

Recommended Practice for Analysis of Oilfield Waters

RECOMMENDED PRACTICE 45
THIRD EDITION, AUGUST 1998

REAFFIRMED, JANUARY 2012



AMERICAN PETROLEUM INSTITUTE

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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:

- The applications of oilfield water analyses.
- The proper collection, preservation, and labeling of field samples.
- A description of the various analytical methods available, including information regarding interferences, precision, accuracy, and detection limits.
- 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:

- 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.
- The prediction of scale formation in surface and downhole equipment.
- Corrosion monitoring and prediction.
- A means of monitoring water treatment system efficiency.
- 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, tempera-

ture 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 ₂ SO 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 ₂ SO 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 HNO₃.

^aThis material was derived in part from the U.S. Environmental Protection Agency, *Rules and Regulations, Federal Register* 49; No. 209, October 26, 1984.

^bContact 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.

^cDissolved 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:

- The equipment may not have been cleaned since its last use.
- 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 brief discussion concerning the constituent (including why it is important in the oilfield).
- General discussion of the method(s).
- Reference(s).
- Summary (if appropriate).
- 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 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 ₂ S 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 ₂ S 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:

^aSM APHA *Standard Methods for the Examination of Water and Wastewater*.²^bASTM 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 ana-

lytical 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 abil-

ity 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

- SM 2320-B, p. 2–26.
- 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

Results	Volume of Standard Acid Corresponding to:		
	Bicarbonate HCO_3	Carbonate CO_3	Hydroxide OH
$P = 0$	T	0	0
$P < \frac{1}{2}T$	$T - 2P$	2P	0
$P = \frac{1}{2}T$	0	2P	0
$P > \frac{1}{2}T$	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:

- Bicarbonate:

$$\text{mg/L } \text{HCO}_3 = \frac{\text{mL acid} \times \text{N acid} \times 61 \times 1,000}{\text{mL sample}}$$

- Carbonate:

$$\text{mg/L } \text{CO}_3 = \frac{\text{mL acid} \times \text{N acid} \times 30 \times 1,000}{\text{mL sample}}$$

- Hydroxyl:

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