Recommended Practice for Analysis of Oilfield Waters

RECOMMENDED PRACTICE 45
THIRD EDITION, AUGUST 1998

American
Petroleum
Institute

Helping You
Get The Job
Done Right.SM

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Exploration and Production Department

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FOREWORD

These recommended practices were prepared by the API Subcommittee on Analysis of Oilfield Waters. This publication is under the administration of the American Petroleum Institute Exploration and Production Department's Executive Committee on Drilling and Production Operations.

The first edition of RP 45, published as "Tentative" in November 1965, was developed by the API Mid-Continent District Study Committee on Analysis of Oilfield Waters. Subsequent to its publication, the Study Committee status was changed to a Subcommittee of the Executive Committee on Drilling and Production Practices and charged with the responsibility of continuing work in certain areas of interest to develop additional procedures for analysis of oilfield water analysis. The Second Edition, published in 1968 and reissued July 1981, contained revisions of, and additions to, First Edition procedures as well as a new section on "Spectroscopic Methods." With the 1968 edition, this publication was advanced from a "Tentative" to a "Standard" Recommended Practice. This Third Edition supersedes and replaces the Second Edition.

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It is intended that these recommended practices serve as a guide to promote standards for analysis of oilfield waters. Users of this publication are reminded that constantly-developing technology, equipment, specific company requirements and policy, and specialized or limited operations do not permit coverage of all possible analyses, practices, or alternatives. This publication is not so comprehensive as to present *all* of the practices for analysis of oilfield waters. Alternative procedures and/or equipment are available and routinely utilized to meet or exceed practices or performance levels set forth herein. Procedures presented in this publication are not intended to inhibit developing technology and equipment improvements or improved operating procedures or analyses. This publication, or portion thereof, cannot be substituted for qualified technical/operations analysis and judgement.

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

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Recommended Practice for Analysis of Oilfield Waters

1 Scope

This document is directed toward the determination of dissolved and dispersed components in oilfield waters (produced water, injected water, aqueous workover fluids, and stimulation fluids). Bacterial analyses, bioassay (toxicity tests for marine animals), NORM determination, and membrane filter procedures are outside the scope of this document.

Biological determination of the species and concentration of bacteria are covered in NACE TM0194-94, *Field Monitoring of Bacterial Growth in Oilfield Systems*.

Determinations of Naturally Occurring Radioactive Materials (NORM) in oilfield waters is discussed in API Bulletin E2, *Bulletin on Management of Naturally Occurring Radioactive Materials (NORM) in Oil and Gas Production*.

Membrane filter procedures are covered in NACE TM01-73, *Test Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters*.

Analyses for residuals of proprietary organic treatment chemicals, such as corrosion inhibitors, demulsifiers, scale inhibitors, water clarifiers, biocides, etc. are also outside the scope of this document. However, analyses for generic components of proprietary chemicals, such as phosphate (scale inhibitor), are included in this document.

Lastly, analyses of nonhazardous oilfield waste (NOW), such as drilling fluid, soil, cores, etc. are outside the scope of this document. However, analyses of separated water (including filtrates) from such sources are within the scope.

The analytical methods presented in this document were selected for their accuracy, reproducibility, and applicability to oilfield systems. For most constituents, several methods of varying degrees of complexity and accuracy are presented to provide the analyst with the opportunity to choose the most appropriate and cost effective method pertinent to his/her needs.

While the cited methods may also be used as indicators of the environmental quality of oilfield waters, regulatory agencies prescribe their own analytical methods that must be followed. These regulatory agencies should be consulted to obtain the relevant analytical procedures for cases in which data is to be used to verify environmental compliance.

2 Acronyms and References

2.1 See Appendix B for a list of acronyms and their definitions.

2.2 See Appendix C for government and industry references.

3 General

3.1 INTRODUCTION

3.1.1 Since the publication of RP 45, *Recommended Practice for Analysis of Oilfield Waters*, Second Edition, 1968, there have been major changes in analytical needs for oilfield waters. The computer age has pushed both oilfield and analytical chemistry technology forward at a rapid rate. Oilfield water analyses data are now used in computer programs to predict such things as water compatibility, scaling tendencies, and fluid movement in reservoirs.

3.1.2 Field instruments to perform analytical procedures onsite have proliferated since 1968. Computers have greatly improved analytical sensitivity for determining dissolved and dispersed constituents in oilfield water. Environmental awareness demands that sophisticated technology be applied to many oilfield water analyses.

3.1.3 The changes since publication of the Second Edition have affected the goals, application, and organization of this document.

3.2 GOALS

The purpose of this document is to provide the user with information on the following:

a. The applications of oilfield water analyses.
b. The proper collection, preservation, and labeling of field samples.
c. A description of the various analytical methods available, including information regarding interferences, precision, accuracy, and detection limits.
d. Appropriate reporting formats for analytical results.

3.3 APPLICATIONS

Although water analyses can be used to resolve technical problems in a wide spectrum of oilfield applications, their use is dominant in several key areas:

a. The prediction of possible formation damage from injection water/formation water incompatibilities in a waterflood or water disposal project and to track the movement of the injection water.
b. The prediction of scale formation in surface and downhole equipment.
c. Corrosion monitoring and prediction.
d. A means of monitoring water treatment system efficiency.
e. A means to diagnose and alleviate a variety of oilfield problems.

Environmental evaluations and regulatory compliance are discussed in 3.4.

A brief discussion of some examples of oilfield water analyses applications follows.

3.3.1 Waterflood Evaluation and Monitoring

3.3.1.1 Water injected into underground formations can result in formation damage if the injected water and connate water are incompatible. Formation damage may be predicted by analyzing injection and connate water prior to initiating injection. Two examples of incompatibilities that can result in formation damage are:

a. The two waters contain dissolved salts and may precipitate solids when mixed. The most damaging precipitated solid is an insoluble scale that plugs the formation, i.e., Ba^{2+} and SO_4^{2-} which form barium sulfate.
b. The two waters differ greatly in total dissolved solids such that upon mixing, ionic concentration changes within the formation result in the swelling of clay minerals and the reduction of formation permeability.

3.3.1.2 During the course of an injection project, a water sample whose composition is identical to that found in situ in the reservoir provides a snapshot of the steady state conditions occurring in the reservoir. However, the process of obtaining a representative reservoir water sample is not a trivial one. While bottom hole samples are most desirable, such samples are seldom available since the act of bringing a sample to the surface creates physical and chemical changes. For example, decreases in temperature and pressure affect both dissolved gas equilibria and individual ionic species equilibria.

3.3.1.3 Water samples collected over a period of time at a producing well can be analyzed to determine if an injected water is entering the borehole, and if the injected and connate waters have specific differences in composition. If the difference is in total salinity or dissolved solids (TDS), a salinity dilution or increase will be seen in samples collected.

3.3.1.4 Differences in ionic ratios (Na/Ca, Na/Mg, Na/K) can also be observed for waters that have marked differences in calcium, magnesium, or potassium concentrations. Anions such as bromide or iodide may occur in much higher concentrations in either the injected or connate water, generating a naturally occurring tracer.

3.3.2 Scale Formation

3.3.2.1 Water analyses are the basis for predicting the occurrence, composition, and location of mineral scale deposits. Scaling is usually the result of the deposition of calcium, magnesium, strontium, and barium in the carbonate or sulfate form. Scaling is induced by pressure drops, temperature changes, flow rate alterations, fluid incompatibilities, and a variety of other factors.

3.3.2.2 Scaling tendencies are predicted by using solubility correlations based on ionic content (Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, HCO_3^-, SO_4^{2-}) of the fluid, in addition to the physical properties such as temperature, pressure, and pH. A variety of available or proprietary scaling-tendency estimate models are used by the various service company, contract, and oil company laboratories. The relative reliability of any particular scaling tendency prediction model must be judged by actual field experience.

3.3.3 Corrosion Studies

Historically, the major uses of water analyses have been corrosion studies, including corrosion monitoring and prediction. For example, dissolved oxygen, carbon dioxide, iron, manganese, sulfide, sulfate, bicarbonate, chlorides, and water pH have been important monitoring and predictive tools.

3.4 ENVIRONMENTAL CONCERNS

The analysis of environmental pollutants in oilfield waters span the range from the simple measurement of solution pH to the identification of an unknown organic constituent in a complex organic/solid/liquid matrix. Although the line of demarcation is not always clear, this document deals with oilfield waters.

Systems dominated by suspended nonhydrocarbon materials such as soil samples and drilling fluids are outside the scope of this document. The procedures in this document, however, *may* be applicable to aqueous filtrates or mineral acid digestates from such samples. A list of acronyms is provided in Appendix B to assist in understanding the jargon used in the industry.

Because regulatory requirements are continuously evolving, it is impossible to identify all of the potential water analyses which operators may want to monitor. *In all cases, whether offshore or onshore, a careful review should be made of pertinent local, state, and federal regulations to make sure that all mandated tests are conducted.*

Many of the procedures given in this document are basically the same as the EPA Methods. *However, for regulatory compliance, a lab performing environmental testing must follow EPA protocol, and meet the required EPA certification. This document only provides an overview of possible environmental analyses useful for monitoring clean-up processes or potential problem areas and gives current representative test procedures.*

Three areas of environmental compliance dominate the need for oilfield water analyses:

a. Oil and grease measurements.
b. Various surface water and soil measurements for environmental assessments and pit closures.
c. Radioactivity measurements for NORM.

In addition, other environmental analyses are becoming more important. Water analysis for toxic heavy metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se), oxygen demand (BOD or COD), hydrogen sulfide, total petroleum hydrocarbons, and certain organic compounds (benzene, phenols, and halocarbons) will be required for most surface-disposed oilfield waters.

3.4.1 Oil and Grease Measurements

3.4.1.1 A most notable environmental oilfield water analysis is the determination of oil and grease content in produced water. The oil and grease analysis historically has been used to determine the operational efficiency of produced water treatment systems and is currently required under EPA's offshore National Pollutant Discharge Elimination System (NPDES) permit on all discharges into the navigable waters of the United States.

3.4.1.2 As a screening tool, many operators conduct their own periodic analysis of produced water quality using either ultraviolet, visible, or infrared techniques on black oils and condensates, respectively. Although these tests do not produce identical gravimetric results, they are sufficiently accurate to provide an index for estimating regulatory compliance and operational efficiency.

3.4.1.3 The organic constituents of crude oil found in produced water contain both insoluble (droplets) and soluble Non-Hydrocarbon Organic Material (NHOM), also called Water Soluble Organics (WSO) fractions.

3.4.1.4 In practice, operators frequently add chemicals to enhance the performance of their water treatment systems. These chemicals can affect either or both fractions in varying degrees. Unfortunately, the previously cited screening methods and the EPA-dictated gravimetric method measure both soluble and insoluble fractions together and cannot distinguish between the two. Consequently, to effectively apply chemical treatments to affect the fraction desired, the operator needs independent determinations of each. A description of methods to do so are cited in 5.3.21.

3.4.2 Pit Closure

3.4.2.1 Typically, native soil samples, pit wall material, and pit contents are tested for pH, Toxic Characteristic Leaching Procedure (TCLP), Total Petroleum Hydrocarbon (TPH), Electrical Conductivity (EC), Sodium Adsorption Ratio (SAR), Exchangeable Sodium Percentage (ESP), and Cation Exchange Capacity (CEC).

3.4.2.2 In the case of property acquisition and/or divestiture, any environmental assessments typically require contaminated soil sampling for benzene, toluene, ethylbenzene, and xylenes (TCLP, TPH, and BTEX). Should the ground water be tested, the above tests are usually conducted, in addition to Target Compound List (TCL) of volatile organic and semi-volatile materials. Many of these soil analyses are outside the scope of this document. However, the analyses of separated water, including filtrates, may be within the scope of this document.

3.4.3 Radioactivity

Another area of increasing importance in the monitoring of water discharges is measurement of radioactivity. API Bulletin E2 discusses methods for measuring Naturally Occurring Radioactive Material (NORM) in the oilfield. Along with the obvious concern of scale deposition, additional environmental concerns have arisen over NORM accumulation in production equipment in conjunction with scale deposition.

4 Sample Collection, Preservation, and Labeling

4.1 INTRODUCTION

4.1.1 No amount of analytical work in the laboratory can compensate for substandard sampling. The objective of sampling is to collect a small portion of material in such a manner that the sample is representative of the whole. Once collected, the sample should be handled in such a manner that significant compositional changes do not occur before analysis. Doing this requires:

a. The careful selection of sample points.

b. Strict attention to sample collection techniques, including selection of sample containers.

c. Proper handling of the sample, including the use of preservatives when required.

4.1.2 *If the samples are being collected for regulatory purposes, the procedures specified by that authority take precedence over the recommendations discussed herein.*

4.2 PRELIMINARY CONSIDERATIONS

4.2.1 Sample Containers

New or carefully-cleaned sample containers are an important component in proper sampling. The type of required sample container varies, depending on the analyses planned for the sample. Specific container requirements for various analyses are listed in Table 1.

4.2.2 Sample Quantity

In general, 500 to 1000 mL sample volumes are sufficient for most physical and chemical analyses. Occasionally larger or multiple samples are necessary. Table 1 shows the sample volume normally required for each analysis.

4.2.3 Types of Samples

Representative samples of some sources can be gathered only by making composites of small samples. For other sources, it is more informative to analyze numerous separate samples instead of a composite. For regulatory purposes, some procedures often specify the type of sample to be collected. Since local conditions vary, no specific recommendation can be universally applied.

4.2.3.1 Grab or Catch Samples

4.2.3.1.1 A sample can only represent the composition of the source at one particular time and place. If the source is known to be fairly constant in composition, then it may be well-represented by a single grab sample. However, when a source is known to vary with time, grab samples collected at intervals and analyzed individually can document the extent, frequency, and duration of the variations.

4.2.3.1.2 In this case, sample intervals must be chosen to capture the extent of the expected changes in composition. When the source's composition varies in space (i.e., by sampling location), collect samples from the appropriate locations and analyze individually.

4.2.3.2 Composite Samples

Composite samples are mixtures of grab samples collected from a sampling point at different times. Composite samples are useful for observing average concentrations of an analyte at the sample point. If appropriate for the user's needs, composite samples represent a substantial savings in laboratory effort and expense. Composite samples are not appropriate for analytes subject to significant and unavoidable changes during storage.

4.3 SAMPLING

The sampled system should be operating at normal conditions of flow rate, pressure, temperature, etc. unless the sampling purpose is to analyze under abnormal conditions. Any departure from normal operating conditions should be noted on the sample identification form.

For distribution systems, flush lines to ensure that the sample is representative. For wells, collect samples only after the well has pumped sufficiently to ensure that reservoir fluid is collected, rather than "stagnant" fluid from the tubing.

4.3.1 Filtration

4.3.1.1 Samples taken for measurement of dissolved components should be field-filtered immediately. This is also true for samples collected for in-field analyses. Filtration is best performed by using a filter holder that can be directly incorporated into the system flow stream (and using system pressure). If in-line system pressure cannot be used, then a large sample should be taken and pressure filtered by an alternate means (all at the sampling location). Membrane filter procedures are covered in NACE TM01-73, *Test Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters*.

4.3.1.2 Filtered samples can be collected by filling and overflowing the sample bottle several times. *However, this can not be done when the containers already contain preservative, nor for samples meant for oil and grease analysis*. Do not filter samples meant for analyses that depend on suspended material, such as microbiological tests, turbidity, oil content, etc.

4.3.1.3 Material removed by the filter may occasionally be used for corrosion and scale product analyses. These analyses are not covered here, but guidance may be found in NACE TM01-73.

4.3.2 Sample Preservation

4.3.2.1 The immediate analysis of samples is ideal; storage at low temperature (4°C) for less than 24 hours is next best, but is not always possible. Therefore, some sample preservation is often required if a sample is to be analyzed at a remote location.

4.3.2.2 Complete preservation of a sample is impossible. At best, preservation techniques can only retard chemical and biological changes that occur after sample collection. Also, almost all preservatives interfere with some tests, so one sample cannot usually be used for every analysis required.

4.3.2.3 Some properties and constituents of oilfield waters cannot be preserved well or easily. For example, temperature, pH and dissolved gases all change rapidly and *must be determined in the field*. Changes in these constituents also affect determinations for calcium, total hardness, and alkalinity. Therefore, these tests are better performed in the field. Likewise, if speciation of the valence states of iron or manganese is required, then analyses for these may be most easily done in the field.

4.3.2.4 When collecting an independent sample for the analysis of organic constituents in water, it is imperative *not to rinse or to overflow the sample bottle with the produced fluid prior to sampling*. Doing this induces deposition of oil on the sides of the bottle which can produce an artificially high organic content level.

4.3.2.5 Table 1 lists the preservatives that should be used for samples that are shipped to the laboratory for later analysis.

4.3.3 Sample Hold Times

4.3.3.1 As stated previously, the quicker an analysis is performed, the better the result obtained. However, some samples must be preserved and sent to a remote laboratory for analyses. All samples, even preserved samples, have a finite hold time. Analyses must be completed within this hold time or the analytical results are likely to be substandard.

4.3.3.2 It is impossible to state exactly how much elapsed time is allowable between sample collection and its analyses. This depends on the sample composition, the analyses required, storage, and shipping conditions. General hold-time guidelines are provided in Table 1. *However, maximum hold times specified in regulatory documents take precedent for regulatory purposes.*

4.4 SAMPLE AND SYSTEM IDENTIFICATION

4.4.1 Sample and system documentation are essential for sample tracking. At a minimum, the following information should appear on each sample label:

a. Sample identification (company, field, well name, etc.).
b. Collected by.
c. Date and time of sample collection.
d. Sample point.
e. Analyses requested.
f. Comments.

4.4.2 Every sample container should be labeled with waterproof ink and the label should be applied to the sample container before the sample is taken.

4.5 FIELD/LABORATORY ANALYSES

Some components and properties of the system change rapidly with time and cannot be adequately preserved or stabilized for later laboratory determinations. These components must be measured or determined in the field as close in time and location to the sample points as possible. Thus, a complete analysis involves field analyses for some components and laboratory analyses (with an unpreserved sample, and also with several specially-treated samples) for the remainder.

4.5.1 Field Measurements

The following components or properties should be measured or determined in the field immediately after sampling and filtration:

a. pH.
b. Temperature.
c. Turbidity (unfiltered sample).
d. Alkalinity.
e. Dissolved oxygen (O_2).
f. Carbon dioxide (CO_2).
g. Hydrogen sulfide (H_2S). (Alternatively, stabilize sample with basic zinc solution for laboratory analysis.)
h. Total and soluble iron (Fe^{2+}), (Fe^{3+}).
i. Total suspended solids. (Primary filtration and washing with distilled water performed in the field; subsequent washing and weighing may be performed in the laboratory.)
j. Bacteria. (Bacteria are filtered or cultured from a sample in the field with subsequent incubation and enumeration in the laboratory.) Bacterial analyses are not covered in this document, but may be found in NACE TM0194-94, *Field Monitoring of Bacterial Growth in Oilfield Systems*.

4.6 QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance (QA) and quality control (QC) are integral parts of any data acquisition or data analysis process. QA and QC are necessary to guarantee the generation of reliable and reproducible results.

Broadly speaking, QA consists of precisely defining the analysis requirements for a specific user application and implementing the measures necessary to ensure that what is required is indeed what is provided by the analyst. For example, if it is necessary to have precise measurements of the sodium concentration, then it is essential that the value be measured, rather than inferred from a difference calculation.

Complementing quality assurance is the equally important QC process that provides the relevant checks to assure that the necessary sampling and analyses protocols have been followed.

Clearly, the amount of QA/QC required for a particular application is dictated by the needs of the user. These needs may span the gamut from a simple field estimation to adjust the amount of a treatment chemical (little QA/QC) to a thorough and complete analysis for regulatory purposes (significant QA/QC).

4.6.1 Field QA/QC Procedures

Specific field procedures that can be invoked to measure and maintain sample QA/QC include the use of trip blanks and sample duplicates, the decontamination of testing equipment and sampling devices, and the calibration of equipment.

4.6.1.1 Trip Blanks

4.6.1.1.1 Trip blanks provide an estimate of the amount of experimental error attributable to interactions between the sample and the container, contaminated laboratory rinse water, and sample handling procedures. If used, a trip blank should be included in the analysis.

4.6.1.1.2 One of each type bottle used in the sample collection is prepared as a trip blank. The trip blank is filled with deionized water at the laboratory, transported to the sampling location and taken back to the laboratory. The trip blank is not opened from the time it leaves the laboratory until it undergoes analysis. Results from this analysis provide an estimate of the amount of background error.

Table 1—Summary of Special Sampling or Handling Requirements[a]

Analysis	Container	Minimum Sample Size (mL)[b]	Preservation	Maximum Storage Recommended
Alkalinity	P,G	200	Refrigerate	24 hours
Ammonia	P,G	200	Refrigerate, add HCl to pH <2	7 days
Bicarbonate			See Alkalinity	
Biochemical Oxygen Demand (BOD)	P,G	1000	Refrigerate	6 hours
Boron	P	100	None required	28 days
Bromide	P,G	200	None required	28 days
Carbon Dioxide	P,G	100	Analyze immediately	—
Chloride	P,G	500	None required	28 days
Chromium	P(A), G(A)	300	Refrigerate	24 hours
Chemical Oxygen Demand (COD)	P,G	100	Analyze as soon as possible, or add H_2SO_4 to pH<2	7 days
Conductivity	P,G	500	Refrigerate	28 days
Fluoride	P	300	None required	28 days
Iodide	P,G	500	None required	28 days
Metals, Dissolved[c]	P(A), G(A)	500	Filter immediately, add HNO_3 to pH<2	6 months
Nitrate	P,G	100	Analyze as soon as possible or refrigerate	48 hours
Oil & Grease, Total	G	1000	Add HCl to pH<2	28 days
Organic Acids	G	500	Refrigerate	Unknown
Oxygen, Dissolved	G	300	Analyze immediately	0.5 hours
pH	P,G	—	Analyze immediately	2 hours
Phosphorus (Phosphate)	G(A)	100	Filter immediately, refrigerate	48 hours
Resistivity			See Conductivity	
Silica	P	500	Refrigerate, do not allow to freeze	28 days
Specific Gravity (SG)	P	500	Refrigerate	28 days
Sulfate	P,G	200	Refrigerate	28 days
Sulfide	P,G	100	Refrigerate; add 4 drops 2N zinc acetate / 100 mL	28 days
Total Dissolved Solids (TDS)	P,G	500	Analyze same day, refrigerate	24 hours
Temperature	P,G	—	Analyze immediately	—
Total Organic Carbon (TOC)	G	100	Analyze immediately; or refrigerate and add H_2SO_4 to pH<2	7 days
Total Suspended Solids (TSS)	P,G	500	Refrigerate	7 days
Turbidity	P,G	—	Analyze immediately	—

Notes:
For determinations not listed, use glass or plastic containers; preferably refrigerate during storage, and analyze *as soon as possible*.
Refrigerate = Storage at 4°C, in dark.

P = plastic (polyethylene or equivalent).
G = glass.
G(A) OR P(A) = rinsed with 1 N HNO_3.

[a] This material was derived in part from the U.S. Environmental Protection Agency, *Rules and Regulations, Federal Register* 49; No. 209, October 26, 1984.
[b] Contact the analytical laboratory for details of sample size to be run. Several analyses can often be done on one sample. Therefore, the listed sample size for any one analysis in this table may be sufficient for several of the analyses desired.
[c] Dissolved metals include: aluminum, barium, calcium, iron, lithium, magnesium, manganese, potassium, sodium, strontium.

4.6.1.2 Sample Duplicates

A field sampling program should include submitting duplicates to the laboratory at a rate of at least 10 percent of the total number of samples collected. The duplicates should be submitted as blind duplicates (i.e., not labeled as duplicate samples) to validate the accuracy of the laboratory findings.

4.6.1.3 Decontamination of Testing Equipment and Sampling Device

4.6.1.3.1 The testing equipment and sampling device used at a sampling site should be checked for contamination prior to use because:

a. The equipment may not have been cleaned since its last use.

b. Since its arrival on-site, the equipment may have been used by someone else.

4.6.1.3.2 One effective way to encourage cleanliness and good technical practices is to use sealed kits, and have access to "blank" sample testing. The latter procedure allows personnel to identify where the contamination first occurred.

4.6.1.4 Calibration of Equipment

4.6.1.4.1 All equipment should be calibrated prior to field use and recalibrated before measuring the parameters for each sample. The protocol used to calibrate the equipment should be referenced in the sample report.

4.6.1.4.2 A satisfactory laboratory QA/QC program includes standard identifications, laboratory notebooks, spikes for calibration, and identification of potential matrix interferences. Adequate statistical procedures (i.e., QC charts) are used to monitor and document performance and resolve testing problems. QC data are used to measure the performance of the collection and analysis or to indicate potential sources of cross-contamination.

4.7 LABORATORY SCREENING

4.7.1 There are ways the user can enhance the quality of reported data to minimize the effect of inaccurate data. Selecting the laboratory or the personnel to perform the analysis is the first step, and probably the most important step, to obtaining quality water analysis data. The user may wish to visit a laboratory and observe such things as cleanliness, orderliness, the age of the equipment, and the attitudes of the technical staff performing the work.

4.7.2 Sending reference standards or duplicate samples with a routine sample set to another laboratory is a way of checking a laboratory's data quality.

4.7.3 A discussion on reporting errors can be found in 6.7.

5 Methods for the Determination of Major Constituents

5.1 INTRODUCTION

The following procedures for determining the major constituents of oilfield waters can produce reliable and reproducible information in the hands of competent analysts. These methods are intended for use in assessing water quality as it relates to scaling, corrosiveness, disposal, formation treatment, etc.

While these methods also may be used as indicators of the environmental quality of oilfield waters, regulatory agencies prescribe their own analytical methods that must be followed. These regulatory agencies should be consulted to obtain the relevant analytical procedures.

The analytical methods cited here were selected for their accuracy, reproducibility, and applicability to oilfield systems. For each constituent, several methods are generally given to provide the analyst with increased flexibility. Using descriptions of the methods and the supplied information on precision and accuracy, the analyst can choose the method most applicable to provide the information needed.

The analytical methods are not presented in detail. More detailed information can be found in the listed references for the methods. Every attempt has been made to select reference material that is commonly available to most laboratories. The following format is followed for each oilfield water constituent covered by this document:

a. A brief discussion concerning the constituent (including why it is important in the oilfield).

b. General discussion of the method(s).

c. Reference(s).

d. Summary (if appropriate).

e. Discussion of the method's precision and accuracy.

Although the methods can artificially be broken down into categories (such as metals, organic, inorganic, hardness, etc.), they are presented in alphabetical order in this document for easy location.

Table 2 also alphabetically lists each constituent addressed in this section. From this table, the user can review the methods available and select the method(s) that meets the user's needs. Also, this table indicates if a test kit (i.e., Hach) is commercially available. However, API makes no claim regarding the quality or precision of such kits. The accuracy and precision of test kits should be determined by the user.

Some of the analyses discussed in this document should be done in the field immediately after sample collection. This information is noted within the referenced method in Table 1. Metals such as aluminum, barium, calcium, etc., have been grouped as one in this table.

Table 2—Summary of Constituents and Analytical Methods

Constituent	Method	Method Reference[a,b]	Detection Limit	Significant Interferences	Field
Alkalinity	Electrometric (Refer to 5.3.1.1)	SM 2320-B, ASTM D 1067-92	1 mg/L as $CaCO_3$	Dissolved gases lost before testing. Soaps, oils, solids may coat electrode	Y
	Indicator (Refer to 5.3.1.2)	SM 2320-B	1 mg/L as $CaCO_3$	Dissolved gases lost before testing. Color & turbidity of sample	Y, Kit
Aluminum	AAS (Refer to 5.3.2.1)	SM 3500-Al B, ASTM D 857-89	0.1 mg/L	Ionizes slightly—can compensate (see method)	—
	ICP (Refer to 5.3.2.2)	SM 3500-Al C	0.04 mg/L	Method compensates	—
	Photometric (Refer to 5.3.2.3)	SM 3500-Al D	0.006 mg/L	Fluorides/Polyphosphates	Kit
Ammonia	Nesslerization (Refer to 5.3.3.1)	SM 4500-NH_3, ASTM D 1426-89	0.02 mg/L	Color, turbidity, Ca, Mg must be removed (see method)	Kit
	Ion Electrode (Refer to 5.3.3.2)	ASTM D 1426-89, SM 4500-NH_3	0.03 mg/L	Amines, Hg, Ag	—
	Titrimetric (Refer to 5.3.3.3)	SM 4500-NH_3	5 mg/L	Alkalinity over 500 mg as $CaCO_3$/l and turbidity must be removed (see method)	—
	Ion Chromatography (Refer to 5.3.3.4)	SM 4110-B, ASTM 4327-91	0.1 mg/L	Any substance with retention time similar to ammonia (sample dilution may be required)	—
Barium	ICP (Refer to 5.3.4.1)	SM 3500-Ba C	0.002 mg/L	None significant	—
	AAS (Refer to 5.3.4.2)	SM 3500-Ba B, ASTM D 3651-92	0.03 mg/L	Ionizes in flame—can compensate (see method)	—
	Turbidimetric (Refer to 5.3.4.3)	See 5.3.4.3 for procedure.	1 mg/L	Organic acids and colored solutions. Polyphosphates—can compensate (see method)	Kit
Bicarbonate	See Alkalinity				
BOD	Biological (Refer to 5.3.5.1)	SM 5210-B	1 mg/L	Reduced forms of nitrogen, substances toxic to microbes used in testing	—
Boron	ICP (Refer to 5.3.6.1)	SM 4500-B D	0.005 mg/L	None significant	—
	Photometric (Refer to 5.3.6.2)	SM 4500-B C	1 mg/L	None significant	—
Bromide	Ion Chromatography (Refer to 5.3.7.1)	SM 4110-B, ASTM 4327-91	0.1 mg/L	Any substance with retention time similar to Bromide (sample dilution may be required)	—
Calcium	ICP (Refer to 5.3.8.1)	SM 3500-Ca C	0.01 mg/L	None significant	—
	AAS (Refer to 5.3.8.2)	SM 3500-Ca B, ASTM D 511-92	0.003 mg/L	Phosphate and aluminum—can compensate (see method)	—
	EDTA Titration (Refer to 5.3.8.3)	SM 3500-Ca D, ASTM D 511-92	1 mg/L	Ba, Sr, orthophosphate	Kit
Carbonate	See Alkalinity				
Carbon Dioxide	Titrimetric (Refer to 5.3.9.1)	SM 4500-CO_2 C	1 mg/L	NH_3, amines, borate, nitrite, PO_4, silicates, and S^{2-}	Y, Kit
Chloride	Mohr/Colorimetric (Refer to 5.3.10.1)	SM 4500-Cl B, ASTM D 4458-85	0.5 mg/L	Bromide, iodide, cyanide. S^{2-}, SCN, SO_3^{2-} can be removed (see method)	Kit
	Mohr/Electrometric (Refer to 5.3.10.2)	SM 4500-Cl D	1 mg/L	Bromide, iodide	—
	Mercuric Nitrate (Refer to 5.3.10.3)	ASTM D 512-89, SM 4500-Cl C	0.5 mg/L	Bromide, iodide, ferric and sulfite ions > 10 mg/L	Kit
	Ion Chromatography (Refer to 5.3.10.4)	ASTM D 4327-91, SM 4110-B	0.1 mg/L	Any substance with retention time similar to chloride (sample dilution may be required)	—

(Table continued on next page.)

Table 2—Summary of Constituents and Analytical Methods (Continued)

Constituent	Method	Method Reference[a,b]	Detection Limit	Significant Interferences	Field
Chromium	AAS (Refer to 5.3.11.1)	SM 3500-Cr B, ASTM D 1687-92	0.02 mg/L	Fe, Ni, Co, Mg—can compensate (see method)	—
	ICP (Refer to 5.3.11.2)	SM 3500-Cr C	0.007 mg/L	None significant	—
	Colorimetric (Refer to 5.3.11.3)	SM 3500-Cr D, ASTM D 1687-92	0.5 mg/L	None significant	—
COD	Open Reflux (Refer to 5.3.12.1)	SM 5220-B	1 mg/L	>2000 mg/L Cl^-, reduced inorganic species	—
Conductivity	Instrumental (Refer to 5.3.13.1)	SM 2510-B, ASTM D 1125-91	0.05 µS/cm	Loss or gain of dissolved gases (primarily fresh waters)	—
Fluoride	Ion Chromatography (Refer to 5.3.14.1)	SM 4110-B, ASTM D 4327-91	0.1 mg/L	Any substance with retention time similar to fluoride (sample dilution may be required)	—
	Ion Selective Electrode (Refer to 5.3.14.2)	SM 4500-F, ASTM D 1179-88	0.02 mg/L	Hydroxyl (OH^-) and polyvalent cations	—
Hydroxide		See Alkalinity			
Iodide	Titration (Refer to 5.3.15.1)	ASTM D 3869-79	0.2 mg/L	Iron, manganese and organic material, which can be removed (see method)	—
	Ion Chromatography (Refer to 5.3.15.2)	SM 4110-A, ASTM D 4327-91	0.1 mg/L	Any substance with retention time similar to iodide (sample dilution may be required)	—
	Ion Selective Electrode (Refer to 5.3.15.3)	ASTM D 3869-79	0.005 mg/L	Sulfide, chloride, and bromide (see method)	—
Iron	Phenanthroline Method (Refer to 5.3.16.1)	SM 3500-Fe D	0.01 mg/L	Cyanide, phosphate, color, and organic material must be removed (see method)	Y
	AAS (Refer to 5.3.16.2)	SM 3500-Fe B	0.02 mg/L	None significant	—
	ICP (Refer to 5.3.16.3)	SM 3500-Fe C	0.007 mg/L	None significant	—
Lithium	AAS (Refer to 5.3.17.1)	SM 3500-Li B, ASTM D 3561-77	0.002 mg/L	None significant	—
	ICP (Refer to 5.3.17.2)	SM 3500-Li C	0.04 mg/L	None significant	—
	Flame Photometric (Refer to 5.3.17.3)	SM 3500-Li D	0.004 mg/L	Barium, strontium, and calcium must be removed (see method)	—
Magnesium	AAS (Refer to 5.3.18.1)	ASTM D 511-92, SM 3500-Mg B	0.0005 mg/L	Phosphate and aluminum—can compensate (see method)	—
	ICP (Refer to 5.3.18.2)	SM 3500-Mg C	0.03 mg/L	None significant	—
	EDTA Titration (Refer to 5.3.18.3)	ASTM D 511-92	1 mg/L	Ba, Sr, orthophosphate	Kit
	Calculation (Refer to 5.3.18.4)	SM 3500-Mg E	1 mg/L	Dependent on results from hardness and calcium determinations	—
Manganese	AAS (Refer to 5.3.19.1)	SM 3500-Mn B, ASTM D 858-90	0.01 mg/L	Silica must be compensated for (see method)	—
	ICP (Refer to 5.3.19.2)	SM 3500-Mn C	0.002 mg/L	None significant	—
	Photometric (Refer to 5.3.19.3)	SM 3500-Mn D	0.02 mg/L	Bromide & iodide. Chloride must be compensated for	Kit
Nitrate	Cadmium Reduction (Refer to 5.3.20.1)	SM 4500-NO_3^- E or F, ASTM D 3867-90	0.01 mg/L	Turbidity, Fe, Ca, oil & grease, chlorine must be compensated for (see method)	—
	Electrode (Refer to 5.3.20.2)	SM 4500-NO_3-D	0.14 mg/L	Cl^-, Br^-, I^-, S^{2-}, CN^-, NO_2^-, HCO_3^- must be compensated for (see method)	—

Table 2—Summary of Constituents and Analytical Methods (Continued)

Constituent	Method	Method Reference[a,b]	Detection Limit	Significant Interferences	Field
Oil & Grease	Infrared (Refer to 5.3.21.1)	SM 5520-C, ASTM D 3921-85	0.2 mg/L	Selection of standard critical	—
	Colorimetric (Refer to 5.3.21.2)	See 5.3.21.2 for Procedure	—	Treating chemicals or other contaminants that cause color change	Y
	Gravimetric (Refer to 5.3.21.3)	SM 5520-B	5 mg/L	Non oil & grease materials may also be extracted	—
	Soxhlet Extraction (Refer to 5.3.21.4)	SM 5520-D	1 mg/L	Organic solvents and certain other organic compounds not considered oil and grease may be extracted	—
	Total Petroleum Hydrocarbon (Refer to 5.3.21.5)	SM 5520-F, ASTM D 3921-85	0.2 mg/L	Organic solvents and certain other organic compounds not considered oil and grease may be extracted	—
Organic Acids	Chromatographic (Refer to 5.3.22.1)	SM 5560-B	Variable	Detergents and soaps	—
	Distillation (Refer to 5.3.22.2)	SM 5560-C	Variable	H_2S and CO_2 must be compensated for (see method)	—
Oxygen, Dissolved	Titrimetric (Refer to 5.3.23.1)	SM 4500-O C, ASTM D 888-92	0.05 mg/L	Ferrous iron	Y
	DO Meter (Refer to 5.3.23.2)	ASTM D 888-92, SM 4500-O G	0.05 mg/L	H_2S causes reduced sensitivity over time	Y
	Colorimetric (Refer to 5.3.23.3)	ASTM D 888-92	0.06 mg/L	See method for limits on interfering species	Y
pH	pH Meter (Refer to 5.3.24.1)	SM 4500-H^+ B, ASTM D 1293-84	—	Temperature (see method)	Y, Kit
Phosphorus (Phosphate)	ICP (Refer to 5.3.25.1)	SM 3120-B	0.1 mg/L	None significant	—
	Pretreatment Conversion to Orthophosphate (Refer to 5.3.25.2)	SM 4500-PB	N/A	Dependent on method selected for measurement of orthophosphate	—
	Colorimetric (Refer to 5.3.25.3)	SM 4500-P, ASTM D 515-88	0.05 mg/L	Ferric iron, copper and silica	Kit
	Ion Chromatography (Refer to 5.3.25.4)	SM 4110, ASTM D 4327-91	0.03 mg/L	Any substance with retention time similar to phosphate (sample dilution may be required)	—
Potassium	AAS (Refer to 5.3.26.1)	SM 3500-K B, ASTM D 3561-77	0.005 mg/L	None significant	—
	ICP (Refer to 5.3.26.2)	SM 3500-K C	0.1 mg/L	None significant	—
	Flame Photometric (Refer to 5.3.26.3)	SM 3500-K D	0.1 mg/L	Na, Ca, Mg	—
Resistivity	See Conductivity			See Appendix A	
Silica	AAS (Refer to 5.3.27.1)	SM 4500-Si B	0.3 mg/L	None significant	—
	ICP (Refer to 5.3.27.2)	SM 4500-Si G	0.02 mg/L	None significant	—
	Colorimetric (Refer to 5.3.27.3)	ASTM D 859-88, SM 4500	0.02 mg/L	Si from glassware and reagents. High levels of color, turbidity, Fe, S^{2-}, PO^-_4	—
	Gravimetric (Refer to 5.3.27.4)	SM 4500-Si D, ASTM D 859-88	0.2 mg/L	Si from glassware or reagents	—
Sodium	AAS (Refer to 5.3.28.1)	SM 3500-Na B, ASTM D 3561-77[3]	0.002 mg/L	None significant	—

Table 2—Summary of Constituents and Analytical Methods (Continued)

Constituent	Method	Method Reference[a,b]	Detection Limit	Significant Interferences	Field
	ICP (Refer to 5.3.28.2)	SM 3500-Na C	0.03 mg/L	None significant	—
	Flame Photometric (Refer to 5.3.28.3)	SM 3500-Na D	0.1 mg/L	Varies by instrument	—
	Calculation (Refer to 5.3.28.4)	See 5.3.28.4 for Procedure	N/A	Dependent on results from measured species	—
Specific Gravity (SG)	Hydrometer (Refer to 5.3.29.1)	ASTM D 1429-86	N/A	None significant	—
	Balance (Refer to 5.3.29.2)	ASTM D 1429-86	N/A	None significant	—
	Pycnometer (Refer to 5.3.29.3)	ASTM D 1429-86	N/A	None significant	—
Strontium	AAS (Refer to 5.3.30.1)	SM 3500-Sr B, ASTM D 3920-92	0.03 mg/L	Ionizes in flame, also Si, Al, and PO_4 (can compensate)	—
	ICP (Refer to 5.3.30.2)	SM 3500-Sr C	0.0005 mg/L	None significant	—
Sulfate	Ion Chromatography (Refer to 5.3.31.1)	ASTM D 4327-91, SM 4500-SO_4 B	0.1 mg/L	Any substance with retention time similar to sulfate (sample dilution may be required)	—
	Turbidimetric (Refer to 5.3.31.2)	SM 4500-SO_4 E, ASTM D4130-82	1 mg/L	Suspended matter and dark colors	Kit
	Gravimetric (Refer to 5.3.31.3)	SM 4500-SO_4 C	1 mg/L	Suspended material, silica, NO_3^-, SO_3^-	—
Sulfide	Iodometric Titration (Refer to 5.3.32.1)	SM 4500-$S^=$ E	1 mg/L	Thiosulfate, sulfite, some organic compounds, which can be removed (see method)	Y
	Ion Electrode (Refer to 5.3.32.2)	ASTM D 4658-92	0.04 mg/L	None significant	Y
	Methylene Blue (Refer to 5.3.32.3)	SM 4500-S^{2-} D	0.01 mg/L	Iodide, thiosulfate and high levels of sulfide, which can be removed (see method)	Y
	Garrett Gas Train (Refer to 5.3.32.4)	API RP 13B-1	Dependent on sample size	Sulfites	Y
Total Dissolved Solids (TDS)	Calculation (Refer to 5.3.33.1)	See 5.3.33.1 for procedure	N/A	Dependent on the detection and measurement of all other ionic species	Y
	Gravimetric (Refer to 5.3.33.2)	SM 2540-C	1 mg/L	Samples high in Ca, Mg, Cl, SO_4 may require longer drying times	Y
Total Organic Carbon (TOC)	Combustion-Infrared (Refer to 5.3.34.1)	SM 5310-B, ASTM D 2579-85	1 mg/L	None significant	—
Total Suspended Solids (TSS)	Filtration (Refer to 5.3.35.1)	SM 2540-D	Variable with sample size	Large floating particle and submerged agglomerates, samples high in dissolved solids	—
Turbidity	Nephelometric (Refer to 5.3.36.1)	ASTM D 1889-88, SM 2130-B	—	Floating or suspended particles, entrained air bubbles, colored solutions	Y

Table Key:

Method Reference:

[a]SM APHA *Standard Methods for the Examination of Water and Wastewater.*[2]
[b]ASTM *1993 Annual Book of ASTM Standards, Volumes 11.01 and 11.02*.

Detection Limits:

Detection limits for the procedure are written as listed. They are presented for comparative purposes only. Detection limits for laboratory analysis of actual oilfield brines may differ significantly due to interfering influences.

Field:

Y Indicates that a constituent should be analyzed in the field or as soon as possible.
Kit Indicates that a test kit (i.e. Hach) is commercially available. However, API makes no claim regarding the quality or precision of such kits. The accuracy and precision of test kits should be determined by the user.

The reference(s) for each method should be consulted for the specific reagent and equipment requirements. Generically, the following recommendations are offered:

a. All reagents should be reagent grade or better, unless otherwise stated.
b. Distilled or deionized water should be used.
c. Only appropriate significant figures should be used.
d. Glassware should be clean, crack-free, and appropriate for the analysis being done.
e. Analysts should become thoroughly familiar with the method before using it for reportable work.

5.1.1 Accuracy, Bias, and Precision

Every analytical method has a number of errors associated with it. Therefore, the reporting of results must include some measure of these errors. Some systematic errors can be reduced by collecting and analyzing replicate samples.

Increasing accuracy is often associated with increasing analytical costs or effort. However, great accuracy may not be required for all analyses and a balance can be struck between accuracy and costs.

For each method detailed in this document, there is an accuracy, bias, and precision associated with it. Where appropriate, and available, one or more of these parameters are reported. However, all these parameters are not available for every method.

Furthermore, even when available, accuracy, bias, and precision are not always presented in the same manner in the literature. Even so, enough information is presented in this document to allow the user to select an analytical method that meets the user's needs. Accuracy, bias, and precision can be defined as follows:

5.1.1.1 accuracy: A measure of the closeness of a measured value with the real value. Both bias and precision are involved in determining the accuracy of a method.

5.1.1.2 bias: A measure of the consistent deviation of the measured values from the true value. Bias measures systematic error due to both the method and to the laboratory's use of the method.

5.1.1.3 precision: Measures the agreement among replicate analyses of a single sample. Precision is usually expressed as a standard deviation. An analysis with a high precision has a small standard deviation.

5.1.2 Emerging Technology

5.1.2.1 One problem recognized in developing this document is that portions of it will soon be out of date. Analytical chemistry is a dynamic science. Established analytical methods are improved. New methods of detection are constantly being developed or are being applied to new areas or in new ways. Instrumentation is becoming more sophisticated, as demonstrated by the continued lowering of minimal detection limits and the increased ability to analyze components of complex mixtures.

5.1.2.2 Many of the reasons discussed in this document for using the analytical tests will change. Some constituents not given much emphasis today will become of greater importance in the future. In turn, some analyses discussed in detail here will someday seem to be trivial or of little importance. Therefore, it is the responsibility of the user of this document to judge the value of emerging analytical methods or of alternative analytical methods proposed in the future. Fortunately, the methods discussed here should provide users with a foundation or basis to test the applicability of new technology for their needs.

5.2 ANALYTICAL METHOD GROUPINGS

Three broad categories of analytical methods (hardness, metals analysis, and ion analysis by ion chromatography) warrant preliminary discussion:

5.2.1 Hardness

Hardness, or total hardness, is a term inherited from the water-treating industry used to describe the soap-consuming power of a water. Historically, the term itself, or variations of it, have been used as a basis for reporting the relative amounts of calcium, magnesium, carbonate, and bicarbonate ions in solution. Among the terms used are the following:

5.2.1.1 Total Hardness

This term is defined as the sum of the calcium and magnesium concentrations expressed as calcium carbonate equivalent in mg/L.

5.2.1.2 Carbonate and Bicarbonate Hardness

5.2.1.2.1 These terms describe the relative amounts of carbonate and bicarbonate ions present under different pH conditions and are commonly referred to as alkalinity.

5.2.1.2.2 A more detailed description of these concepts is included in Standard Methods 2340. All ionic species are reported in mg/L as they exist in solution. Consequently, they will not compare directly to previously cited hardness values for the same species expressed in terms of calcium carbonate equivalents in mg/L.

5.2.2 Metals Analysis

Two of the most common laboratory analytical methods for determination of most dissolved metals in oilfield waters are:

a. Flame Atomic Absorption Spectrometry (AAS).
b. Inductively Coupled Plasma Spectroscopy (ICP).

5.2.2.1 AAS Method

5.2.2.1.1 Principle

In flame atomic absorption spectrometry the sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element. Because each metal has its own characteristic absorption wavelength, the amount of energy absorbed at that wavelength (by the flame) is proportional to the element's concentration in the sample over a known concentration range.

5.2.2.1.2 Interferences

The method is relatively free of spectral or radiation interferences. The most troublesome interference is termed "chemical" and results from the lack of absorption by atoms becoming bound in molecular combinations within the flame. Such interferences can be reduced or eliminated by adding specific elements or compounds to the sample solution.

Alternatively, using a hotter nitrous oxide-acetylene flame can minimize many of these interferences. Finally, extraction procedures are available where salt matrix interferences are present. This also concentrates the sample so that the detection limits are extended.

5.2.2.1.3 Procedure Reference

SM 3111, p. 3–9.

5.2.2.2 ICP Method

Emission spectroscopy using ICP was developed as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples. Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion.

5.2.2.2.1 Principle

An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 Mhz. An aerosol of the sample is injected into the ICP and subjected to temperatures of about 6000° to 8000°K.

The high temperature results in almost complete dissociation of molecules, thus eliminating most chemical interferences. The dissociated ions produce an ionic emission spectrum. The spectrum is focused onto a monochromator to affect dispersion. After dispersion, characteristic wavelengths are detected by a photomultiplier.

5.2.2.2.2 Interferences

Spectral and non-spectral interferences can occur. Spectral interferences are generally handled by selecting alternate analytical wavelengths or by the subtraction of background spectra. Non-spectral interferences generally arise from the physical properties of the sample, such as viscosity and surface tension. High dissolved solids can also cause problems. Most interferences can be handled by careful selection of operating conditions.

5.2.2.2.3 Procedure Reference

SM 3120-B, p. 3–34.

5.2.3 Ion Chromatography (IC)

5.2.3.1 Principle

When the ion chromatograph is conventionally configured, a filtered water sample is injected into a stream of carbonate-bicarbonate passing through a series of low capacity, strongly basic anion exchange columns. Anions in the water are separated based on their relative affinity for the exchange sites. The separated anions are converted to their acid forms and are measured using an electrical-conductivity cell. Each anion is identified by its retention time in comparison to standards. Quantitation is obtained by comparative measurements of peak height or peak area.

Many cations also can be analyzed by employing similar procedures. While these cation analysis IC procedures have not yet achieved "standard" status, quantitative cationic ion exchange can be done with confidence. Literature from the instrument manufacturer should be consulted for more information.

5.2.3.2 Interferences

Any substance that has a retention time coinciding with that of any anion or cation to be determined will interfere. A high concentration of any one ion also interferes with the resolution of others. To resolve uncertainties of identification, use the method of known additions.

5.2.3.3 Procedure Reference

The references below discuss ion chromatography as it applies to the analysis of anions. With this information and literature from the instrument manufacturer, cation analysis often can be performed in a similar manner.

a. SM 4110-B.
b. ASTM D 4327-91, Vol. 11.01, p. 386.

5.3 ANALYTICAL METHODS

5.3.1 Alkalinity

Alkalinity in oilfield waters is caused by the presence of a number of different ions but is usually attributed to the presence of bicarbonate (HCO_3), carbonate (CO_3), and hydroxyl (OH) ions. Alkalinity can be defined as a measure of the ability of components of a sample to react with hydrogen ions from an added acid.

A common test for alkalinity consists of sequentially titrating the sample with a standard acid using phenolphthalein and then methyl purple as indicators. The end points of the titrations represent pH values of approximately 8.1 and 4.5, respectively.

The alkalinity of water to the phenolphthalein titration is considered to be caused by the presence of the hydroxides plus one-half the carbonates, whereas the alkalinity to the methyl purple titration is the result of the presence of all ions. Alkalinity as measured by the phenolphthalein end point usually is absent in oilfield waters and most surface waters.

Once alkalinity is measured, the concentrations of HCO_3, CO_3, and OH in the water can be calculated. The HCO_3, CO_3, and OH may then be used in one of the many scaling tendency models to predict the possibility of scale formation.

5.3.1.1 Alkalinity (Electrometric Method)

5.3.1.1.1 Principle

An electrotitrator or pH meter is used to determine the amount of acid necessary to reach pH 8.1 and 4.5, respectively. These pH values approximate the points where the hydroxide and bicarbonate ions are neutralized.

5.3.1.1.2 Interferences

Alkalinity is commonly reported as carbonate, bicarbonate, or hydroxide. However, the alkalinity resulting from the presence of borate, silicate, sulfide, phosphate, and other bases will be included in the values for carbonate and bicarbonate. No attempt is made to identify or compensate for the specific ions included in the alkalinity determination.

5.3.1.1.3 Procedure References

a. SM 2320-B, p. 2–26.
b. ASTM D1067-92, Vol. 11.01, p. 241.

5.3.1.1.4 Summary

The results obtained from the foregoing method offer a means for the stoichiometric classification of the three principal forms of alkalinity. The concentration of each ion is calculated by the relationships shown in Table 3.

5.3.1.1.5 Precision and Accuracy

The precision of the method is approximately 2 to 3 percent of the amount present. Because alkalinity is imparted by unstable water constituents which are measured at the surface, the agreement of the measured alkalinity with the actual alkalinity in the well is uncertain.

Table 3—Volume Relationships for Alkalinity Calculations

	Volume of Standard Acid Corresponding to:		
Results	Bicarbonate HCO_3	Carbonate CO_3	Hydroxide OH
$P = 0$	T	0	0
$P < {}^1/_2T$	$T - 2P$	2P	0
$P = {}^1/_2T$	0	2P	0
$P > {}^1/_2T$	0	$2(T - P)$	$2P - T$
$P = T$	0	0	T

Notes:
P = titration to pH 8.1 in mL.
T = total titration to pH 4.5 in mL.

5.3.1.2 Alkalinity (Indicator Method)

5.3.1.2.1 Principle

The basic constituents in the sample are determined by titrating with standard acid to end points indicated by acid-base indicators.

5.3.1.2.2 Interferences

Refer to 5.3.1.1.2.

5.3.1.2.3 Procedure Reference

SM 2320-B, p. 2–26.

5.3.1.2.4 Precision and Accuracy

Refer to 5.3.1.1.5.

Using the relationships expressed in Table 3, the ionic calculations are as follows:

a. Bicarbonate:

$$\text{mg/L } HCO_3 = \frac{\text{mL acid} \times \text{N acid} \times 61 \times 1{,}000}{\text{mL sample}}$$

b. Carbonate:

$$\text{mg/L } CO_3 = \frac{\text{mL acid} \times \text{N acid} \times 30 \times 1{,}000}{\text{mL sample}}$$

c. Hydroxyl:

$$\text{mg/L OH} = \frac{\text{mL acid} \times \text{N acid} \times 17 \times 1{,}000}{\text{mL sample}}$$

5.3.2 Aluminum

Aluminum is the third most abundant element of the earth's crust, occurring in minerals, rocks, and clays. This wide distribution accounts for the presence of aluminum in nearly all natural water as a soluble salt, a colloid, or an insoluble compound.

5.3.2.1 Aluminum (AAS Method)

5.3.2.1.1 Principle

Refer to 5.2.2.1.1 for discussion of Flame Atomic Absorption Spectrometry (AAS). This method is applicable for aluminum concentrations from 5 to 100 mg/L. The upper limit can be increased by serial dilution.

5.3.2.1.2 Interferences

The AAS method is free from common interferences such as fluoride and phosphate. Aluminum ionizes slightly in the nitrous oxide-acetylene flame, but the addition of sodium chloride suppresses this interference.

5.3.2.1.3 Procedure References

a. SM 3500-Al B, p. 3–43.
b. ASTM D857-89, Vol. 11.01, p. 371.

5.3.2.1.4 Precision and Accuracy

Typically, this method will yield a relative standard deviation of 4.2 percent and a relative error of 8.4 percent, depending on the skill of the operator.

5.3.2.2 Aluminum (ICP Method)

5.3.2.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principle of ICP.

5.3.2.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of the interferences of ICP.

5.3.2.2.3 Procedure Reference

SM 3500-Al C, p. 3–44.

5.3.2.2.4 Precision and Accuracy

The precision and accuracy are described by the following:

$$X = 0.9273C + 3.6,$$

$$S_t = 0.0559X + 18.6,$$

$$S_o = 0.0507X + 3.5,$$

where

X = concentration of aluminum determined, µg/L,

C = true value, µg/L,

S_t = overall precision,

S_o = single-operator precision.

5.3.2.3 Aluminum (Photometric Method)

5.3.2.3.1 Principle

With Eriochrome cyanine R dye, dilute aluminum solutions buffered to a pH of 6.0 produce a red to pink complex that exhibits maximum absorption at 535 nm. The intensity of the developed color is influenced by the aluminum concentration, reaction time, temperature, pH, alkalinity, and concentration of other ions in the sample.

To compensate for color and turbidity, the aluminum in one portion is complexed with EDTA to provide a blank. The interference of iron and manganese is eliminated by adding ascorbic acid. The optimum aluminum range lies between 20 and 300 µg/L but can be extended upward by sample dilution.

5.3.2.3.2 Interferences

Negative errors are caused by both fluoride and polyphosphates. Because the fluoride concentration often is known or can be obtained readily, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. Orthophosphate does not interfere in concentrations under 10 mg/L. The interference caused by small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulfate does not interfere up to a concentration of 2000 mg/L.

5.3.2.3.3 Procedure Reference

SM 3500-Al D, p. 3–44.

5.3.2.3.4 Precision and Accuracy

Depending on the various ions in the sample, the relative standard deviation varies from about 20 percent to 50 percent, while the relative error varies from about 2 percent to 20 percent. Thus, AAS or ICP may be preferred for analysis of certain samples.

5.3.3 Ammonia

The two major factors that influence selection of the method to determine ammonia are concentration and presence of interferences.

In general, direct manual determination of low concentrations of ammonia is confined to drinking water, and good quality, nitrified wastewater effluent. In other instances, and where interferences are present and greater precision is necessary, a preliminary distillation step is required. For high ammonia concentrations, a distillation and titration technique is preferred.

5.3.3.1 Ammonia (Nesslerization Method)

5.3.3.1.1 Principle

Direct nesslerization is suitable for determination of ammonia in purified drinking waters, natural water, and highly purified wastewater effluents, all of which should be low in color and have ammonia concentrations exceeding 0.02 mg/L. Pretreatment, before direct nesslerization with zinc sulfate and alkali, precipitates calcium, iron, magnesium, and sulfide, which results in turbidity when treated with nessler reagent. The floc also removes suspended matter and, sometimes, colored matter.

5.3.3.1.2 Interferences

Glycine, urea, glutamic acid, cyanates, and acetamide hydrolyze very slowly in solution on standing, but, of these, only urea and cyanates will hydrolyze on distillation at a pH of 9.5. Glycine, hydrazine, and some amines will react with nessler reagent to give the characteristic yellow color in the time required for the test. Similarly, volatile alkaline compounds such as hydrazine and amines will influence titrimetric results.

Some organic compounds, such as ketones, aldehydes, alcohols, and some amines, may cause a yellowish or greenish off-color or a turbidity on nesslerization following distillation. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH before nesslerization. Remove residual chlorine by sample pretreatment.

5.3.3.1.3 Procedure References

a. SM 4500-NH_3 C, p. 4–78.
b. ASTM D1426-89, Vol. 11.01, p. 379.

5.3.3.1.4 Precision and Accuracy

Direct nesslerization of a concentration of 1 mg/L yields a relative standard deviation of about 12 percent and a relative error of less than 1 percent. At concentrations near 0.2 mg/L the RSD is approximately double at 22 percent.

5.3.3.2 Ammonia (Selective Ion Electrode Method)

5.3.3.2.1 Principle

The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($NH_{3(aq)}$ and NH_4^+) is converted to $NH_{3(aq)}$ by raising the pH with a strong base to above 11.

The ammonia thus formed diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter.

This method is applicable to the measurement of 0.03 to 1400 mg/L of ammonia in potable and surface waters, and domestic and industrial wastes.

5.3.3.2.2 Interferences

Volatile amines are a positive interference. Mercury and silver interfere by complexing with ammonia. High concentrations of dissolved ions affect the measurement, but color and turbidity do not.

5.3.3.2.3 Procedure References

a. SM 4500-NH_3 F, p. 4–81.
b. ASTM D1426-89, Vol. 11.01, p. 379.

5.3.3.2.4 Precision and Accuracy

The precision and accuracy vary greatly with concentration. At low concentrations (<0.1 mg/L NH_3), errors of 100 percent or more are possible, while at about 20 mg/L and above the precision and the accuracy are better than 5 percent.

5.3.3.3 Ammonia (Titrimetric Method)

5.3.3.3.1 Principle

The titrimetric method is used only on samples that have been carried through preliminary distillation using boric acid as the absorbent. The distillate is titrated with standard sulfuric acid titrant to the referenced end-point. A blank should be carried through all steps of the procedure and the necessary correction applied to the results.

5.3.3.3.2 Interferences

Interferences from cyanates and organic nitrogen compounds are minimized by buffering the distillation solution at pH 9.5.

5.3.3.3.3 Procedure Reference

SM 4500-NH_3 E, p. 4–81.

5.3.3.3.4 Precision and Accuracy

For a concentration of 0.2 mg/L the reported relative standard deviation is 69.8 percent and the relative error is 20.0 percent. As the concentration is raised to 1.5 mg/L the RSD is 21.6 percent and the RE is 2.6 percent.

5.3.3.4 Ammonia (Ion Chromatography Method)

Ion chromatography has been successfully applied to the analysis of low ppm and ppb levels of ammonia and several amines. Species identification is made by comparison of retention times with those of standards. Quantitation is performed using a method of external standards.

5.3.3.4.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.3.4.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.3.4.3 Procedure References

Refer to 5.2.3.3 for discussion of references.

5.3.4 Barium

Barium in the form of barium sulfate scale is a frequent cause of operating difficulties. It is unlikely that a water could contain high concentrations of both barium and sulfate ions. Therefore, if the routine water analysis shows a high sulfate concentration, the barium content should be low. Barium is determined by ICP, AAS, or gravimetrically. A quick routine determination may be made turbidimetrically.

Scale deposits cause serious problems in oilfield operations. These deposits usually result from the mixing of two or more oilfield waters. Mixing can occur on the surface, as in secondary-recovery operations, or downhole, as in casing failures. In any case, it is desirable to know whether waters have scale-forming tendencies. The sulfate scales are the most difficult to combat because of their lack of solubility.

5.3.4.1 Barium (ICP Method)

5.3.4.1.1 Principle

Refer to 5.2.2.2.1 for discussion of the principle of ICP.

5.3.4.1.2 Interferences

Refer to 5.2.2.2.2 for discussion of the interferences of ICP.

5.3.4.1.3 Procedure Reference

SM 3500-Ba C, p. 3–52.

5.3.4.1.4 Precision and Accuracy

The detection limit is about 0.002 mg/L. The precision is approximated by:

$$S_t = 0.1819X + 2.78,$$

$$S_o = 0.1285X + 2.55,$$

where

S_t = overall precision,

S_o = single-operator precision,

X = concentration of barium determined, µg/L.

The bias is given by: $X = 0.7683C + 0.47$,

where

X = mean recovery, µg/L,

C = true value, µg/L.

5.3.4.2 Barium (AAS Method)

5.3.4.2.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS.

5.3.4.2.2 Interferences

Refer to 5.2.2.1.2 for general discussion of AAS interferences. The addition of an excess of potassium (2 mL of a 2.5 percent KCl solution per 100 mL of sample) will reduce the ionization effect of barium in the flame. This method is applicable for barium concentrations from 1.0 to 20.0 mg/L. The upper limit can be increased by serial dilution techniques.

5.3.4.2.3 Procedure References

a. SM 3500-Ba B, p. 3–52.
b. ASTM D3651-92, Vol. 11.02, p. 461.

5.3.4.2.4 Precision and Accuracy

The precision and accuracy of the method, for undiluted samples in the range of 1.0 to 20.0 mg/L, is 8.9 percent and 2.7 percent, respectively. The detection limit is about 0.03 mg/L.

5.3.4.3 Barium (Turbidimetric Method)[1]

5.3.4.3.1 Principle

This procedure has been devised to measure the tendency of water to form a precipitate in the presence of sulfate ions. This tendency is called a P.S. (Precipitated by Sulfate) value and is reported as barium sulfate. Since this is primarily a measure of scale-forming tendency, the ability of the P.S. value to include calcium and strontium sulfate is of no particular concern.

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[1] Robertson, R.S. and Walesa, A.C.

5.3.4.3.2 Interferences

Polyphosphate is the most common interference and 2.0 mg/L or more can inhibit the formation of turbidity. Polyphosphate interference can be eliminated by boiling 50 mL of sample with 15 drops of 6 N hydrochloric acid for 1 hour. Maintain volume during boiling. The sample is neutralized (approximate pH of 7) with 1 N sodium hydroxide, cooled, and diluted to the original volume.

Interference can also be expected from high concentrations of organic acids or organic complexing agents, such as scale or other treating chemicals.

5.3.4.3.3 Equipment

a. Photometer, violet filter or 420 nm.
b. Buret, automatic, 25-, 50-mL.
c. Beaker, 250-mL.
d. Stop watch.
e. Volumetric flask, 1-liter.
f. Gelatin capsule, No. 000.

5.3.4.3.4 Reagents

a. Acid reagent: Dissolve 900 mg of $MgCl_2{\bullet}6H_2O$, 0.040 g $BaCl_2{\bullet}2\ H_2O$, and 0.005 g of sodium citrate dihydrate in approximately 300 mL of distilled water in a liter volumetric flask. Add 10.0 mL of a 2,500 mg/L Aerosol OT (dioctyl ester of sodium sulfosuccinic acid) solution, 50.0 mL of concentrated hydrochloric acid, and dilute to volume.

b. Sulfate reagent: Fill No. 000 gelatin capsule with 1.15 ±0.05 g of $MgSO_4{\bullet}7\ H_2O$. This weight can be approximated by filling the body of the capsule level full before capping. The magnesium sulfate should be clear, fine, needle-like crystals without opaque spots.

5.3.4.3.5 Procedure

a. The sample must be clear and the calcium content shall not exceed 4,500 mg/L. Filter to remove turbidity and dilute to reduce calcium concentration, if necessary.

b. Pipet 15-mL sample into each of two matched cells. (If cells will not hold 15 mL, use suitable containers and transfer to cells).

c. Add 2 mL of acid reagent to each cell and mix. Reserve one cell for blank.

d. Add contents of one capsule to cell and begin mixing immediately (within 5 sec), first with sudden motion to disperse crystals followed by slow rhythmic motions. Continue mixing for approximately $1^1/_2$ min. Avoid entraining excessive amounts of air.

e. Five minutes after the addition of sulfate, zero the instrument with blank, and take a reading on the test cell. A wavelength of 420 µm is used. A violet filter should be used with a filter photometer.

f. Read P.S. value from calibration curve.

5.3.4.3.6 Preparation of Calibration Curve

a. Prepare 1 liter of standard solution containing 200 mg/L strontium sulfate added as strontium chloride, 4,000 mg/L calcium carbonate, added as calcium chloride, and 75,000 mg/L sodium chloride added as sodium chloride. The strontium and calcium salts are prepared by dissolving the appropriate amount of the carbonate in concentrated hydrochloric acid, evaporating to dryness, and dissolving in distilled water.

b. Using convenient volumes of the standard solution, prepare a series of samples containing from 10 to 200 mg/L of barium. The barium is added as $BaCl_2{\bullet}2H_2O$.

c. The turbidity of the samples is measured. The readings (percent absorption, or optical density) versus barium sulfate (P.S.) content in mg/L are graphed on coordinate paper.

5.3.4.3.7 Reference

Robertson, R. S. and Walesa, A. C.[1]

5.3.5 Biochemical Oxygen Demand (BOD)

BOD is the oxygen demand that is required for bacterial activity in oxidizing organic material. Its determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluent, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems.

5.3.5.1 BOD

5.3.5.1.1 Principle

Dilutions of the sample are made in dilution buffer containing bacterial growth nutrients such as nitrogen, phosphorus, trace metals, and oxidizing bacteria. The dilutions are sealed and incubated (5 days is typical). Initial dissolved oxygen content is subtracted from final dissolved oxygen measurements.

5.3.5.1.2 Interferences

Any material that will interfere with bacterial growth will interfere with the BOD test. The presence of readily oxidizable nitrogenous compounds will lead to erroneous BOD results.

5.3.5.1.3 Procedure Reference

SM 5210-B, p. 5–20.

5.3.5.1.4 Summary

The results of this analysis method are heavily dependent on sampling and storage conditions. Other chemicals exhibiting an oxygen demand, such as sulfide and ferrous iron, will bias the results. The results are also affected by the "seed" cultures used (which may vary from locale to locale).

5.3.5.1.5 Precision and Accuracy

There is no measurement for establishing bias for the BOD procedure.

5.3.6 Boron

Boron may prove useful in identifying the sources of intrusive brines. Boron is present in oilfield brines as boric acid, borates, and organic borates. When it exists as associated boric acid, it is important in the buffer mechanisms, second only to the carbonate system. It may be precipitated as relatively insoluble calcium and magnesium borates.

Boron, together with bromine and iodine, is generally associated with waters accompanying petroleum. Like chlorine, it is an element of marine origin. The solubility of most boron compounds, the hydrolytic cleavage of boron salts, and their ability to be occluded and co-precipitated with other compounds aid the extensive migration of boron. Soluble complex boron compounds in brines and connate waters probably are a result of the decay of the same plants and animals that were the source of petroleum.

5.3.6.1 Boron (ICP Method)

5.3.6.1.1 Principle

Refer to 5.2.2.2.1 for discussion of the principle of ICP.

5.3.6.1.2 Interferences

Refer to 5.2.2.2.2 for discussion of the interferences of ICP. The detection limit is about 0.02 mg/L.

5.3.6.1.3 Procedure Reference

SM 4500-B D, p. 4–10.

5.3.6.1.4 Precision and Accuracy

The precision and accuracy are described by the following:

$$X = 0.8807C + 9.0,$$

$$S_t = 0.1150X + 14.1,$$

$$S_o = 0.0742X + 23.2,$$

where

X = concentration of boron determined, µg/L,

C = true value, µg/L,

S_t = overall precision, µg/L,

S_o = single-operator precision, µg/L.

5.3.6.2 Boron (Photometric Method)

5.3.6.2.1 Principle

Boron reacts with carminic acid in concentrated sulfuric acid to form a bluish-red substance whose intensity is proportional to the boron concentration.

5.3.6.2.2 Interferences

The ions commonly found in water and wastewater do not interfere. The minimum detectable quantity is 2µg of boron.

5.3.6.2.3 Procedure Reference

SM 4500-B C, p. 4–10.

5.3.6.2.4 Precision and Accuracy

An analysis by nine laboratories of a synthetic sample containing 180 µg/L B, 50 µg/L As, 400 µg/L Be, and 50 µg/L Se in distilled water yielded a relative standard deviation of 35.5 percent and a relative error of 0.6 percent.

5.3.7 Bromide

Bromide analysis may be useful in identifying the source of oilfield waters and differentiating between subsurface formations.

5.3.7.1 Bromide (Ion Chromatography Method)

5.3.7.1.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.7.1.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.7.1.3 Procedure References

Refer to 5.2.3.3 for discussion of references.

5.3.7.1.4 Summary

Bromide is one of seven common anions readily determined by ion chromatography in a single analytical operation. The others are F^-, SO_4^-, NO_2^-, PO_4^-, Cl^-, and NO_3^-. Anion combinations which may be difficult to distinguish by other analytical methods are readily separated by IC.

5.3.7.1.5 Precision and Accuracy

The detection limit for this method is 0.1 mg/L. The precision and accuracy for this method is 5 to 6 percent and 4 to 5 percent respectively.

5.3.8 Calcium

Calcium contributes to the severe carbonate and sulfate scales associated with oilfield waters. Carbonate scales are readily treated with acid. Sulfate scale problems are difficult to handle, because there are very few chemicals that will dissolve the scale after it has been deposited.

Calcium is determined by the ICP, AAS, Permanganate Method, and Compleximetric Method. The Permanganate and Compleximetric Methods are subject to interferences from barium and strontium. Therefore, the preferred method of analysis is ICP or AAS.

5.3.8.1 Calcium (ICP Method)

5.3.8.1.1 Principle

Refer to 5.2.2.2.1 for discussion of the principle of ICP.

5.3.8.1.2 Interferences

Refer to 5.2.2.2.2 for discussion of the interferences of ICP.

5.3.8.1.3 Procedure Reference

SM 3500-Ca C, p. 3–57.

5.3.8.1.4 Precision and Accuracy

The detection limit is about 0.01 mg/L. The precision is approximated by:

$$S_t = 0.1228X + 10.1,$$

$$S_o = 0.0189X + 3.7,$$

where

S_t = overall precision,

S_o = single-operator precision,

X = concentration of calcium determined, µg/L.

The bias is given by: $X = 0.9182C - 2.6$,

where

X = mean recovery, µg/L,

C = true value, µg/L.

5.3.8.2 Calcium (AAS Method)

5.3.8.2.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS.

5.3.8.2.2 Interferences

Refer to 5.2.2.1.2 for discussion of AAS interferences. This method is applicable for calcium concentrations from 0.2 to 20.0 mg/L. The upper limit can be increased by serial dilution techniques.

5.3.8.2.3 Procedure References

a. SM 3500-Ca B, p. 3-57.
b. ASTM D511-92, Vol. 11.01, p. 435.

5.3.8.2.4 Precision and Accuracy

The precision and accuracy of the method, for undiluted samples, is 4.2 percent and 0.4 percent respectively. The detection limit is about 0.003 mg/L.

5.3.8.3 Calcium (Compleximetric Titration Method)

5.3.8.3.1 Principle

Calcium and magnesium are both complexed by EDTA at pH 10, while only calcium is complexed at pH 12 because of precipitation of magnesium as the hydroxide. Consequently, by titrating a sample with standard EDTA at pH 12, the calcium concentration of the sample can be determined.

5.3.8.3.2 Interferences

Ions commonly present in oilfield waters that interfere with this method are iron, barium, and strontium. Barium and strontium are included with the calcium determination and usually are present in quantities smaller than the calcium.

5.3.8.3.3 Procedure References

a. SM 3500-Ca D, p. 3–57.
b. ASTM D511-92, Vol. 11.01, p. 435.

5.3.8.3.4 Summary

This method is applicable to most waters in the range from 1 to 1000 mg/L of calcium. Upper limits may be extended by dilution. The titration endpoint may be difficult to see and some operator practice is required. Several reliable field test kits exist for this testing. As with all test kits, the accuracy and precision should be determined by the user.

5.3.8.3.5 Precision and Accuracy

The detection limit for this method is 1 mg/L. The precision and accuracy for this method is 9.2 percent and 1.9 percent, respectively.

5.3.9 Carbon Dioxide

Surface waters normally contain less than 10 mg free carbon dioxide (CO_2) per liter while ground waters may easily contain several hundred milligrams per liter. The CO_2 content of a water contributes to its alkalinity, scaling tendency, and to corrosion. Since carbon dioxide is a dissolved gas, it is important that the analysis be done promptly (on site preferred).

5.3.9.1 Carbon Dioxide (Titrimetric Method)

5.3.9.1.1 Principle

Free CO_2 reacts with sodium hydroxide to form sodium bicarbonate. Completion of the reaction is indicated potentiometrically or by the development of the pink color characteristic of phenolphthalein indicator.

5.3.9.1.2 Interferences

Cations and anions that quantitatively disturb the normal CO_2-carbonate equilibrium interfere with the determination. Metal ions that precipitate in alkaline solution, such as aluminum, chromium, copper, and iron, contribute to high results. Ferrous iron should not exceed 1 mg/L. Positive errors also are caused by weak bases, such as ammonia or amines, and by salts of weak acids and strong bases, such as borate, nitrite, phosphate, silicate, and sulfide.

5.3.9.1.3 Procedure Reference

SM 4500-CO_2 C, p. 4–17.

5.3.9.1.4 Summary

Carbon dioxide is an important parameter within oilfield waters. Its presence has an effect on scaling, pH, and corrosion.

5.3.9.1.5 Precision and Accuracy

Precision and accuracy are on the order of 10 percent.

5.3.10 Chloride

Chloride is present in practically all oilfield waters. The concentration of chloride ranges from very dilute to saturated and may cause a serious disposal problem.

The chloride concentration can be used to estimate the resistivity of formation waters and differentiate between subsurface formations.

Chloride is determined by Mohr/Colorimetric titration, Mohr/Electrometric titration, Mercuric Nitrate titration, and Ion Chromatography (IC).

5.3.10.1 Chloride (Mohr/Colorimetric Method)

5.3.10.1.1 Principle

The Mohr Method is based on the reaction of the indicator, potassium chromate, with the first excess of standard silver nitrate titrant forming an insoluble red silver chromate precipitate at the end point. Because of the lower solubility of silver chloride, all the chloride reacts with the silver nitrate before any silver chromate forms. This method is suitable for analyzing solutions whose pH is between 6.0 and 8.5. This makes it directly applicable to most oilfield waters without making any pH adjustment.

5.3.10.1.2 Interferences

The Mohr Method is subject to interference from bromides, iodides, thiocyanate, phosphates, carbonates, and sulfides, that also precipitate silver ions. Of these, bromides, iodides, and sulfides are often present in oilfield waters. Usually no attempt is made to compensate for bromide and iodide, because they are not present in sufficient quantity to affect the chloride results.

Sulfides are removed by acidifying the solution with nitric acid and boiling. Cyanides and thiosulfates are rarely present, but would interfere by forming soluble silver complexes. Iron, barium, lead, and bismuth precipitate with the chromate indicator. Of these, iron is most frequently encountered. If necessary, iron can be removed by precipitation with sodium hydroxide or sodium peroxide and filtering, or by a cation exchange resin.

5.3.10.1.3 Procedure References

a. SM 4500-Cl^- B, p. 4–49.
b. ASTM D4458-85, Vol. 11.02, p. 473.

5.3.10.1.4 Precision and Accuracy

The detection limit for this method is 0.5 mg/L. The precision and accuracy for this method is 4.2 percent and 1.7 percent, respectively.

5.3.10.2 Chloride (Mohr/Electrometric Method)

5.3.10.2.1 Principle

The Mohr/Electrometric Method is based on the potentiometric titration with silver nitrate using a glass and silver-silver chloride electrode system. During the titration, the change in potential between the glass and silver-silver chloride electrodes is measured by means of an electronic voltmeter. The endpoint of the titration is determined when the greatest change in voltage has occurred while adding silver nitrate at a constant rate.

5.3.10.2.2 Interferences

The Mohr/Electrometric Method is subject to interference from bromides, iodides, thiocyanate, and sulfides, which also precipitate silver ions. Of these, bromides, iodides, and sulfides are often present in oilfield waters. Usually, no attempt is made to compensate for bromide and iodide because they are not present in sufficient quantity to affect the chloride results.

Sulfides are removed by acidifying the solution with nitric acid and boiling. Cyanides and thiosulfates are rarely present, but would interfere by forming soluble silver complexes. Ferric iron, if present at substantially higher levels than the chloride, will interfere.

5.3.10.2.3 Procedure Reference

SM 4500-Cl^- D, p. 4-51.

5.3.10.2.4 Precision and Accuracy

The detection limit for this method is 1 mg/L. The precision and accuracy for this method is 2.5 percent and 2.5 percent, respectively.

5.3.10.3 Chloride (Mercuric Nitrate Method)

5.3.10.3.1 Principle

The Mercuric Nitrate Method is based on the reaction of mercuric nitrate with chloride to form a soluble, slightly dissociated mercuric chloride. As the titration proceeds, the first excess mercuric nitrate forms a purple complex with the indicator, diphenylcarbazone, in the pH range of 2.3 to 2.8.

5.3.10.3.2 Interferences

The Mercuric Nitrate Method is subject to interference from bromides, iodides, chromates, ferric iron, and sulfite. Of these, bromides, iodides, and sulfites may be present in oilfield waters. Usually, no attempt is made to compensate for bromide and iodide, because they are not present in sufficient quantity to affect the chloride results.

5.3.10.3.3 Procedure References

a. SM 4500-Cl^- C, p. 4-50.
b. ASTM D512-89, Vol. 11.01, p. 449.

5.3.10.3.4 Precision and Accuracy

The detection limit for this method is 0.5 mg/L. The precision and accuracy for this method are 3.3 percent and 2.9 percent, respectively.

5.3.10.4 Chloride (Ion Chromatography Method)

5.3.10.4.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.10.4.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.10.4.3 Procedure References

Refer to 5.2.3.3 for discussion of references.

5.3.10.4.4 Summary

Chloride is one of seven common anions readily determined by ion chromatography in a single analytical operation. The others are F^-, SO_4^-, NO_2^-, PO_4^-, Br^-, and NO_3^-. Anion combinations that may be difficult to distinguish by other analytical methods are readily separated by IC.

5.3.10.4.5 Precision and Accuracy

The detection limit for this method is 0.1 mg/L. The precision and accuracy for this method are 5 to 6 percent and 4 to 5 percent, respectively.

5.3.11 Chromium

Chromium is important in oilfield water analysis because of its toxicity and environmental issues.

5.3.11.1 Chromium (AAS Method)

5.3.11.1.1 Principle

Refer 5.2.2.1.1 for discussion of AAS. Dissolved chromium is determined by aspiration of a filtered sample without pretreatment. Total chromium is measured by using a hydrochloric-nitric acid digestion before the filtration step.

5.3.11.1.2 Interferences

General interferences are few as discussed in 5.2.2.1.2. Ionization interference is controlled by adding large excesses of easily ionized sodium. Iron, nickel, and cobalt at 100 µg/L and magnesium at 30 µg/L interfere. Using 8-hydroxyquinoline at 10,000 mg/L eliminates these interferences.

5.3.11.1.3 Procedure References

a. SM 3500-Cr B, p. 3–59.
b. ASTM D1687-92, Vol. 11.01, p. 460.

5.3.11.1.4 Precision and Accuracy

The detection limit for chromium is 0.02 mg/L. ASTM D1687-92 reports that the overall precision (S_T) varied linearly with the chromium concentration, x, in mg/L. For selected water matrices:

$$S_T = 0.079x + 0.019.$$

5.3.11.2 Chromium (ICP Method)

5.3.11.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.11.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of the interferences of ICP.

5.3.11.2.3 Procedure Reference

SM 3500-Cr C, p. 3–59.

5.3.11.2.4 Precision and Accuracy

The detection limit is about 0.007 mg/L. The precision and bias were given as:

$$X = 0.9544C + 3.1,$$

$$S_t = 0.0499X + 4.4,$$

$$S_o = 0.0009X + 7.9,$$

where

X = mean recovery, µg/L,

C = true value, µg/L,

S_t = overall precision, µg/L,

S_o = single operator precision, µg/L.

5.3.11.3 Chromium (Colorimetric Method)

5.3.11.3.1 Principle

All chromium is converted to hexavalent chromium by potassium permanganate. Chromium is then determined via its reaction with diphenylcarbazide in acid solution. To determine total chromium, the sample is first digested with sulfuric-nitric acid before adding the permanganate.

5.3.11.3.2 Interferences

Minor interferences are possible from molybdenum, vanadium, iron, and copper. If encountered, these are easily removed.

5.3.11.3.3 Procedure References

a. SM 3500-Cr D, p.3-59.
b. ASTM D1687-92, Vol. 11.01, p. 460.

5.3.11.3.4 Summary

This method covers total and hexavalent chromium in most waters and waste waters over the range of 0.5 to 5.0 mg/L. This range is extended upward by dilution.

5.3.11.3.5 Precision and Accuracy

Standard Methods Section 3500-Cr D reports a relative standard deviation of 47.8 percent and a relative error of 16.3 percent. The minimum detection limit is about 0.5 mg/L.

5.3.12 Chemical Oxygen Demand (COD)

COD is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. COD is often used as an indicator of water “pollution” by organic materials.

5.3.12.1 COD (Open Reflux Method)

5.3.12.1.1 Principle

A sample is refluxed in a strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulfate to determine the $K_2Cr_2O_7$ consumed.

5.3.12.1.2 Interferences

This method cannot be used for samples containing more than 2000 mg/L Cl^-. Other techniques must be used. Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent. Reduced inorganic species, such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively.

5.3.12.1.3 Procedure Reference

SM 5220-B, p. 57.

5.3.12.1.4 Precision and Accuracy

The minimum detection concentration is 1 mg/L carbon. Precision is about 10 percent, bias about 5 percent.

5.3.13 Conductivity

The conductivity of an oilfield water is a measure of the ability of ions in the water to carry (conduct) an electric current. The current carried through the water is a function of the relative velocities with which the different ions move. Various ions differ widely in their velocity and in their effect on resistivity. In addition, temperature of the electrolyte affects the ionic velocities and, consequently, the conductivity.

Conductivity measurements are often converted to resistivity measurement for use in the interpretation of electric well logs. Such log interpretations are beyond the scope of this document. However, the graph in Appendix A has been retained from earlier versions of this standard to assist those users who still desire to use a resistivity measurement to interpret well resistivity logs. This graph estimates resistivity by plotting equivalent sodium chloride concentration and temperature.

5.3.13.1 Conductivity (Instrumental Method)

5.3.13.1.1 Principle

A dip cell (conductivity cell) containing two platinum electrodes of a fixed area and at a fixed distance apart are immersed in the sample. The conductance is measured with a Wheatstone bridge-type instrument and expressed in 1µohm-cm.

5.3.13.1.2 Interferences

Oil or organic compounds can coat the electrodes and interfere. Exposure of the sample to the atmosphere will result in loss or gain of dissolved gases, which change the conductivity. A flow-through or in-line cell limits this change.

5.3.13.1.3 Procedure Reference

a. SM 2510-B, p. 2–43.
b. ASTM D1125-91, Vol. 11.01, p. 253.

5.3.13.1.4 Summary

If conductivity is measured at 25°C, no temperature correction is necessary, thus eliminating a major source of error. At other temperatures, corrections are needed and are provided by the reference method.

5.3.13.1.5 Precision and Accuracy

Precision and accuracy depend entirely on the instrument used and can best be obtained from the manufacturer.

5.3.14 Fluoride

Fluoride is useful in identifying the source of oilfield waters and differentiating between subsurface formations.

5.3.14.1 Fluoride (Ion Chromatography Method)

5.3.14.1.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.14.1.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.14.1.3 Procedure References

Refer to 5.2.3.3 for discussion of references.

5.3.14.1.4 Summary

Fluoride is one of seven common anions readily determined by ion chromatography in a single analytical operation. The others are Br^-, SO_4^-, NO_2^-, PO_4^-, Cl^-, and NO_3^-. Anion combinations that may be difficult to distinguish by other analytical methods are readily separated by IC.

5.3.14.1.5 Precision and Accuracy

The detection limit for this method is 0.1 mg/L. The precision and accuracy for this method are 5 to 6 percent and 4 to 5 percent, respectively.

5.3.14.2 Fluoride (Ion Selective Electrode Method)

5.3.14.2.1 Principle

Fluoride ion is measured potentiometrically using an ion-selective fluoride electrode in combination with a standard reference electrode and a pH meter with an expanded millivolt scale, or a selective ion meter having a direct concentration scale for fluoride. Fluoride concentrations from 0.1 to 1000 mg/L may be measured by this method.

5.3.14.2.2 Interferences

Interferences from extremes of pH and polyvalent cations (Si^{+4}, Fe^{+3}, and Al^{+3}) are controlled by addition of a pH 5.0 buffer containing citrate ion.

5.3.14.2.3 Procedure References

a. SM 4500-F^- C, p. 4–61.
b. ASTM D1179-88, Vol. 11.01, p. 515.

5.3.14.2.4 Precision and Accuracy

Precision varies with concentration and is graphically presented in ASTM D1179-88. Using the citrate buffer, typically, the relative standard deviation is less than 4 percent and the relative error is less than 2 percent.

5.3.15 Iodide

Iodide is frequently added to injection water to act as a chemical tracer, which is useful in identifying the source of oilfield waters and differentiating between subsurface formations.

5.3.15.1 Iodide (Titration Method)

5.3.15.1.1 Principle

Iodide is oxidized to iodate with bromine water, the excess bromine is decomposed with sodium formate. The iodate is reacted with iodide to form iodine which is then titrated with sodium thiosulfate.

5.3.15.1.2 Interferences

Iron, manganese, and organic material can interfere. These interferences are removed by precipitation and filtration.

5.3.15.1.3 Procedure Reference

ASTM D3869-79, Vol. 11.02, p. 468.

5.3.15.1.4 Precision and Accuracy

The precision and accuracy of the method was found to be about 1 to 2 percent of the amount of iodide present in the range of 10 to 50 mg/L. The detection limit of the method is 0.2 mg/L.

5.3.15.2 Iodide (Ion Chromatography Method)

5.3.15.2.1 Principle

Refer to 5.2.3.1 for discussion of IC principle.

5.3.15.2.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.15.2.3 Procedure Reference

Refer to 5.2.3.3 for discussion of references.

5.3.15.2.4 Summary

Ion Chromatography has been successfully applied to the analysis of low ppm levels of iodide. Species identification is made by comparison of retention times with those of standards. Quantitation is performed using a method of external standards.

5.3.15.3 Iodide (Ion Selective Electrode Method)

5.3.15.3.1 Principle

Iodide is determined by a method of standard addition. An iodide selective electrode and a standard reference electrode are placed in a solution and the potential is recorded. Additional potential values are generated after each of two standard additions. The electrode slope is determined from the potential measurements of the iodide solutions of known concentration. The iodide concentration of the original unknown solution is then calculated. This method is applicable to oilfield waters containing 1 to 2000 mg/L iodide.

5.3.15.3.2 Interferences

Ions commonly found in oilfield waters that interfere with the method are Cl^-, Br^-, and S^{-2}. The maximum allowable ratio of interfering ion to iodide is as follows: Cl^-, 10^6; Br^-, 5×10^3; S^{-2}, $<10^{-6}$. Sulfide interference can be eliminated by buffering the sample at pH 6 or lower.

5.3.15.3.3 Procedure Reference

ASTM D3869-79, Vol. 11.02, p. 478.

5.3.15.3.4 Precision and Accuracy

The precision varies with the quantity being tested in accordance with a graph contained in ASTM D3869-79. A positive bias of 8.7 percent or less was determined from four solutions containing iodide in the range 12 to 1375 mg/L.

5.3.16 Iron

There are many methods available for determining iron concentrations in oilfield water. Most methods have interference problems with other ions. In addition, analysis is complicated by various combinations of chemical and physical forms in which the iron can exist (ferrous, ferric, or both; suspended, colloidal, and undissolved).

Under reducing conditions, iron exists in the ferrous state. In the absence of complex-forming substances, ferric iron is not significantly soluble unless the pH is very low. On exposure to air or addition of oxidants, ferrous iron is readily oxidized to the ferric state and may hydrolyze to form insoluble hydrated ferric oxide. Because of this instability, determination of ferrous iron requires special precautions and may need to be done in the field at the time of sample collection.

5.3.16.1 Iron (Phenanthroline Method)

5.3.16.1.1 Principle

Iron is brought into solution, reduced to the ferrous state, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form a an orange-red complex. The colored solution obeys Beer's law.

5.3.16.1.2 Interferences

Known interferences are strong oxidizing agents, cyanide, nitrate, and polyphosphates.

Other interfering ions include chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L, and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdenum, and silver precipitate phenanthroline. Boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrate interferences. Adding excess hydroxylamine eliminates errors induced by strong oxidizers. Excess phenanthroline can eliminate interferences by most metal ions.

5.3.16.1.3 Procedure References

SM 3500-Fe D, p. 3–66.

5.3.16.1.4 Summary

This method provides iron determinations of sufficient precision and accuracy for oilfield waters. It should be noted that sample variability and instability affect precision and accuracy more than will analysis errors. To obtain maximum precision and accuracy, ferrous iron may be determined in the field during sample collection. Several field test methods (iron test kits) exist for such testing. As with all test kits, the sufficiency of the accuracy and precision should be determined by the user.

5.3.16.1.5 Precision and Accuracy

Precision and accuracy depend on the method of sample collection and storage, the iron concentration, and the presence of interfering color, turbidity, and foreign ions. Visual colorimetry methods have a precision of 5 percent. Photometric measurements have a precision of 3 percent or 3 microgram, whichever is greater. Because of sampling and storage problems, a relative error of 13 percent can be expected. The detection limit is about 0.01 mg/L.

5.3.16.2 Iron (AAS Method)

5.3.16.2.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS.

5.3.16.2.2 Interferences

Refer to 5.2.2.1.2 for discussion of the interferences of AAS.

5.3.16.2.3 Procedure Reference

SM 3500-Fe B, p. 3–66.

5.3.16.2.4 Summary

This method provides iron determinations of sufficient precision and accuracy for oilfield waters. Sample preparation techniques are available, depending on the need to measure dissolved iron (ferrous) only or total iron. However, due to iron's ready oxidation during sample transit and storage, only total iron is measured in the laboratory.

To measure ferrous iron present in the field water, the sample must be immediately filtered (preferably by in-line filtration) upon collection to remove ferric iron. All the iron subsequently measured by AAS was originally ferrous iron.

If iron oxidizes and precipitates between the time of sampling/filtration and the time of analysis, the precipitate must be redissolved before analysis when measuring total iron.

5.3.16.2.5 Precision and Accuracy

The precision of the method is about 5.8 percent and the accuracy is about 2.3 percent. The detection limit is about 0.02 mg/L. However, precision and accuracy depend heavily on sample collection and storage.

5.3.16.3 Iron (ICP Method)

5.3.16.3.1 Principle

Refer to 5.2.2.2.1 for discussion of ICP.

5.3.16.3.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.16.3.3 Procedure Reference

SM 3120-C, p, 3–66.

5.3.16.3.4 Summary

The sample preparation techniques utilize relatively concentrated acid solutions. Therefore, only total iron can be determined at analysis time. To measure the ferrous iron present in a field water, the sample must be immediately filtered (in-line filtration preferred) upon collection to remove ferric iron. All the iron subsequently measured by ICP is ferrous iron.

5.3.16.3.5 Precision and Accuracy

The precision and accuracy of the method are dependent on the iron concentration. These values are calculated from a linear regression equation (refer to 5.3.16.3.3). For iron concentrations found in oilfield waters, the precision of the method is about 5 percent and the accuracy is about 2 percent. The detection limit is about 0.007 mg/L. However, precision and accuracy depend heavily on sample collection and storage.

5.3.17 Lithium

Lithium is a minor constituent of minerals, present in fresh waters in concentrations below 0.2 mg/L. Brines and thermal waters may contain higher levels. The atomic adsorption spectrometric method and the inductively coupled plasma method are preferred.

5.3.17.1 Lithium (AAS Method)

5.3.17.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for lithium concentrations from 0.1 to 70,000 mg/L. The determination of lithium in brackish water, sea water, and brine is easily accomplished, but may require the use of the method of additions described in ASTM D3561-77.

5.3.17.1.2 Interferences

Refer to 5.2.2.1.2 for discussion of the interferences of AAS. Ionization interference is controlled by adding large excesses of easily ionized sodium.

5.3.17.1.3 Procedure References

a. SM 3500-Li B, p. 3–71.
b. ASTM D3561-77, Vol. 11.02, p. 486.

5.3.17.1.4 Precision and Accuracy

The detection limit for lithium is 0.002 mg/L. ASTM D3561-77 gives the precision as:

$$S_t = 0.0677X + 3.127,$$

$$S_o = 0.0486X + 1.936,$$

where

S_t = overall precision,
S_o = single-operator precision,
X = concentration of lithium determined, mg/L.

The bias was given as 5 percent.

5.3.17.2 Lithium (ICP Method)

5.3.17.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.17.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.17.2.3 Procedure Reference

SM 3500-Li C, p. 3–71.

5.3.17.2.4 Precision and Accuracy

The detection limit is 0.04 mg/L. The precision and bias data were not given.

5.3.17.3 Lithium (Flame Emission Photometry)

5.3.17.3.1 Principle

Trace amounts of lithium can be determined by flame emission photometry at a wavelength of 670.8 nm. The sample is sprayed into a gas flame and excited under carefully controlled and reproducible conditions. The desired spectral line is isolated and its intensity is measured. The value determined is compared to a standard curve.

5.3.17.3.2 Interferences

High concentrations of barium, strontium, and calcium interfere; sodium sulfate-sodium carbonate solutions precipitate these ions. The magnesium content must not exceed 10 mg in the portion of the sample taken for analysis.

5.3.17.3.3 Procedure Reference

SM 3500-Li D, p. 3–71.

5.3.17.3.4 Precision and Accuracy

The detection limit for lithium is 0.004 mg/L. Precision is 5 percent and accuracy is 1.38 percent.

5.3.18 Magnesium

Magnesium is the eighth most common element and is a common constituent of oilfield waters. It is an important constituent of water hardness which can cause pipe or tube scaling.

5.3.18.1 Magnesium (AAS Method)

5.3.18.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for magnesium concentrations from 0.25 to 3.5 mg/L. The upper limit can be increased by serial dilution techniques. The determination of magnesium in brackish water, sea water, and brines requires the use of the method of additions described in ASTM D511-92.

5.3.18.1.2 Interferences

Refer to 5.2.2.1.2 for discussion of AAS references. Aluminum interferes. The addition of lanthanum in the procedure eliminates the interference effect of up to 100 mg/L aluminum. The use of a nitrous oxide-acetylene flame has been reported to remove the interference when used with the addition of potassium to control ionization interference.

5.3.18.1.3 Procedure References

a. SM 3500-Mg B, p. 3–73.
b. ASTM D511-92, Vol. 11.01, p. 435.

5.3.18.1.4 Precision and Accuracy

The detection limit for magnesium is 0.0005 mg/L.

ASTM D511-92 gives the precision as:

$$S_t = 0.078X + 0.03,$$

$$S_o = -0.001X + 0.01,$$

where

S_t = overall precision,
S_o = single-operator precision,
X = concentration of magnesium determined, mg/L.

The bias given ranged from 0 to –11.5 percent.

5.3.18.2 Magnesium (ICP Method)

5.3.18.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.18.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.18.2.3 Procedure Reference

SM 3500-Mg C, p. 3–73.

5.3.18.2.4 Precision and Accuracy

The detection limit is about 0.03 mg/L. The precision is given by:

$$S_t = 0.0607X + 11.6,$$

$$S_o = 0.0298X - 0.6,$$

where

S_t = overall precision,

S_o = single-operator precision,

X = concentration of magnesium determined, mg/L.

5.3.18.3 Magnesium (EDTA Titration Method)

5.3.18.3.1 Principle

Calcium and magnesium are complexed by ethylenediamine tetraacetic acid (EDTA) after pH has been adjusted to 10. The EDTA initially complexes the calcium, then the magnesium. Magnesium is determined by the difference between an aliquot titrated with EDTA at pH 10 and one titrated at pH 12 to 13.

5.3.18.3.2 Interferences

EDTA reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. The addition of hydroxylamine and cyanide reduce the interferences. About 5 mg/L iron and 10 mg/L manganese, copper, zinc, and lead can be tolerated. The possible interference from commonly used polyphosphates, organic phosphonates, and EDTA/NTA compounds in water treatment should be recognized. Refer to ASTM D511-92 for more information on interferences.

5.3.18.3.3 Procedure Reference

ASTM D511-92, Vol. 11.01, p. 435.

5.3.18.3.4 Summary

This test method is applicable to most waters in a range from 1 to 1000 mg/L of calcium plus magnesium. Upper limits may be extended by dilution. The titration endpoints may be difficult to see and some operator practice is required. The operator should be aware that there are many possible interferences. Several reliable field test kits exist for this testing. As with all test kits, the accuracy and precision provided should be determined by the user.

5.3.18.3.5 Precision and Accuracy

The detection limit for magnesium is 1 mg/L. The precision for this test method for magnesium ranging in concentration from 2.5 to 36 mg/L is:

$$S_t = 0.017X + 0.85,$$

$$S_o = 0.002X + 0.70,$$

where

S_t = overall precision,

S_o = single-operator precision,

X = concentration of magnesium determined.

Precision ranged from –1.8 to 6.7 percent.

5.3.18.4 Magnesium (Calculation Method)

5.3.18.4.1 Principle

Magnesium may be estimated as the difference between hardness (SM 3500-Ca D) and calcium, as $CaCO_3$ (SM 2340-C).

5.3.18.4.2 Interferences

Interfering metals must be present in non-interfering concentrations in the calcium titration (SM 3500-Ca D) and suitable inhibitors must be used in the hardness titration (SM 2340-C).

5.3.18.4.3 Procedure Reference

SM 3500-Mg E, p. 3–74.

5.3.18.4.4 Summary

Magnesium(mg/L) = [total hardness (as mg/L $CaCO_3$) – hardness (as mg/L $CaCO_3$] x 0.243. Several reliable field test kits exist for both components of this testing. As with all test kits, the accuracy and precision provided should be determined by the user.

5.3.18.4.5 Precision and Accuracy

The precision and accuracy of the magnesium determination are determined by the precision and accuracy of the calcium titration, which is about 9.2 percent and 1.9 percent respectively. The detection limit for magnesium by this method is about 1.0 mg/L.

5.3.19 Manganese

The redox potential of most in situ oilfield brines is reducing and in such an environment manganese is present as Mn^{2+}. If the redox potential of the brine becomes oxidizing, the manganese in solution may precipitate. Therefore, manganese must be determined at the sampling site or the sample must be acidified before transporting it back to a central laboratory for analysis.

5.3.19.1 Manganese (AAS Method)

5.3.19.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for manganese concentrations from 0.1 to 10 mg/L. The upper limit can be increased by serial dilution techniques.

5.3.19.1.2 Interferences

Manganese absorption is depressed in the presence of phosphate, perchlorate, iron, nickel, and cobalt when using a reducing air-acetylene flame. In an oxidizing air-acetylene or a nitrous oxide-acetylene flame, these interferences are not present.

5.3.19.1.3 Procedure References

a. SM 3500-Mn B, p. 3–74.
b. ASTM D858-90, Vol. 11.01, p. 553.

5.3.19.1.4 Precision and Accuracy

This method will typically yield a relative standard deviation of 7.8 percent and a relative error of 1.3 percent, depending on the skill of the operator.

5.3.19.2 Manganese (ICP Method)

5.3.19.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.19.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.19.2.3 Procedure Reference

SM 3500-Mn C, p. 3–74.

5.3.19.2.4 Precision and Accuracy

The precision and accuracy are described by the following:

$$X = 0.9417C + 0.13,$$

$$S_t = 0.0324X + 0.88,$$

$$S_o = 0.0153X + 0.91,$$

where

X = concentration of manganese, µg/L,

C = true value, µg/L,

S_t = overall precision, µg/L,

S_o = single-operator precision, µg/L.

5.3.19.3 Manganese (Photometric Method)

5.3.19.3.1 Principle

Persulfate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate. The resulting color is stable for at least 24 hours if excess persulfate is present and organic matter is absent.

5.3.19.3.2 Interferences

Reducing constituents, such as chloride, bromide, iodide, and organic matter can interfere. Much of the interference is removed by digestion of the sample with nitric and sulfuric acids. The addition of mercuric sulfate prevents the interference of chloride.

5.3.19.3.3 Procedure Reference

SM 3500-Mn D, p. 3–75.

5.3.19.3.4 Precision and Accuracy

A synthetic sample containing 120 µg/L Mn and various other ions in distilled water was analyzed in 33 laboratories by the persulfate method, with a relative standard deviation of 26.3 percent and a relative error of 0 percent.

5.3.20 Nitrate

Nitrate is usually not present in formation waters. The presence of nitrate may indicate contamination by surface or shallow ground water or the deliberate addition of nitrate to the injection water.

Determination of nitrate is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges.

5.3.20.1 Nitrate (Cadmium Reduction Method)

5.3.20.1.1 Principle

A filtered sample is passed through a column containing copper coated cadmium granules to reduce nitrate to nitrite ion. The combined nitrite-nitrate nitrogen is determined by diazotizing the total nitrite ion with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form a highly colored azo dye that is measured spectrophotometrically.

5.3.20.1.2 Interferences

Turbid samples must be filtered prior to analysis to eliminate particulate interference and to prevent flow reduction through the column. Oil and grease (in the sample) coat the surface of the cadmium and prevent the complete reduction of nitrate to nitrite.

Certain metal ions, in concentrations above 35 mg/L, may lower reduction efficiency and form interfering colored complexes. Residual chlorine interferes by oxidizing the cadmium column, thus reducing its efficiency. Low pH samples should be adjusted between 6 and 8 to ensure effective reduction of nitrate to nitrite.

5.3.20.1.3 Procedure References

a. SM 4500-NO_3^- E or F, p. 4–89.
b. ASTM D3867-90, Vol. 11.01, p. 579.

5.3.20.1.4 Summary

The test method is applicable for nitrite determinations as well as nitrate. After performing the procedure, omit the cadmium reduction step. Nitrite is calculated as the difference between the two tests. Procedures are listed for manual and automated techniques.

5.3.20.1.5 Precision and Accuracy

Standard deviations for both techniques determined in nonreagent water matrix are listed below:

Standard Manual Automated Deviation Method:

Overall, S_t 0.057 mg/L 0.0437 mg/L.

Single Operator, S_o 0.038 mg/L 0.0300 mg/L.

5.3.20.2 Nitrate (Electrode Method)

5.3.20.2.1 Principle

The nitrate ion electrode is a selective sensor that develops a potential across a thin membrane that holds in place a water-immiscible liquid ion exchanger. The electrode responds to nitrate ion activity between about 10^{-5} and 10^{-1} M (0.14 to 1400 mg/L nitrate).

5.3.20.2.2 Interferences

Chloride and bicarbonate ions interfere when their weight ratios to nitrate are >10 and >5, respectively. Other ions that are potential interferences are nitrite, cyanide, sulfide, bromide, iodide, chlorate, and perchlorate. The electrode functions best at a constant pH and ionic strength.

5.3.20.2.3 Procedure Reference

SM 4500-NO_3^- , p. 4–88.

5.3.20.2.4 Precision and Accuracy

Over the range of the method, precision of ±0.4 mV, corresponding to 2.5 percent in concentration, is expected.

5.3.21 Oil and Grease

In general, crude oils are complex mixtures of hydrocarbons that contain a wide variety of chemical constituents, a large portion of which are insoluble in water. However, some crude oils contain a significant amount of chemical constituents that are soluble in water.

As a result of this solubility, different oil-in-water analytical techniques can give different results, depending on which crude oil fraction or fractions are being analyzed. The methods used for determining and the terminology used to identify each of these fractions is given below:

a. Constituent—total oil and grease (refer to 5.3.21.1 or 5.3.21.3 for further information).
    1. Methods used—either SM 5220-B (gravimetric) or SM 5220-C (infrared).
    2. Measures—soluble plus insoluble fraction.
b. Constituent—total petroleum hydrocarbons (TPH) (refer to 5.3.21.5 for further information).
    1. Method used—SM 5520-F.
    2. Measures—insoluble fraction.
c. Constituent—water soluble organics (WSOs).
    1. Method Used—calculation of difference between 5.3.21.a and 5.3.21.b.
    2. Measures—soluble fraction.

When results from an analysis of organic constituents in water are reported, it is essential that the user clearly understand which fractions were measured.

It is important to note that two different methods are available for determining total oil and grease (gravimetric method SM 5220-B and infrared method SM 5220-C). Usually, the amount of oil and grease determined by the infrared method is different than that measured in the gravimetric method, with the extent of the difference related to the composition of the crude oil.

This difference occurs because of volatilization of crude light ends from solution as solvent is evaporated in the gravimetric method. The "correct" amount of oil and grease in a given sample is determined by the analytical method used.

5.3.21.1 Oil and Grease (Infrared Method)

Oil and grease determinations are frequently performed as a measure of oil carryover in production operations. The following method is fast, convenient, and sufficiently accurate for measuring oil carryover as a result of normal production operations.

5.3.21.1.1 Principle

An acidified sample of water is extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. A portion is examined by infrared spectroscopy to measure the absorbance due to oil and grease in the original sample.

5.3.21.1.2 Interferences

Organic solvents and certain other organic compounds not considered as oil and grease may be extracted and measured as oil and grease. Heavier hydrocarbons may not be soluble in the solvent.

5.3.21.1.3 Procedure References.

a. SM 5520-C, p. 5–44.
b. ASTM D3921-85, Vol. 11.02, p. 62.

5.3.21.1.4 Summary

The measurement of oil and grease is one of the most common analytical tests performed. It should be remembered that “oil and grease” is any material recovered from an acidified sample by extraction with trichlorotrifluoroethane and having infrared absorption bands in the same regions as those of the carbon-hydrogen bonds. Unlike other analyses, the analyte (oil and grease) is defined by the method used.

5.3.21.1.5 Precision and Accuracy

The precision for oil and grease given in ASTM D3921-85 were:

$$S_t = 0.167X + 0.333,$$

$$S_o = 0.122X + 0.148,$$

where

S_t = overall precision, mg/L,

S_o = single-operator precision, mg/L,

X = concentration of oil and grease determined, mg/L.

The bias is given as 2.4 percent. The precision for petroleum hydrocarbons given in ASTM D3921-85 is:

$$S_t = 0.160X + 0.329,$$

$$S_o = 0.141X + 0.048,$$

where

S_t = overall precision, mg/L,

S_o = single-operator precision, mg/L,

X = concentration of oil and grease determined, mg/L.

5.3.21.2 Oil and Grease (Colorimetric Method)

5.3.21.2.1 Principle

A visible photometer with a fixed wavelength in the 400 to 550 nm range can be used to quantify most crude oils in 1,1,1-trichloroethane extracts of water.

This method is practical for field use because many colorimeters are available with capabilities for this wavelength range. The method can be fine tuned by using a scanning spectrophotometer to determine the most sensitive wavelength setting for a particular oil.

However, most oils will produce a visible color and a suitable calibration near 450 nm. The exact wavelength setting is not critical as long as it is consistent from calibration to sample determination.

Other solvents (such as hexane) can be substituted as long as the crude oil being determined is completely soluble.

5.3.21.2.2 Interferences

Treating chemicals or other contaminants in the water that impart a color in the solvent may interfere.

5.3.21.2.3 Equipment

a. Photometer capable of reading in the 400–550 nm range.
b. Pipets.
c. Volumetric flasks, 50 to 100 mL.
d. Separatory funnel, 1 liter.
e. Graduated cylinders.

5.3.21.2.4 Reagents

a. Solvent- 1,1,1-trichloroethane.
b. Sample of crude oil.

5.3.21.2.5 Procedure

a. Measure 500 mL of water sample into a 1 liter separatory funnel, add 50 mL of solvent, and shake for 2 minutes.
b. Allow the solvent layer to separate. Transfer a portion of the solvent layer to a clean, dry photometer cell.
c. Place the cell in the photometer and make a reading at the selected wavelength. The photometer should be calibrated and a blank reference set prior to the reading (for double beam instruments, the reference cell should contain a solvent blank).
d. Determine the oil-in-water concentration from the calibration data.

5.3.21.2.6 Preparation of Calibration Data

a. Prepare a 100 mg/L standard solution by weighing 0.1 grams of the crude oil (produced from field where sample originates) into a 100 mL volumetric flask and diluting to the mark with solvent.
b. A series of standards can be prepared by making dilutions of the 100 mg/L standard. For example, 10 mL of standard diluted to 100 mL produces a 10 mg/L standard solution. By making a table or plot of standard concentrations and corresponding photometer readings, a reference curve can be created.

5.3.21.2.7 Calculation

a. Determine sample extract concentration by plotting sample photometer reading on reference calibration curve.

b. Multiply sample extract concentration X 10 to determine final sample oil-in-water concentration.

5.3.21.2.8 Summary

The measurement of oil and grease is one of the most common analytical tests performed. It should be remembered that "oil and grease" is any material recovered as a substance soluble in 1,1,1- trichloroethane. Unlike other analyses, the analyte (oil and grease) is defined by the method used.

5.3.21.2.9 Precision and Accuracy

Depends on the particular oil and photometer in use. The method is generally applicable for oil and grease levels in the 1 to 100 mg/L range.

5.3.21.3 Oil and Grease (Gravimetric Method)

5.3.21.3.1 Principle

An acidified sample of water is extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. The extract is dried and the oil content obtained by weight.

5.3.21.3.2 Interferences

Organic solvents and certain other organic compounds not considered as oil and grease may be extracted and measured as oil and grease. Solvent drying may result in the loss of volatile hydrocarbons. Heavier hydrocarbons may not be soluble in the solvent.

5.3.21.3.3 Procedure Reference

SM 5520-B, p. 5–43.

5.3.21.3.4 Summary

The measurement of oil and grease is one of the most common analytical tests performed. It should be remembered that "oil and grease" is any material recovered as a substance soluble in trichlorotrifluoroethane and not lost by evaporation under the analysis conditions. Unlike other analyses, the analyte (oil and grease here) is defined by the method used.

5.3.21.3.5 Precision and Accuracy

The precision for oil and grease given in SM 5520-B from a standard oil is 93 percent with a standard deviation of 0.9 mg/L.

5.3.21.4 Oil and Grease (Soxhlet Extraction Method)

The Soxhlet Extraction Method is often used for samples that contain hydrocarbons mixed with other solid materials. The method is also useful for the higher molecular weight hydrocarbons often found mixed with solids.

5.3.21.4.1 Principle

An acidified sample is filtered through diatomaceous silica filter aid to collect the oil and grease. The filter-trapped material is extracted in a Soxhlet apparatus with 1,1,2-trichloro-1,2,2-trifluoroethane. The extract is dried and the oil content obtained by weight.

5.3.21.4.2 Interferences

Organic solvents and certain other organic compounds not considered as oil and grease may be extracted and measured as oil and grease. Solvent drying will result in the loss of volatile hydrocarbons. Heavier hydrocarbons may not be soluble in the solvent. Duplicate results can only be obtained by strict adherence to all details.

5.3.21.4.3 Procedure Reference

SM 5520-D, p. 5–45.

5.3.21.4.4 Summary

The Soxhlet Method is widely used to determine oil and grease in solids containing samples such as tank bottoms, sludge, soil, etc. Similar to the other methods described here, it should be remembered that "oil and grease" is any material recovered as a substance soluble in trichloro-trifluoroethane. Unlike other analyses, the analyte (oil and grease) is defined by the method used.

5.3.21.4.5 Precision and Accuracy

The precision for oil and grease given in SM 5520-D is 98 percent with a standard deviation of 1.1 mg.

5.3.21.5 Oil and Grease (Total Petroleum Hydrocarbon)

The objective of many oil and grease determinations is to estimate the hydrocarbon content of the sample. An example is the measurement of oil carryover in production operations. The following method is fast, convenient, and sufficiently accurate for measuring oil carryover as a result of normal production operations.

5.3.21.5.1 Principle

An acidified sample of water is extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. The extract is treated with silica gel to remove polar substances, thereby providing a solution of petroleum hydrocarbons. This extract is then examined by infrared spectroscopy.

5.3.21.5.2 Interferences

Organic solvents and certain other organic compounds not considered as oil and grease may be extracted and measured as oil and grease. Those not absorbed by silica gel will be measured as petroleum hydrocarbons.

5.3.21.5.3 Procedure References

a. SM 5520-F, p. 5–47.
b. ASTM D3921-85, Vol. 11.02, p. 62.

5.3.21.5.4 Summary

The measurement of hydrocarbons in water is one of the most common analytical tests performed. In this method, any material recovered by trichlorotrifluoroethane and not absorbed by silica gel is defined as total petroleum hydrocarbons (TPH).

5.3.21.5.5 Precision and Accuracy

The precision for oil and grease given in ASTM D3921-85 is:

$$S_t = 0.167X + 0.333,$$

$$S_o = 0.122X + 0.148,$$

where

S_t = overall precision, mg/L,
S_o = single-operator precision, mg/L,
X = concentration of oil and grease determined, mg/L.

The bias is given as 2.4 percent. The precision for petroleum hydrocarbons given in ASTM D3921-85 is:

$$S_t = 0.160X + 0.329,$$

$$S_o = 0.141X + 0.048,$$

where

S_t = overall precision, mg/L,
S_o = single-operator precision, mg/L,
X = concentration of oil and grease determined, mg/L.

5.3.22 Organic Acids

Oilfield waters frequently contain organic acids that may be important in corrosion. A distinction is noted between organic acids and volatile acids. A chromatographic separation method is presented for organic acids, while a method using distillation is presented for volatile acids.

5.3.22.1 Organic Acids (Chromatographic Method)

5.3.22.1.1 Principle

An acidified aqueous sample containing organic acids is adsorbed on a column of silicic acid and the acids are eluted with n-butanol in chloroform. The eluate is collected and titrated with standard base. Short-chain (C_1 to C_6) organic acids are eluted by this solvent system and are reported collectively as total organic acids.

5.3.22.1.2 Interferences

The chloroform-butanol solvent system is capable of eluting organic acids other than the volatile acids and also some synthetic detergents. In addition to the so-called volatile acids (crotonic, adipic, pyruvic, phthalic, fumaric, lactic, succinic, malonic, gallic, aconitic, and oxalic acids), alkyl sulfates, and alkyl-aryl sulfonates are adsorbed by silicic acid and eluted.

5.3.22.1.3 Procedure Reference

SM 5560-B, p. 5–42.

5.3.22.1.4 Summary

The organic acid content is calculated as follows and is designated mg acetic acid/L.

Total Organic Acids (mg as acetic acid) =

$$\frac{(a - b) \times N \times 60{,}000}{\text{mL sample}},$$

where

a = NaOH used for sample, mL,
b = NaOH used for blank, mL,
N = normality of NaOH.

5.3.22.1.5 Precision and Accuracy

Average recoveries of about 95 percent are obtained for organic concentrations above 200 mg as acetic acid/L. Individual tests generally vary from the average by approximately 3 percent. A greater variation results when lower concentrations of organic acids are present. Titration precision expressed as the standard deviation is about ±0.1 mL (approximately ±24 mg as acetic acid/L).

5.3.22.2 Organic Acids (Distillation Method)

5.3.22.2.1 Principle

This technique recovers acids containing up to six carbon atoms. Fractional recovery of each acid increases with increasing molecular weight. The method is empirical and should be carried out exactly as described.

5.3.22.2.2 Interferences

Hydrogen sulfide and CO_2 are liberated during distillation and will be titrated to give a positive error. Eliminate this error by discarding the first 15 mL of distillate and account for this in the recovery factor.

5.3.22.2.3 Procedure Reference

SM 5560-C, p. 5–44.

5.3.22.2.4 Summary

Calculations and reporting are on the basis of mg as acetic acid.

Volatile Acids (mg as acetic acid) =

$$\frac{\text{mL NaOH} \times N \times 60{,}000}{\text{mL sample} \times f},$$

where

N = normality of NaOH,

f = recovery factor.

5.3.22.2.5 Precision and Accuracy

No precision or accuracy is expressed for this method.

5.3.23 Oxygen, Dissolved

Dissolved oxygen must be determined on location. This alone limits the methods that can be used, because only a few are adaptable to field use on oilfield waters. To further complicate matters, it is necessary that the method be accurate for the determination of trace amounts of oxygen.

5.3.23.1 Oxygen, Dissolved (Titrimetric Method)

5.3.23.1.1 Principle

The azide modification of the Winkler (iodometric) method is the most frequently used method for oilfield waters. The procedure relies on the oxidative property of dissolved oxygen, which culminates with the titration of iodine by thiosulfate.

5.3.23.1.2 Interference

The azide modification effectively removes interference caused by nitrite. Ferric iron interferes unless potassium fluoride is added, in which case 100 to 200 mg/L can be tolerated. Ferrous iron interferes, but that interference is eliminated by the use of potassium permanganate solution. High levels of organic material or dissolved oxygen can be accommodated by use of the concentrated iodide-azide solution.

5.3.23.1.3 Procedure References

a. SM 4500-O C, p. 4–100.
b. ASTM D888-92, Vol. 11.01, p. 593.

5.3.23.1.4 Summary

Various modifications of the iodometric method have been developed to eliminate or minimize effects of interferences; nevertheless, the method still is applicable to a variety of industrial and domestic waste waters. Moreover, the iodometric method is not suited for field testing and cannot be adapted for continuous monitoring or for dissolved oxygen in situ.

5.3.23.1.5 Precision and Accuracy

Dissolved oxygen can be determined with a precision, expressed as a standard deviation, of about 20 µg/L in distilled water and about 60 µg/L in waste water and secondary effluents. In the presence of appreciable interference, even with proper modifications, the standard deviation may be as high as 100 µg/L.

5.3.23.2 Oxygen, Dissolved (Instrumental Probe)

5.3.23.2.1 Principle

Oxygen-sensitive electrodes of the polarographic or galvanic type are composed of two solid metal electrodes in contact with supporting electrolyte, which is separated from the test solution by a selective membrane. The probes are commercially available in some variety. In all these instruments the “diffusion current” is linearly proportional to the concentration of molecular oxygen. The current can be converted easily to concentration units by a number of calibration procedures.

5.3.23.2.2 Interferences

Plastic films used with membrane electrode systems are permeable to a variety of gases besides oxygen, although none is depolarized easily at the indicator electrode. Prolonged use in waters containing such gases as hydrogen sulfide tends to lower cell sensitivity. Eliminate this interference by frequently changing and recalibrating the membrane electrode.

5.3.23.2.3 Procedure References

a. SM 4500-O G, p. 4–103.
b. ASTM D888-92, Vol. 11.01, p. 593.

5.3.23.2.4 Summary

Dissolved oxygen electrodes provide an excellent method for analysis in polluted waters, highly colored waters, and strong waste effluents. They are recommended for use, especially under conditions that are unfavorable for use of the iodometric method, or when that test and its modifications are subject to serious errors caused by interferences.

5.3.23.2.5 Precision and Accuracy

With most commercially available membrane electrode systems, an accuracy of ±0.1 mg/L and a precision of ±0.05 mg/L can be obtained.

5.3.23.3 Oxygen, Dissolved (Colorimetric Method)

5.3.23.3.1 Principle

Dissolved oxygen reacts under alkaline conditions with the indigo carmine solution to produce a progressive color change from yellow-green through red to blue and blue-green. The result of each test can be determined by comparison of color developed in the sample with color standards made to represent different concentrations of dissolved oxygen.

5.3.23.3.2 Interferences

Tannin, hydrazine, and sulfite do not interfere in concentrations up to 1.0 mg/L. Ferric iron, cyclohexylamine, and morpholine in concentrations up to 4.0 mg/L can be tolerated. Ferrous iron will produce low results and copper will cause high results. In samples where ferrous iron and copper are present, their combined interference is frequently zero. Highly colored, turbid waters, and nitrate interfere.

5.3.23.3.3 Procedure Reference

ASTM D888-92, Vol. 11.01, p. 593.

5.3.23.3.4 Summary

This test method is applicable to water containing less than 60 µg/L of dissolved oxygen, such as steam condensate and deaerated boiler feedwater only. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

5.3.23.3.5 Precision and Accuracy

The overall precision and bias has not been determined because of the instability of shipped solutions. The single-operator precision of this method may be expressed as follows:

$$S_o = 0.052X + 0.7,$$

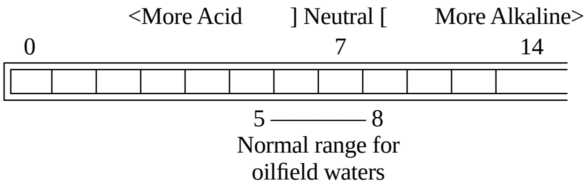
where

S_o = single-operator precision, µg/L,

X = concentration of dissolved oxygen determined, µg/L.

5.3.24 pH

The term "pH" is defined as the log of the reciprocal of the hydrogen ion concentration expressed in moles per liter or pH = $log_{10}\left(\frac{1}{[H^+]}\right)$. Simply explained, the pH is a number between 0 and 14 that indicates the degree of acidity or alkalinity, as shown in the following example:



Some fluid constituents that control pH of water are dissolved solids, precipitation reactions, carbon dioxide, bicarbonate, borate, and hydrogen sulfide.

The pH of a water affects the formation of several types of mineral scales found in the oilfield. At a lower pH, the corrosiveness of the water is increased.

The pH measurement can be made colorimetrically or electrometrically; however, the electrometric method is most suitable for oilfield waters because it is not affected by colored or opaque solutions.

5.3.24.1 pH (Electrometric Method)

5.3.24.1.1 Principle

The electrometric method is essentially a measurement of the potential between an indicator electrode and a reference electrode. The most common electrode system for technical use is the glass and saturated calomel pair.

5.3.24.1.2 Interferences

Very accurate pH determinations require corrections for temperature and dissolved solids in oilfield waters. However, this degree of accuracy is seldom required. Temperature corrections can be made automatically using a thermocompensator or can be calculated from information supplied with the instrument. Errors due to dissolved solids or "salt error" can be calculated, obtained from a chart supplied with the electrode or compensated for by using a special glass electrode.

5.3.24.1.3 Procedure References

a. SM 4500-H^+ B, p. 4–65.
b. ASTM D1293-84, p. 324.

5.3.24.1.4 Summary

The pH is read directly from the meter and it is usually assumed that the determination was made at room temperature, approximately 25°C. The determination of pH at temperatures other than room temperature should either be corrected or reported with the temperature. Temperature corrections are usually made in one of three ways:

a. Use a meter equipped with a thermocompensator.
b. Standardize the pH meter with buffer solutions at sample temperature.
c. Calculate the temperature corrections.

5.3.25 Phosphorus (Phosphate)

Phosphorus is determined in oilfield waters as a means of monitoring chemical treatment with phosphorus containing organic compounds used for inhibiting scale and corrosion.

Three methods are listed for the determination of phosphorus: ICP, Colorimetric, and Ion Chromatography. If ICP is used, no chemical pretreatment is necessary. However, the Colorimetric and Ion Chromatography methods respond to dissolved orthophosphate; therefore, phosphorus in any form other than dissolved orthophosphate must be converted to orthophosphate by a preliminary hydrolysis or oxidative digestion step.

5.3.25.1 Phosphorus (ICP Method)

5.3.25.1.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.25.1.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.25.1.3 Procedure Reference

SM 3120-B, p. 3–34, discusses ICP as it applies to the analysis of various elements. With this information and literature from the instrument manufacturer, phosphorus analysis is performed in a similar manner.

5.3.25.2 Phosphorus (Pretreatment: Hydrolysis Oxidative Digestion)

5.3.25.2.1 Principle

In general, polyphosphates (such as pyro, tripoly, hexametaphosphate) can be converted to dissolved orthophosphate by means of a less vigorous acid hydrolysis pretreatment. Phosphorus-containing organic compounds (such as phosphate esters and phosphonates) require a more vigorous oxidative digestion pretreatment.

5.3.25.2.2 Interferences

Interferences will depend on the method selected for the measurement of orthophosphate.

5.3.25.2.3 Procedure Reference

SM 4500-P B, p. 4–111.

5.3.25.3 Phosphorus (Colorimetric Method)

5.3.25.3.1 Principle

Orthophosphate reacts with ammonium molybdate and potassium antimonyl tartrate under acidic conditions to form phosphomolybdic acid, which is reduced to molybdenum blue by ascorbic acid.

5.3.25.3.2 Interferences

Arsenates, as low as 0.1 mg/L As, are a positive interference. Hexavalent chromium and NO^{2-} interfere to give low results. Sulfide interferes by giving high results, however this interference is removed if an oxidative digestion pretreatment is performed.

5.3.25.3.3 Procedure References

a. SM 4500-P E, p. 4–115.
b. ASTM D515-88, Vol. 11.01, p. 601.

5.3.25.4 Phosphorus (Ion Chromatography)

5.3.25.4.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.25.4.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.25.4.3 Procedure References

Refer to 5.2.3.3 for discussion of references.

5.3.26 Potassium

Potassium is the seventh most common element and is a common constituent of oilfield waters. It is useful for identifying brackish water, seawater, or brine.

5.3.26.1 Potassium (AAS Method)

5.3.26.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for potassium concentrations from 0.1 to 70,000 mg/L. The determination of potassium in brackish water, sea water, and brine is easily accomplished, but may require the use of the method of additions described in ASTM D3561-77.

5.3.26.1.2 Interferences

General interferences are few as discussed in 5.2.2.1.2. Ionization interference is controlled by adding large excesses of easily ionized sodium.

5.3.26.1.3 Procedure References

a. SM 3500-K B, p. 3–80.
b. ASTM D3561-77, Vol. 11.02, p. 486.

5.3.26.1.4 Precision and Accuracy

The detection limit for potassium is 0.005 mg/L. ASTM D3561-77 gives the precision as:

$$S_t = 0.1443X - 2.317,$$

$$S_o = 0.0847X - 61.15,$$

where

S_t = overall precision, mg/L,
S_o = single-operator precision, mg/L,
X = concentration of potassium determined, mg/L.

The bias is given as 11 to 25 percent.

5.3.26.2 Potassium (ICP Method)

5.3.26.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.26.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.26.2.3 Procedure Reference

SM 3500-K C, p. 3–80.

5.3.26.2.4 Precision and Accuracy

The detection limit is about 0.1 mg/L. The precision is given as:

$$S_t = 0.0934X + 77.8,$$

$$S_o = -0.0099X - 144.2,$$

where

S_t = overall precision, µg/L,
S_o = single-operator precision, µg/L,
X = concentration of potassium determined, µg/L.

The bias was given as: $X = 0.8669C - 36.4$,

where

X = mean recovery, µg/L,
C = true value, µg/L.

5.3.26.3 Potassium (Flame Emission Photometry)

5.3.26.3.1 Principle

Trace amounts of potassium can be determined by flame emission photometry at a wavelength of 766.5 nm. The sample is sprayed into a gas flame and excited under carefully controlled and reproducible conditions. The desired spectral line is isolated and its intensity is measured. The value determined is compared to a standard curve.

5.3.26.3.2 Interferences

High concentrations of chloride, sulfate, and bicarbonate may interfere. Radiation buffers are added to suppress this interference. The use of a standard addition technique can also be used.

5.3.26.3.3 Procedure Reference

SM 3500-K D, p. 3–80.

5.3.26.3.4 Precision and Accuracy

The detection limit for potassium is 0.1 mg/L. Precision is 15.5 percent and accuracy is 2.3 percent.

5.3.27 Silica

Silica is a major component of rocks and minerals, particularly those of igneous origin. In water, it is undesirable for many industrial applications. Silica is especially damaging in high-pressure, high-temperature processes where silicate scales are formed.

5.3.27.1 Silica (AAS Method)

5.3.27.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for more than one form of silica. It determines dissolved silica and some colloidally dispersed silica. The optimal use limits are 20 to 300 mg/L. This range can be extended upward by dilution. The method is rapid and does not require timing steps required in other methods.

5.3.27.1.2 Interferences

General interferences are few as discussed in 5.2.2.1.2. Ionization interference is controlled by adding large excesses of easily ionized sodium.

5.3.27.1.3 Procedure Reference

SM 4500-Si B, p. 4–118.

5.3.27.1.4 Precision and Accuracy

The detection limit for silica is 0.3 mg/L. SM 4500-Si B did not specifically address the precision for silica, but errors are expected to be less than 10 percent.

5.3.27.2 Silica (ICP Method)

5.3.27.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.27.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.27.2.3 Procedure Reference

SM 4500-Si G, p. 4–123.

5.3.27.2.4 Precision and Accuracy

The detection limit is about 0.02 mg/L. The precision and bias are given as:

$$X = 0.5742C - 35.6,$$

$$S_t = 0.4160X + 37.8,$$

$$S_o = 0.1987X + 8.4,$$

where

X = mean recovery, µg/L,

C = true value, µg/L,

S_t = multi-laboratory standard deviation, µg/L,

S_o = single-analyst standard deviation, µg/L.

5.3.27.3 Silica (Colorimetric Method)

5.3.27.3.1 Principle

Ammonium molybdate at pH 1.2 reacts with silica and any phosphate present to form hetero-poly acids. Oxalic acid is used to destroy the molybdophosphoric acid, leaving molybdosilicic acid. An intense yellow color is produced.

5.3.27.3.2 Interferences

One form of silica is known not to react with molybdate. It is not known to what extent “unreactive” silica occurs in nature. Glassware should be used sparingly to prevent leaching of silica into the analysis. Tannins, iron, sulfide, phosphate, color, and turbidity interfere.

5.3.27.3.3 Procedure References

a. SM 4500-Si D, 4–119.
b. ASTM D859-88, Vol. 11.01, p. 627.

5.3.27.3.4 Summary

Due to the complexity of silica chemistry, the form of silica measured here is only that silica that reacts with molybdate.

5.3.27.3.5 Precision and Accuracy

$$S_t = 0.03X + 1.3,$$

$$S_o = 0.005X + 0.7,$$

where

S_t = overall precision, µg/L SiO_2,

S_o = single-operator precision, µg/L SiO_2,

X = concentration of silica determined, µg/L SiO_2.

The bias ranged from –2.5 to +0.2 percent. The minimum detection limit is about 0.02 mg/L.

5.3.27.4 Silica (Gravimetric Method)

5.3.27.4.1 Principle

Hydrochloric acid decomposes silicates and forms silicic acids that are precipitated during drying. Ignition followed by volatilization of silicon tetrafluoride (by reaction with hydrofluoric acid) leaves impurities behind. Total silica is determined by weight loss.

5.3.27.4.2 Interferences

Glassware should be used sparingly to prevent leaching of silica into the analysis.

5.3.27.4.3 Procedure References

a. SM 4500-Si C, p. 4–118.
b. ASTM D859-88, Vol. 11.01, p. 627.

5.3.27.4.4 Summary

Silicon compounds dissolved or suspended in water are concentrated and precipitated as partially dehydrated silica (by reaction with HCl). Ignition completes the dehydration and the silica is volatilized by HF (to silica tetrafluoride). Complex silicate residues may have to be dissolved by alkali fusion before dehydration.

5.3.27.4.5 Precision and Accuracy

$$S_t = (0.0085X + 0.55) / V,$$

$$S_o = (0.005X + 0.4) / V,$$

where

S_t = overall precision, mg/L Si,

S_o = single-operator precision, mg/L Si,

X = concentration of silica determined, mg/L Si,

V = liters of sample used.

The bias ranges from –24 to –1.6 percent. The minimum detection limit is about 0.2 mg/L.

5.3.28 Sodium

Sodium is the sixth most common element and is a major constituent of oilfield waters. It is useful for identifying brackish water, seawater, or brine.

5.3.28.1 Sodium (AAS Method)

5.3.28.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for sodium concentrations from 0.1 to 70,000 mg/L. The determination of sodium in brackish water, sea water, and brine is easily accomplished, but may require the use of the method of additions described in ASTM D3561-77.

5.3.28.1.2 Interferences

General interferences are few as discussed in 5.2.2.1.2. Ionization interference is controlled by adding large excesses of easily ionized potassium.

5.3.28.1.3 Procedure References

a. SM 3500-Na B, p. 3–93.
b. ASTM D3561-77, Vol. 11.02, p. 486.

5.3.28.1.4 Precision and Accuracy

The detection limit for sodium is 0.002 mg/L. ASTM D3561-77 gives the precision as:

$$S_t = 0.08905X - 729,$$

$$S_o = 0.02950X - 195,$$

where

S_t = overall precision, mg/L,

S_o = single-operator precision, mg/L,

X = concentration of sodium determined, mg/L.

The bias is reported as 5.7 to 8.3 percent.

5.3.28.2 Sodium (ICP Method)

5.3.28.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.28.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.28.2.3 Procedure Reference

SM 3500-Na C, p. 3–93.

5.3.28.2.4 Precision and Accuracy

The detection limit is about 0.03 mg/L. The precision is approximated by:

$$S_t = 0.2097X + 33.0,$$

$$S_o = 0.0280X - 105.8,$$

where

S_t = overall precision, µg/L,

S_o = single-operator precision, µg/L,

X = concentration of sodium determined, µg/L.

The bias is given by: $X = 0.9581C + 39.6$,

where

X = mean recovery, µg/L,

C = true value, µg/L.

5.3.28.3 Sodium (Flame Emission Photometry)

5.3.28.3.1 Principle

Trace amounts of sodium can be determined by flame emission photometry at a wavelength of 589 nm. The sample is sprayed into a gas flame and excited under carefully controlled and reproducible conditions. The desired spectral line is isolated and its intensity is measured. The value determined is compared to a standard curve.

5.3.28.3.2 Interferences

High concentrations of chloride, sulfate, and bicarbonate may interfere; radiation buffers are added to suppress this interference. The use of a standard addition technique can also be used.

5.3.28.3.3 Procedure Reference

SM 3500-Na D, p. 3–93.

5.3.28.3.4 Precision and Accuracy

The detection limit for sodium is 0.1 mg/L. Precision is 17.3 percent and accuracy is 4.0 percent.

5.3.28.4 Sodium (Calculation Method)

Sodium historically received little consideration in the analyses of oilfield waters, except in the determination of total dissolved solids. The sodium calculation served as a "catch-all," in that it included sodium and potassium and was used to balance the cations with the anions for the dissolved solids calculation.

5.3.28.4.1 Principle

Sodium is calculated as the stoichiometric difference between the sum of the anions and the sum of the cations. In practice, this is limited to the difference in the milliequivalents of the anions and the cations determined.

5.3.28.4.2 Interferences

Errors are introduced because unmeasured elements, such as potassium and lithium, are reported as sodium. Any analytical errors or omissions in the other components will result in errors in the calculated sodium.

5.3.28.4.3 Procedure

The values obtained for the common ions are converted to milliequivalents per liter (meq/L). This is done by dividing each ion concentration (mg/L) by its milliequivalent weight (mg/meq) to give the meq/L of each ion present. After adding the meq/L for both the anions and the cations, the difference is multiplied by the milliequivalent weight of sodium to give the mg/L sodium present.

5.3.28.4.4 Calculations

This method is demonstrated in the following calculation:

a. Anions:

$$\text{Chloride: } \frac{50{,}000 \text{ mg/L}}{35.5 \text{ mg/meq}} = 1{,}410 \text{ meq/L,}$$

$$\text{Sulfate: } \frac{1,290 \text{ mg/L}}{48.0 \text{ mg/meq}} = 27 \text{ meq/L,}$$

$$\text{Bicarbonate: } \frac{204 \text{ mg/L}}{61.0 \text{ mg/meq}} = 3 \text{ meq/L,}$$

Total Anions: 1,440 meq/L.

b. Cations:

$$\text{Calcium: } \frac{5{,}900 \text{ mg/L}}{20.0 \text{ mg/meq}} = 295 \text{ meq/L,}$$

$$\text{Magnesium: } \frac{2{,}000 \text{ mg/L}}{12.2 \text{ mg/meq}} = 164 \text{ meq/L,}$$

Total Cations: 459 meq/L.

c. Sodium:

$$(1{,}440 - 459) \text{ meq/L} \times 23.0 \text{ mg/meq} = 22{,}600 \text{ mg/L.}$$

5.3.28.4.5 Precision and Accuracy

The precision and accuracy of this method depend upon the methods used and the technique of the analyst.

5.3.29 Specific Gravity (SG)

Specific gravity is the ratio of a weight of any volume of a substance at a given temperature to the weight of an equal volume of some other substance at a specified temperature taken as a standard. Water is the usual standard for solids and liquids. For convenience, the specific gravity of oilfield water is usually determined at room temperature and corrected to 60°F.

The specific gravity of waters can be determined with a hydrometer, specific gravity balance, or pycnometer, depending upon the accuracy desired. Hydrometers are not as accurate as the specific gravity balance or pycnometer; but for many uses of these data, the accuracy is acceptable.

Accurate results can be obtained with a specific gravity balance or a pycnometer. The specific gravity balance is faster than the pycnometer; however, the results must be corrected for temperature. No temperature correction is necessary with the pycnometer if the measurements are made with the sample and distilled water at the same temperature.

5.3.29.1 Specific Gravity (Hydrometer Method)

5.3.29.1.1 Principle

The hydrometer is a weighted bulb with a graduated stem. The depth to which the hydrometer sinks is determined by the density of the fluid. The specific gravity is read directly from the graduated stem. Some hydrometers are equipped with thermometers so that temperature corrections can be made, if necessary.

5.3.29.1.2 Interferences

Any oil present in the sample will interfere with this determination; therefore, only freshly filtered samples should be used.

5.3.29.1.3 Procedure Reference

ASTM D1429-86, Vol. 11.01, p. 351.

5.3.29.1.4 Summary

The specific gravity may be corrected to 60°F by adding 0.0002 for each degree above 60°F.

5.3.29.1.5 Precision and Accuracy

The overall precision and single-operator precision of this test method vary with the quantity being tested. A graphical representation of the precision is found in ASTM D1429-86. Similarly, the bias is tabulated in the same reference.

5.3.29.2 Specific Gravity (Balance Method)

5.3.29.2.1 Principle

The specific gravity balance is essentially an analytical balance, which uses a plummet to determine the weight of a liquid by displacement. The plummet is calibrated in a standard liquid (usually distilled water) before the determination is made.

5.3.29.2.2 Interferences

Oil present in the sample will interfere with this determination; therefore, only freshly filtered samples should be used.

5.3.29.2.3 Procedure Reference

ASTM D1429-86, Vol. 11.01, p. 351.

5.3.29.2.4 Precision and Accuracy

The overall precision and single-operator precision of this test method vary with the quantity being tested. A graphical representation of the precision is found in ASTM D1429-86. Similarly, the bias is tabulated in the same reference.

5.3.29.3 Specific Gravity (Pycnometer Method)

5.3.29.3.1 Principle

A pycnometer is essentially a calibrated stoppered flask. The sample is introduced into a pycnometer, stabilized at the desired temperature, and weighed. The specific gravity is calculated from this weight and the previously determined weight of reagent water that was required to fill the pycnometer at the same temperature.

5.3.29.3.2 Interferences

Oil present in the sample will interfere with this determination; therefore, only freshly filtered samples should be used.

5.3.29.3.3 Procedure Reference

ASTM D1429-86, Vol. 11.01, p. 351.

5.3.29.3.4 Summary

No temperature correction is necessary if the measurements of the sample water and the reagent water are made at the same temperature.

5.3.29.3.5 Precision and Accuracy

The overall precision and single-operator precision of this test method vary with the quantity being tested. A graphical representation of the precision is found in ASTM D1429-86. Similarly, the bias is tabulated in the same reference.

5.3.30 Strontium

Strontium is frequently found in waters or brines containing barium. Their mixing with fluids high in sulfate ion forms a very insoluble scale that causes serious problems in oilfield operations.

5.3.30.1 Strontium (AAS Method)

5.3.30.1.1 Principle

Refer to 5.2.2.1.1 for discussion of AAS. This method is applicable for strontium concentrations from 0.1 to 5.0 mg/L. The upper limit can be increased by serial dilution techniques.

5.3.30.1.2 Interferences

A nitrous oxide-acetylene flame is used to reduce interferences from other elements. Potassium chloride or potassium nitrate is added to combat ionization in the flame.

5.3.30.1.3 Procedure References

a. SM 3500-Sr B, p. 3–96.
b. ASTM D3920-92, Vol. 11.01, p. 647.

5.3.30.1.4 Precision and Accuracy

This method will typically yield a relative standard deviation of 5.0 percent and a relative error of 0.2 percent, depending on the skill of the operator.

5.3.30.2 Strontium (ICP Method)

5.3.30.2.1 Principle

Refer to 5.2.2.2.1 for discussion of the principles of ICP.

5.3.30.2.2 Interferences

Refer to 5.2.2.2.2 for discussion of ICP interferences.

5.3.30.2.3 Procedure Reference

SM 3500-Sr C, p. 3–96.

5.3.30.2.4 Precision and Accuracy

No statement of precision and accuracy is expressed. The detection limit is 0.0005 mg/L.

5.3.31 Sulfate

Sulfate (SO_4^{2-}) is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter. Seawater contains about 2300 mg/L sulfate. Sulfate is an important parameter in determining the amount of scale that might form from a water or mixture of waters.

5.3.31.1 Sulfate (Ion Chromatography Method)

5.3.31.1.1 Principle

Refer to 5.2.3.1 for discussion of IC principles.

5.3.31.1.2 Interferences

Refer to 5.2.3.2 for discussion of IC interferences.

5.3.31.1.3 Procedure References

Refer to Par. 4.2.3.3 for discussion of references.

5.3.31.1.4 Summary

Sulfate is one of seven common anions readily determined by ion chromatography in a single analytical operation. The others anions are F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, and NO_3^-. Anion combinations which may be difficult to distinguish by other analytical methods are readily separated by IC.

5.3.31.1.5 Precision and Accuracy

The detection limit for sulfate is 0.1 mg/L. SM 4110-B gives the overall and single operator precision for very low sulfate concentrations as 0.07 and 0.03 mg/L, respectively. For higher concentrations of sulfate, the overall and single operator precision are 2.5 and 2.2 mg/L, respectively. No significant bias (95 percent confidence level) was noted.

5.3.31.2 Sulfate (Turbidimetric Method)

5.3.31.2.1 Principle

Sulfate ion is converted to barium sulfate under controlled conditions. A glycerin-acid solution is added to acidify and stabilize the suspension of barium sulfate. Sodium chloride is also added to adjust the ionic strength of the solution. The turbidity (resulting from addition of barium chloride to the sample containing sulfate) is determined by a photoelectric colorimeter and compared to a standard curve.

5.3.31.2.2 Interferences

Suspended matter in the sample must be removed. Dark colors that cannot be compensated for in the procedure interfere with the measurement of suspended barium sulfate.

5.3.31.2.3 Procedure References

a. SM 4500-SO_4^{2-} E, p. 4–143.
b. ASTM D4130-82, Vol. 11.02, p. 493.

5.3.31.2.4 Summary

This test covers the turbidimetric determination of sulfate ion in brackish water, seawater, and brines. It is applicable to waters having an ionic strength greater than 0.65 mol/L and a sulfate ion concentration greater than 25 mg/L. A concentration less than 25 mg/L can be determined by using a standard addition method.

5.3.31.2.5 Precision and Accuracy

The detection limit for sulfate is about 1 mg/L. ASTM D4130-82 presents a graph of the overall and single operator precision. For the overall test, the precision varies from 1.1 percent to 5.8 percent, when going from sulfate concentration of 25 mg/L to 160 mg/L. For the single operator, the precision varies from 1.2 percent to 3.4 percent for the same sulfate concentration range. The bias ranged from 2.32 percent to –2.17 percent as the sulfate concentrations increased.

5.3.31.3 Sulfate (Gravimetric Method)

5.3.31.3.1 Principle

Sulfate is precipitated in a hydrochloric acid solution as barium sulfate by the addition of barium chloride. The precipitate is filtered, washed, dried, ignited, and weighed as barium sulfate.

5.3.31.3.2 Interferences

The gravimetric determination of sulfate is subject to many errors, both positive and negative. Sources of some of these errors include suspended matter, silica, $BaCl_2$ precipitate, NO_3^-, SO_3^{2-}, and the presence of alkali metals.

5.3.31.3.3 Procedure Reference

SM 4500-SO_4^{2-} C, p. 4–132.

5.3.31.3.4 Summary

This test covers the gravimetric determination of sulfate ion. It should not be used for sulfate concentrations less than 10 mg/L.

5.3.31.3.5 Precision and Accuracy

The detection limit for sulfate is about 1 mg/L. The reference presents the precision and bias as about 4.7 percent and 1.9 percent, respectively.

5.3.32 Sulfide

Hydrogen sulfide and other sulfides are present in some oilfield waters. They form where sulfur compounds have decomposed under anaerobic conditions. Hydrogen sulfide ordinarily can be detected by its characteristic odor of rotten eggs. The accurate determination of small amounts of sulfide is difficult, and no published method is entirely applicable to all types of water samples. The determination is complicated, because the sulfides oxidize to sulfur in the presence of air (or oxygen).

The qualitative detection of sulfide is comparatively easy, by putting a sample in a 100-mL glass-stoppered conical flask, acidifying, and suspending a piece of slightly moist lead acetate paper between the stopper and the neck. As little as 0.01 mg/L of hydrogen sulfide can be detected in a 50 mL sample by this method. A brown stain on the paper indicates the presence of sulfide.

Three methods are in general use for the determination of sulfide. All three measure total sulfides. Each can be used for soluble sulfide determination by removing iron sulfide and other precipitated sulfides before the test is run. Each procedure has advantages and disadvantages and selection of a particular method should be dependent upon conditions encountered and the desired results.

5.3.32.1 Sulfide (Iodometric Method)

5.3.32.1.1 Principle

Sulfide is oxidized quantitatively by iodine to elemental sulfur. Excess iodine is titrated with standardized thiosulfate solution using starch for the end-point indicator.

5.3.32.1.2 Interferences

Any other materials present which can be oxidized by iodine will yield an excessive value for the sulfide content. These materials can be appreciable in waters with a sulfide content lower than 20 mg/L and will cause a serious error in the sulfide value.

5.3.32.1.3 Procedure Reference

SM 4500-S^{2-} E, p. 4–127.

5.3.32.1.4 Summary

A titration based on this reaction is an accurate method for determining sulfide at concentrations above 1 mg/L, if interferences are absent and if loss of hydrogen sulfide is avoided.

5.3.32.1.5 Precision and Accuracy

When 0.1 N sodium thiosulfate is used and a 50-mL sample is taken, the accuracy of the method is about ±1.5 mg/L sulfide.

5.3.32.2 Sulfide (Ion Selective Electrode)

5.3.32.2.1 Principle

Sulfide ion is measured potentiometrically using a sulfide ion-selective electrode in conjunction with a double-junction, sleeve type reference electrode. Potentials are read using a pH meter (having an expanded scale capable of being read to the nearest 0.1 mV) or a specific ion meter having a direct concentration scale for sulfide ion.

5.3.32.2.2 Interferences

The analysis for sulfide ion is essentially free from interference by other ions.

5.3.32.2.3 Procedure Reference

ASTM D4658-92, Vol. 11.01, p. 655.

5.3.32.2.4 Summary

The ion-selective electrode method for the determination of sulfide in water is applicable for concentrations in the range of 0.04 to 4000 mg/L sulfide.

5.3.32.2.5 Precision and Accuracy

Single-operator precision as listed in ASTM D4658-92 is as follows:

Concentration Range, mg/L	Average Standard Deviation, ±mV	Concentration Variation, ±%
0.05 to 1.0	0.75	6.5
1.0 to 100	0.42	2.6
100 to 4000	0.33	2.0

5.3.32.3 Sulfide (Methylene Blue Method)

5.3.32.3.1 Principle

The methylene blue method is based on the reaction of sulfide, ferric chloride, and dimethyl-p-phenylenediamine to produce methylene blue. Ammonium phosphate is added after color development to remove ferric chloride color. The procedure is applicable at sulfide concentrations up to 20 mg/L.

5.3.32.3.2 Interferences

Strong reducing agents, such as sulfite, thiosulfate, and hydrosulfite, interfere by reducing the blue color or by preventing its development. High concentrations of sulfide may inhibit full color development, requiring a dilution of the sample. Some loss of sulfide may occur when the sample is diluted.

5.3.32.3.3 Procedure Reference

SM 4500-S^{2-} D, p. 4–126.

5.3.32.3.4 Summary

This test method is available in kit form.

5.3.32.3.5 Precision and Accuracy

The accuracy as reported in SM 4500-S^{2-} is approximately ±10 percent.

5.3.32.4 Sulfide (Garrett Gas Train Method)

5.3.32.4.1 Principle

The concentration of soluble sulfides can be quantitatively determined by acidifying a solids-free, filtered water in a Garrett Gas Train. Sulfides convert to hydrogen sulfide (H_2S) which is carried by an inert gas into a Drager tube. The tube changes color in direct proportion to the amount of H_2S produced. Soluble sulfides include H_2S, sulfide (S^{-2}) ion, and bisulfide (HS^-) ion.

5.3.32.4.2 Interferences

No contaminant common to the oilfield will cause a similar color change inside the Drager tube. The carrier gas should be nitrogen, but carbon dioxide is acceptable. Avoid air or other oxygen-containing gases.

5.3.32.4.3 Procedure Reference

API RP 13B-1, Second Edition.

5.3.32.4.4 Precision and Accuracy

With proper sample sizing and volumes of gas through the tubes, the accuracy is approximately 10 percent.

5.3.33 Total Dissolved Solids (TDS)

Solids refer to matter dissolved (Total Dissolved Solids) or suspended (Total Suspended Solids) in water or wastewater. Solids may affect water quality in a number of ways. Waters with high dissolved solids generally are of inferior quality to waters with low dissolved solids for any number of industrial processes.

The total dissolved solids determination is used as a check on specific gravity and resistivity. Charts have been prepared by a number of laboratories to compare these values and, unless the values are relatively close, the results are checked. If the difficulty cannot be resolved, the analysis is re-run. These charts are based on experience and are very useful in avoiding gross errors.

5.3.33.1 TDS (Calculation Method)

5.3.33.1.1 Principle

Most oilfield brines are water solutions of sodium chloride, with lesser amounts of calcium chloride, magnesium chloride, and other metal salts. This calculation method determines total dissolved solids from the sum of the concentrations of the individual ions.

5.3.33.1.2 Interferences

Calculation of the total dissolved solids is subject to error, because all the cations and anions are not determined in an oilfield brine analysis.

5.3.33.1.3 Procedure

The results of the analyses in mg/L for all of the cations and anions are added. The procedure is not applicable, unless a complete mineral analysis of the water is available.

5.3.33.1.4 Example Calculation

Ions Determined	Concentration, mg/L
Sodium	14,000
Calcium	2,100
Magnesium	500
Sulfate	1,200
Bicarbonate	1,300
Chloride	24,100
Total Dissolved Solids:	43,200

5.3.33.1.5 Precision and Accuracy

The precision and accuracy of this method depend upon the quality of the analytical data. However, the accuracy is usually within ±5 percent of the amount calculated.

5.3.33.2 TDS (Gravimetric Method)

5.3.33.2.1 Principle

A well mixed sample is filtered through a standard glass-fiber filter. The filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids.

5.3.33.2.2 Interferences

Highly mineralized waters may contain hygroscopic minerals that require prolonged drying, proper desiccation, and rapid weighing. Limit the sample to no more than 200 mg residue to minimize water trapping in the residue.

5.3.33.2.3 Procedure Reference

SM 2540-C, p. 2–55.

5.3.33.2.4 Summary

Total dissolved solids is an important water quality parameter, especially for oilfield water compatibility issues.

5.3.33.2.5 Precision and Accuracy

The precision as listed in SM 2540-C had a standard deviation of 21.2 mg/L.

5.3.34 Total Organic Carbon (TOC)

The total organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) may be used to characterize these fractions. However, the presence of organic carbon that does not respond to either the BOD or COD test makes them unsuitable for the measurement of total organic carbon.

Total organic carbon (TOC) is a more convenient and direct expression of organic matter than either BOD or COD, but does not provide the same kind of information. Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and does not measure other inorganically bound elements, such as nitrogen and hydrogen. TOC also does not measure inorganic bound elements that can contribute to the oxygen demand measured by BOD and COD. TOC does not replace BOD and COD testing.

5.3.34.1 TOC (Combustion-Infrared Method)

5.3.34.1.1 Principle

The sample is injected into a heated reaction chamber packed with an oxidative catalyst. Water is vaporized and organic carbon is oxidized to CO_2 and water. The CO_2 is carried to a nondispersive infrared analyzer for measurement of total carbon. Inorganic carbon is determined by oxidizing another sample in a separate reaction chamber (where organic carbon is not oxidized). Total organic carbon is determined by subtraction.

5.3.34.1.2 Interferences

Removal of carbonate and bicarbonate by acidification and purging with a purified gas results in loss of volatile organic substances. Any contact with organic material may contaminate the sample.

5.3.34.1.3 Procedure References

a. SM 5310-B, p. 5–11.
b. ASTM D2579-85, Vol. 11.02, p. 40.

5.3.34.1.4 Summary

The results of this analysis method is heavily dependent on sampling and storage conditions. Specific sample container cleaning procedures are given in both references.

5.3.34.1.5 Precision and Accuracy

The minimum detection concentration is 1 mg/L carbon. The difficulty in sampling particulate matter on unfiltered samples limits the precision to about 5 to 10 percent. On clear samples, precision approaches 1 to 2 percent.

5.3.35 Total Suspended Solids (TSS)

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water quality in a number of ways. Waters with high suspended solids generally are of inferior quality to waters with low suspended solids for most oilfield uses.

Membrane filter procedures are covered in NACE TM01-73.

5.3.35.1 TSS

5.3.35.1.1 Principle

A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103° to 105°C. The increase in the weight of the filter represents the total suspended solids.

5.3.35.1.2 Interferences

Exclude large floating particles or submerged agglomerates of nonhomogeneous materials if they are not thought to be part of the suspended solids of the water being analyzed. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of salts. Excessive residue on the filter may cause clogging and produce high results.

5.3.35.1.3 Procedure Reference

SM 2540-D, p. 2–56.

5.3.35.1.4 Summary

Total suspended solids is an important water quality parameter, especially for oilfield injection waters. Total suspended solids are a convenient measure of water quality changes across many types of process equipment.

5.3.35.1.5 Precision and Accuracy

The precision as listed in SM 2540-D had a standard deviation of 6.0 mg/L.

5.3.36 Turbidity

Clarity of water is important for many industrial processes. Water turbidity is caused by suspended matter, such as clays, organic or inorganic matter, and microscopic organisms. Turbidity is a measure of the amount of light scattered and absorbed, rather than transmitted through a sample. Correlation of turbidity with the weight concentration of suspended material is difficult. However, turbidity is useful for comparative purposes.

5.3.36.1 Turbidity (Nephelometric Method)

5.3.36.1.1 Principle

A comparison of the intensity of light scattering of a sample is made to the scattering exhibited by a reference standard. The reference standard is prepared from formazin suspensions.

5.3.36.1.2 Interferences

Dirty glassware, gas bubbles, and surface vibrations can interfere. Colored materials can cause measured turbidity to be reported low. This is not usually a problem in treated waters.

5.3.36.1.3 Procedure References

a. SM 2130-B, p. 2–9.
b. ASTM D1889-88a, Vol. 11.01, p. 359.

5.3.36.1.4 Summary

Turbidity results are reported in nephelometric turbidity units (NTU). Since there is no direct relationship between NTU and weight percent of suspended matter, the best use of nephelometry is for process control and QA/QC.

5.3.36.1.5 Precision and Accuracy

No information was provided on precision and accuracy.

6 Reporting and Documentation

6.1 INTRODUCTION

Water analysis report forms are as varied as the number of laboratories performing water analyses. However, most reports contain the same fundamental parts. Many analytical laboratories have adopted their own standard report format. Laboratory Information Management Systems (LIMS) are in common usage. These computer systems can electronically generate reports from instrument output.

6.2 RECOMMENDED REPORT FORMATS

Figures 1 and 2 are API recommended formats for laboratory and field water analysis reporting, respectively. These recommended formats are presented as guides for preparing report forms. The following list of information should be included in a report form to meet the recommended criteria for a Water Analysis Report Form:

a. Requestor of analysis: Company, organization, agency, individual, etc.
b. Sample identification: Field, location (lease, site, project, etc.), sample point (well, tank pit, etc.).
c. Date and time collected.
d. Person collecting the sample.
e. Units for measured values: (mg/L, ohm-m, °C, etc.).
f. Analytical methods: (SM 407-C, EPA Method 6010, ASTM D 512, Hach kit, etc.).

6.3 REGULATORY COMPLIANCE REPORT FORMAT

The report formats recommended in this document are not intended for regulatory compliance reporting, where the regulatory agency may specify additional quality control and quality assurance parameters in the report format. These agencies (EPA, state or local water boards, etc.) usually have their own guidelines or requirements for reporting.

6.4 WATER PATTERNS

Water pattern usually refers to any graphical representation of water analysis data. Water patterns are a convenient way to present analytical data for comparative purposes. However, their use is not as common today as in past years. Water patterns are mentioned here for historical purposes. Water comparisons today are more likely to be done by computer programs or by determining accessory constituents in the water samples.

6.5 API WATER ANALYSIS LABORATORY REPORT FORM

Each laboratory has a water analysis report form that is designed to suit the needs of that particular laboratory. The API Water Analysis Laboratory Report Form (refer to Figure 1) serves the purpose of illustrating typical information usually requested and the generally accepted way of reporting the analytical data.

6.6 API WATER ANALYSIS FIELD REPORT FORM

The API Water Analysis Field Report Form (Figure 2) serves the purpose of illustrating typical information usually required to be run in the field and the generally accepted way of reporting the analytical data.

6.7 QUALITY OF WATER ANALYSIS RESULTS

The recipient of a water analysis report usually assumes the data to be of good quality. This is not always a correct assumption and erroneous data can cause more problems than no data. Furthermore, once water analysis data has been reported and filed, it usually becomes fact to all subsequent users.

6.8 APPRAISAL OF THE LABORATORY REPORT

There are ways of improving the quality of analytical data on the report form. Examples of report elements that can be quickly screened are as follows:

a. The major constituents should be listed.
b. The proper units should be reported (mg/L, etc.).
c. The methods used should be given for each analyte.
d. Conditions for the determination should be given when applicable (example: temperature for resistivity).
e. The use of significant figures should be consistent.
f. The reported data should be internally consistent. For example:

1. The cation/anion ratio should balance near unity.
2. The TDS should generally agree with a resistivity or conductivity measurement.
3. A low pH value would not be possible with a high carbonate alkalinity.
4. A high barium concentration would not be likely in a high sulfate brine.
5. Natural waters do not generally give pH values near the extremes (1 or 14).

Lab Report Form

Company	Field	Date Time	Sampled By
Sample Number	Sample Point	Well Depth	API Well Number

Other Information: ____________

Dissolved Solids Other Properties

Cations	**mg/L**	**meq/L**	**Method**	**Property**	**Value**	**Units**	**Method**
Sodium, Na				pH			
Calcium, Ca				Density (20°C)		g/mL	
Magnesium, Mg				Conductivity		µohm-cm @ temp.	
Barium, Ba				Resistivity		ohm/cm @ temp.	
Strontium, Sr				TDS		mg/L	
Iron, Fe							
Potassium, K				**Other Tests**	**Value**	**Units**	**Method**
Total Cations							
Anions	**mg/L**	**meq/L**	**Method**				
Chloride, Cl							
Sulfate, SO_4							
Alkalinity							
Bicarb., HCO_3							
Carbonate, CO_3							
Hydroxide, OH							
Total Anions							

Comments: ____________________________

Figure 1—API Water Analysis Laboratory Report Form

Field Report Form

Company	Field	Date Time	Sampled By
Sample Number	Sample Point	Well Depth	API Well Number

Other Information: ____________

Test	Value	Units	Method	Other Tests	Value	Units	Method
Alkalinity		mg/L					
Hydroxide (calculated)		mg/L					
Carbonate (calculated)		mg/L					
Bicarbonate (calculated)		mg/L					
Iron		mg/L					
Sulfide		mg/L					
Dissolved O_2		mg/L					
Dissolved CO_2		mg/L					
pH							
Temperature		°C					
Turbidity		NTU					

Comments: ___________________________

Figure 2—API Water Analysis Field Report Form

APPENDIX A—RESISTIVITY GRAPH

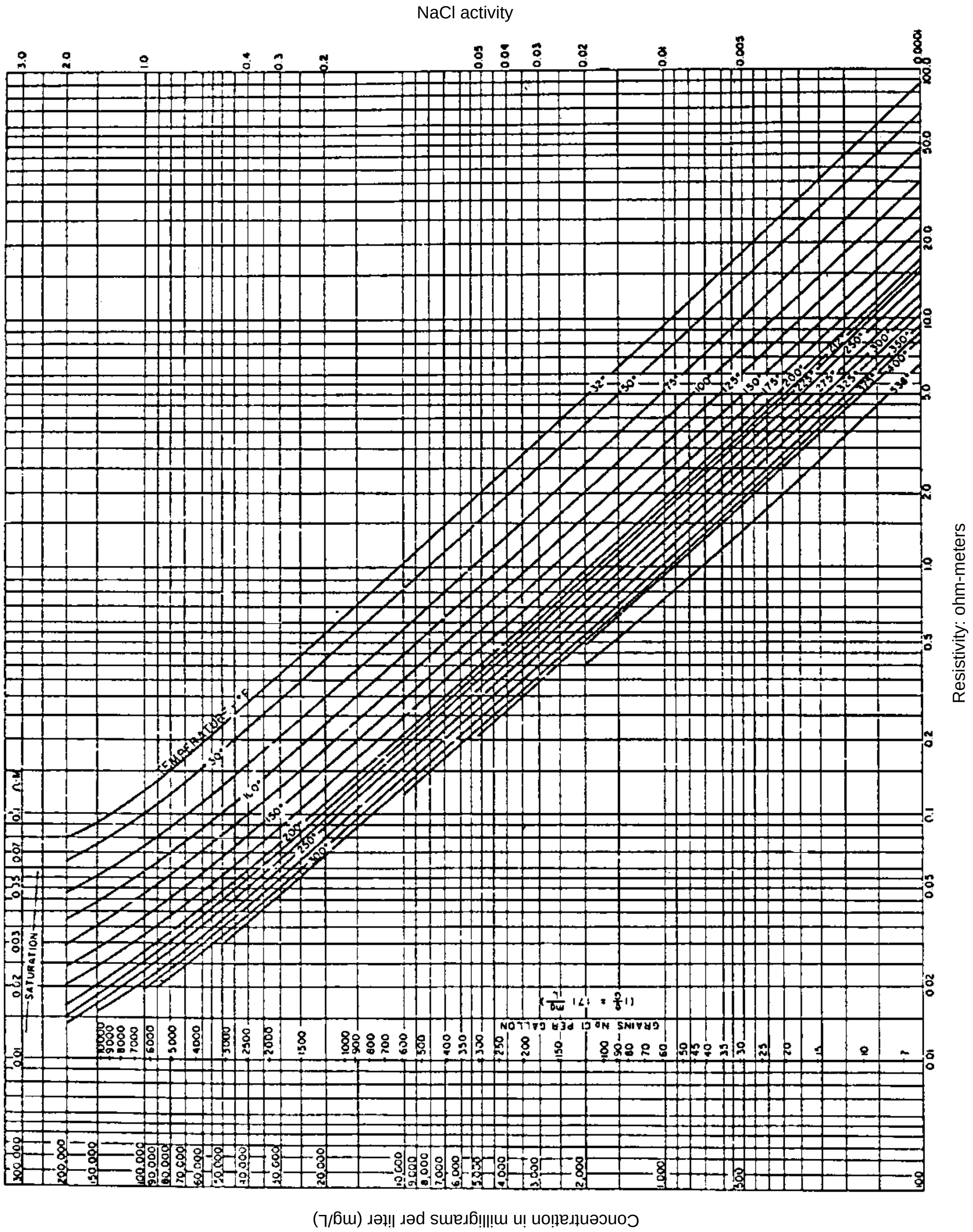


Figure A-1—Resistivity Graph for Salinity and Temperature of NaCl Solution

APPENDIX B—LIST OF ACRONYMS*

Acronym	Term	Definition
AAS	Flame Atomic Absorption Spectrophotometry	Primary technique to measure single metallic elements. AAS uses the hollow cathode lamp source, AC amplified detection, and special sample introduction techniques such as flame aspiration and graphite furnace thermal discharge.
ACS	American Chemical Society	Professional society of chemists in the United States.
API	American Petroleum Institute	Research institute established by the petroleum companies in the United States.
ASTM	American Society for Testing Materials	Society which establishes industrial test standards in the United States.
BAT	Best Available Technology	Technology commercially available for wastewater pollution abatement.
BDL	Below Detection Limit	An analyte not detected at a concentration established as the measurement detection limit for the analytical technique used.
BNA	Base-Neutral and/or Acidic Organic Priority Pollutants	The priority pollutants are extracted as two extracts; base-neutral (BN) analytes, and the phenolic organic analytes which are slightly acidic (A).
BOD	Biochemical Oxygen Demand	Measure of the oxygen removal capacity of polluted water supplies using a biochemical test procedure.
BQL	Below Quantification Limit	An analyte not detected at a concentration established as the measurement detection limit for the analytical technique used.
CAS#	Chem Abstract Service Number	Unique number that the Chemical Abstract Service (a division of the American Chemical Society) assigns to individual chemical species. The CAS number is useful in database searching to obtain information about individual analytes.
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act	The original “Superfund” Act, CERCLA is designed to implement clean-up at major U.S. uncontrolled hazardous waste sites.
COD	Chemical Oxygen Demand	Measure of the oxygen removal capacity of polluted water using a chemical test procedure.
CVAAS	Cold Vapor Atomic Absorption Spectrophotometry	Technique to measure mercury by converting all mercury in the sample to the elemental form and then using an inert gas to sparge the mercury vapor into the light path irradiated by a hollow cathode tube.
CWA	Clean Water Act	Legislation intended to control industrial and polluted discharges in the United States.
EPA	Environmental Protection Agency	Federal agency responsible to Congress for protecting the quality of the environment in the United States.
GC	Gas Chromatography	Analytical technique which uses an inert gas and open-tube column to selectively separate organic compounds contains a stationary phase, either coated on an inert bed or on the column walls. Organic molecules migrate through the column at different rates and separate.
GC/MS	Gas Chromatograph/Mass Spectrometry	GC/MS is gas chromatography with mass spectrometric detection. MS is a primary technique to detect and measure organic analytes in complex sample matrices, or where a large number of organic compounds need to be analyzed at the same time.
GC/MS/DS	Gas Chromatography/Mass Spectrometry/Data System	Technique whereby GC is used with mass spectrometric detection to selectively analyze large numbers of organic analytes in single samples and a computer data system (DSO) handles in the large amount of analysis information.

Acronym	Term	Definition
GFAAS	Graphite Furnace AAS	Sample introduction for AAS using staged heating of the sample solution from a small graphite tube.
GLP	Good Laboratory Practice	Standards established by the U.S. Food and Drug Administration (FDA) for maintaining laboratory records, laboratory practices, and reporting laboratory data.
HGAAS	Hydride Generation	Technique for improving sensitivity of AAS and ICAP for volatile metals (e.g., Se).
HPLC	High Performance Liquid Chromatography	Uses a liquid mobile phase and packed column (e.g., 10 to 20 cm long) to separate organic analytes. HPLC is useful for polar, thermally labile, and/or large organic molecules.
IC	Ion Chromatography	Liquid chromatographic technique that measures anion concentration.
ICP or ICAP	Inductively Coupled Argon Plasma	A primary technique to measure multiple metallic elements serially or simultaneously. ICP uses an argon plasma “torch” to excite elements and complex optics to isolate line emission spectra.
IR	Infrared	IR analysis involves energy absorption due to bond vibrational and rotational interactions in molecules. IR is the spectral region used for functional group analysis.
IS	Internal Standard	Calibration standard added to a sample extract at the time of analysis. Native analyte concentrations are calculated by measuring their analytical response.
ISE	Ion Selective Electrode	Electrochemical detector that directly senses individual ionic species (e.g., H+ in aqueous systems).
LC/MS	Liquid Chromatography/Mass Spectrometry	Liquid chromatography with mass spectrometric detection.
LDB	Land Disposal Ban	A regulation that requires TCLP analysis of certain waste samples.
LIMS	Laboratory Information Management System	A system that accepts input from a variety of laboratory devices as well as humans, and efficiently facilitates laboratory data handling.
LOD	Limit of Detection	Lower concentration at which a signal can be differentiated from instrument noise.
LOQ	Limit of Quantitation	Lower concentration at which an instrumental technique initiates a linear response with increasing concentration for the analyte under analysis.
MCAWW	Methods for Chemical Analysis of Water and Wastes	EPA Report 600/4-79-020 (revised March 1983). Manual of methods for the sampling and analysis of inorganic species in wastewater and drinking water.
MCC	Maximum Concentration of Contaminants	Regulatory action levels for eight elements, and six organic compounds, used to classify hazardous wastes.
MCL	Maximum Contaminant Levels	Concentration levels described in drinking water regulations. Selection of the MCLs uses health and occurrence considerations to set drinking water action levels.
MCLG	Maximum Contaminant Level Goals	Concentration levels described in drinking water regulations. Selection of MCLGs uses health and analytical methodology to set drinking water action levels.
MDL	Method Detection Limit	MDL is the lowest concentration of analyte that can be detected above instrumental or random (noise) signals.
MSD	Mass Selective Detector	Simple mass spectrometer detector for gas chromatography based on quadrupole technology.
NEPA	National Environmental Protection Act	Primary legislation establishing the regulatory authority of the U.S. Environmental Protection Agency.

Acronym	Term	Definition
NIOSH	National Institute for Occupational Safety & Health	United States agency responsible for fundamental research on worker safety.
NHOM	Non-Hydrocarbon Organic Material	Found in oilfield produced water. The EPA oil and grease test includes these water soluble organic (WSO) materials as part of the measured oil and grease.
NIST	National Institute of Standards and Technology	United States agency which establishes physical and chemical standards of measurement. NIST also facilitates technology transfer in the U.S.
NORM	Naturally Occurring Radioactive Material	Usually associated with scale deposition in equipment in the production of oil, gas, and water.
NO_x	Oxides of Nitrogen	Gaseous pollutants, mainly NO and NO_2, that contain nitrogen and oxygen.
NPDES	National Pollution Discharge Elimination System	The permitting program (established in 1973 by the Clean Water Act) to set discharge limits on industrial and municipal wastewater.
NTIS	National Technical Information Service	Source for all U.S. federal reports and documents.
OSHA	Occupational Safety and Health Administration	United States agency responsible for regulating industrial health and safety standards.
PAH	Polynuclear Aromatic Hydrocarbons	Fused-ring aromatic compounds produced by combustion of carbonaceous fuels.
PCB	Polychlorinated Biphenyls (includes mono-)	Products of the chlorination of biphenyl that are widely regulated in the United States as harmful to the environment.
PP	Priority Pollutant	129 listed pollutants used to demonstrate pollution levels in wastewater.
PQL	Practical Quantitation Limit	The lowest level of analyte that can be reliably reported by a laboratory reporting a standard method.
PRP	Principal Responsible Parties (from Superfund)	Those parties liable and responsible for restoring a CERCLA hazardous waste site.
QA	Quality Assurance	Program plan to ensure defensibility of data.
QC	Quality Control	Direct measure taken to maximize quality of reported data.
RCRA	Resource Conservation and Recovery Act	Primary legislation that regulates the production, handling, disposal (e.g., incineration) and reporting of hazardous waste.
RF	Response Factor	Instrumental response for unit mass of an individual chemical analyte.
SOP	Standard Operating Procedure	Written procedure that describes individual laboratory operations.
Sox	Total Gaseous Sulfur Compounds	Gaseous pollutants containing sulfur and oxygen (e.g., SO_2).
SW-846	SW-846	(Third Edition, 1988) EPA manual of RCRA waste analysis methods.
TCLP	Toxicity Characteristic Leaching Procedure	The method used to generate leachate samples for “land ban” and RCRA analyses. TCLP uses a tumbling extractor to collect aqueous leachate from pH adjusted solid waste samples.
TDS	Total Dissolved Solids	Those solid materials in a water sample that will pass through a 0.45 µm filter.
TOC	Total Organic Carbon	The sum of organic species in a water sample.
TOD	Total Oxygen Demand	Measure of the total oxygen removal capacity, chemical and biochemical, of polluted water.

Acronym	Term	Definition
TOX	Total Organic Halogen	The sum of halogenated organic species in an aqueous sample.
TPH	Total Petroleum Hydrocarbon	The amount of hydrocarbon materials extracted from a sample. The extracting solvent may vary but should not remove non-petroleum hydrocarbons.
TSCA	Toxic Substances Control Act	Primary legislation that regulates the manufacture of toxic materials.
TSD	Treatment, Storage, and Disposal Facility	Facilities for treating, storing and disposal of hazardous waste. RCRA imposes stringent restrictions on these facilities.
TSS	Total Suspended Solids	Those solid materials in a water sample that are retained on a 0.45 µm filter.
UV	Ultraviolet	Spectral region used for organic analysis. UV involves light absorption caused by molecular electronic transitions.
VOAs	Volatile Organic Analytes	Term used for volatile organic pollutants.
VOC	Volatile Organic Compound	Volatile analytes measured in drinking water samples.
VOCCS	Volatile Organic Compound Canister Sampler	Evacuated stainless steel canister used to collect volatile ambient pollutants.
WSO	Water Soluble Organics	Materials found in oilfield produced water. The EPA oil and grease test includes these non-hydrocarbon organic materials (NHOM) as part of the measured oil and grease.

*Reprinted by special permission from the American Chemical Society (ACS), Department of Continuing Education, “List of Acronyms,” *ACS Short Course, Environmental Analytical Chemistry: Water and Waste*, 1990.

APPENDIX C—REFERENCES

The following publications are referenced in this recommended practice.

API

Bulletin E2	*Bulletin on Management of Naturally Occurring Radioactive Materials (NORM) in Oil and Gas Production*
RP 13B-1	*Standard Procedure for Field Testing Drilling Fluid Materials*, Second Edition, 1997.

APHA[2]

Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

SM 5
SM 407-C
SM 2130
SM 2320
SM 2340
SM 2510
SM 2540
SM 3111
SM 3120
SM 3500
SM 4110
SM 4500
SM 5210
SM 5220
SM 5310
SM 5520
SM 5560

ASTM[3]

1993 *Annual Book of ASTM Standards*, Volumes 11.01 and 11.02.

D 511-92	*Standard Test Methods for Calcium and Magnesium in Water*
D 512-89	*Standard Test Methods for Chloride Ion in Water*
D 515-88	*Standard Test Methods for Phosphorus in Water*
D 857-89	*Standard Test Methods for Aluminum in Water*
D 858-90	*Standard Test Methods for Manganese in Water*
D 859-88	*Standard Test Methods for Silica in Water*
D 888-92	*Standard Test Methods for Dissolved Oxygen in Water*
D 1067-92	*Standard Test Methods for Acidity or Alkalinity of Water*
D 1125-91	*Standard Test Methods for Electrical Conductivity and Resistivity of Water*
D 1179-88	*Standard Test Methods for Fluoride Ion in Water*
D 1293-84	*Standard Test Methods for pH of Waters*
D 1426-89	*Standard Test Methods for Ammonia Nitrogen in Water*
D 1429-86	*Standard Test Methods for Specific Gravity of Water and Brine*
D 1687-92	*Standard Test Methods for Chromium in Water*
D 1889-88	*Standard Test Methods for Turbidity of Water*
D 2579-93	*Standard Test Methods for Total and Organic Carbon in Water*
D 3561-77	*Standard Test Methods for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brine by Atomic Absorption Spectrophotometry*
D 3651-92	*Standard Test Methods for Barium in Brackish Water, Seawater, and Brines*
D 3867-90	*Standard Test Methods for Nitrite-Nitrate in Water*
D 3869-79	*Standard Test Methods for Iodide and Bromide in Brackish Water, Seawater, and Brines*
D 3920-92	*Standard Test Methods for Strontium in Water*
D 3921-85	*Standard Test Methods for Oil and Grease and Petroleum Hydrocarbons in Water*
D 4130-82	*Standard Test Methods for Sulfate Ion in Brackish Water, Seawater, and Brines*
D 4327-91	*Standard Test Methods for Anions in Water by Chemically Suppressed Ion Chromatography*
D 4458-85	*Standard Test Methods for Chloride Ion in Brackish Water, Seawater, and Brines*
D 4658-92	*Standard Test Method for Sulfide Ion in Water*

---

[2] American Public Health Association, 1015 15th Street, N.W., 3rd Floor, Washington, D.C. 20005.

[3] American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

EPA[4]

EPA Method 6010

Rules and Regulations, *Federal Register* 49; No. 209, October 26, 1984, pg. 43250.

NACE[5]

TM0194-94	*Field Monitoring of Bacterial Growth in Oilfield Systems*
TM01-73	*Test Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters*

Robertson, R. S. and Walesa, A.C., “Rapid Turbidimetric Method Limits Need for Barium Determination in Oilfield Brines,” *Proc.* 134th meeting, American Chemical Society, Chicago, 1958.

---

[4] U.S. Environmental Protection Agency. *Federal Register (FR)* publications are available from the U.S. Printing Office, Washington, DC 20402.

[5] NACE International, 1440 S. Creek Drive, P.O. Box 218340, Houston, TX 77218.

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