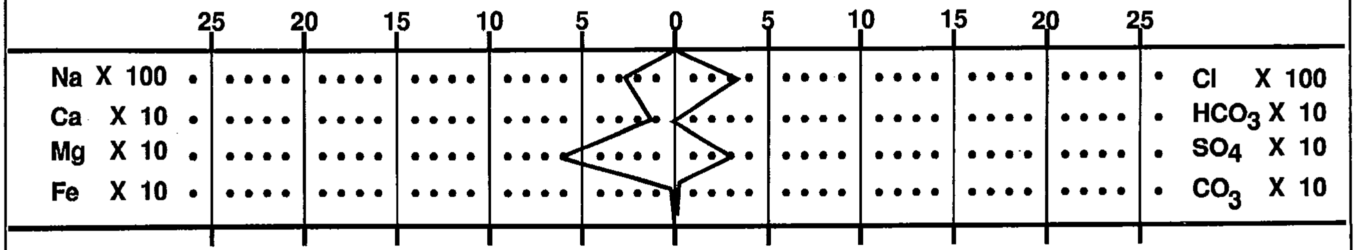
	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	463	16,400	16,826
Bicarbonate	2	137	141
Sulfate	45	2,150	2,206
Carbonate	0	0	0
CATIONS			
Sodium + Potassium (Calc)	400	9,190	9,429
Calcium	18	358	367
Magnesium	92	1,120	1,149
Iron	0.002	0.5	1.0
Barium	0.004	0.3	0.3

Magnesium/Calcium Ratio	3.1
Total Dissolved Solids (calculated)	29,356
Total Dissolved Solids (experimental)	29,600

Figure A-5—Continued

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	PASCAGOULA-OFFSHORE LIGHTERING		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY	1.016	pH	6.9	RESISTIVITY (ohm/cm)	155	@	-0-

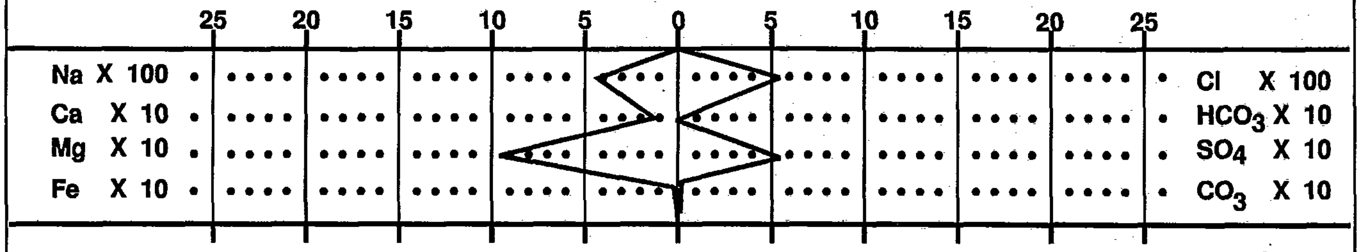
	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	319	11,300	11,481
Bicarbonate	2	97	99
Sulfate	28	1,330	1,351
Carbonate	0	0	0
CATIONS			
Sodium + Potassium (Calc)	275	6,328	6,430
Calcium	12	238	242
Magnesium	61	741	753
Iron	0.03	1.0	1.0
Barium	0.002	0.2	0.2

Magnesium/Calcium Ratio	3.1
Total Dissolved Solids (calculated)	20,035
Total Dissolved Solids (experimental)	21,200

Figure A-5—Continued

COMPANY NAME	NO NAME		
SAMPLE NAME (I.D.)	JAPAN-KEIYPO SEA-BERTH		
DATE/TIME SAMPLED	-0-		
LABORATORY NUMBER	-0-	**SEAL NUMBER**	-0-

MINERAL PATTERN MEQ/LITER
BASIC REPORT FORM



SPECIFIC GRAVITY	1.0283	pH	7.6	RESISTIVITY (ohm/cm)	14.8	@ -0-

	meq/L	mg/L	ppm/wt
ANIONS			
Chloride	527	18,700	19,229
Bicarbonate	1	65	67
Sulfate	53	2,550	2,622
Carbonate	0	0	
CATIONS			
Sodium + Potassium (Calc)	466	10,704	11,007
Calcium	19	383	394
Magnesium	97	1,180	1,213
Iron	0.03	1.0	1.0
Barium	0.01	1.0	1.0

Magnesium/Calcium Ratio	3.1
Total Dissolved Solids (calculated)	33,584
Total Dissolved Solids (experimental)	NOT RUN

Figure A-5—Continued

APPENDIX B—COMPREHENSIVE INVESTIGATIVE PROGRAM

B.1 General Statements

B.1.1 If the evaluation of data derived by 17.3.6 (Basic Sampling and On-Site Testing Procedure) and 17.3.7 (Basic Analytical Procedures) does not indicate the sources of the contaminant water, then it may be necessary to derive additional qualitative and quantitative data of the minor components present in the samples through more complex analyses. This appendix addresses that need.

B.1.2 These recommendations only address the aqueous phase constituents and not such parameters as solids, emulsions, or oils.

B.2 Selection of Analytical Methodology

B.2.1 Methods of analysis define the determined results. Therefore, a given component analyzed by different analytical methods will not necessarily provide the same quantitative result.

B.2.1.1 The use of nonstandardized methods of analysis can compound the problem of interpreting results. *Therefore, a component analyzed by both a standard and a nonstandard technique, on the same sample, can yield significantly different levels of this component.*

B.2.1.2 In order to establish a uniform basis of comparison, each sample component in a series must be analyzed using the same test method. *Therefore, the nonstandard technique should be run on all of the samples, even though some of the components might have been successfully run using standard techniques. The extent of the bias should be determined.*

B.2.2 Analytical methods involving the use of sophisticated analytical instrumentation to detect trace elements (ions) that are not normally associated with water contaminated by crude oil have not been subjected to rigorous standardization. Thus, acceptable precision statements for this type of sample are not available. These methods must therefore be referenced when reporting the analytical data.

B.2.3 If it is impossible to get a sufficient volume of sample to perform the standard methods of analysis for major components (for example, HCO_3^- by titration), then very sophisticated analytical techniques can be performed on less sample even though the veracity of the standard methods will be lacking.

B.2.4 It may be necessary to investigate the composition of the nonaqueous phases—the solids, the emulsions, and even the oil itself—for clues as to the source of contaminated water.

B.3 Sample Preparation

B.3.1 Any sample can consist of two or more phases—oil, liquid, emulsion, or solid—and there is no known way to render the sample homogeneous. Therefore, the magnitude of any given component on a total sample basis cannot be determined by analysis of only one phase.

B.3.2 Various techniques such as the use of separatory funnels, filters, centrifuge, and chemical additives have been used to force separation of phases in order to prepare samples of the various phases for analysis. It is extremely difficult to obtain a true weight or component balance even when internal standards and such techniques as successive dilution are used. *Consequently, all of the separations must be performed in exactly the same fashion* on each of the samples, even though there could be sufficient sample to run some separations without resorting to these additional techniques.

B.3.3 Composite of samples to comply with sample volumes must be attempted carefully. The inclusion of atmospheric oxygen or CO_2 can result in the formation of precipitates and other deleterious side reactions. Precautions must be observed for each particular methodology that will be performed in the laboratory.

B.3.4 Dilution should not be used to extend the volume of sample in order to perform a more extensive battery of tests. *Destroying the natural buffering that exists in these samples can result in large errors due to changes in solubility (concentration).*

B.4 Water Characteristics (Components) to Be Determined

B.4.1 Any or all of the 13 items listed in Table 1 must be determined.

B.4.2 Additional water characteristics include strontium, iodine, bromine, sulfide, silica, phosphate, sulfite, TDS, and numerous secondary trace metals and salts.

B.5 Expression of Analytical Results

The procedure for expression of analytical results is the same as the procedure in A.2.

B.6 Report Form

The report form is prepared as described in A.3, but the appropriate components should be added to the report form and plots (see Figure A-2).

B.7 Interpretation of Results

B.7.1 The interpretation of the nonstandard testing data will require considerably more expertise, since there are not as many historical data to support the conclusions. *Therefore, it is an absolute necessity to perform these specialized tests on samples of a known "like" composition to ensure that the resulting data can be inserted into existing data bases for comparison.* Pollution, contamination, or mishandling of samples when using highly sophisticated techniques increase the probability of errors in interpretation.

B.7.2 The information in B.7.1 should be used in conjunction with the historical data provided in A.4.

B.8 Additional Sampling

If after performing the more complex analytical techniques, the source(s) of the contaminate water still cannot be determined, it may then be necessary to conduct a more comprehensive sampling and testing program on subsequent movements of a similar cargo under consideration.

Order No. 852-30407

1-1700— 4/92—2.5C (5A)

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005