Materials Department

SAMPLING AND ANALYSIS METHODS FOR GEOTHERMAL FLUIDS AND GASES

J.C. Watson

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To: Recipients of manual "Sampling and Analysis Methods for Geothermal Fluids and Gases, July 1978"

This document is the culmination of efforts to assemble a manual of sampling and analysis methods for geothermal fluids and gases. Although an effort has been made to eliminate grammatical errors in the content, some will undoubtedly appear in this edition.

The sampling and analysis methods contained have been evaluated under field situations. The appendices contain the data generated during field evaluations. Appendix 1 dealing with the field evaluation of sampling methods at the Republic Geothermal, Inc., East Mesa, CA, site is currently being written and will be mailed separately.

Comments on the content of this manual are welcome and should be submitted to:

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INTRODUCTION

This manual is the third document issued in the process of formulating a manual of sampling and analysis methods for geothermal fluids and gases. This document is the result of efforts begun in 1975 to assemble a manual of recommended methods of sampling and analysis.

The first manual issued in August 1976 as a "Comment Issue,"(a) included tables of analytic options for liquids and gases and summaries of standard methods of analysis. They were selected from standard references for constituents of interest to geothermal investigators, however, no attempt was made to recommend or rank their suitability. It was a place to start and in this role served its purpose in stimulating interest and comment. Also included was a graphic presentation of the concentration ranges of constituents found in a variety of brines and a matrix devised to relate constituents or properties of interest to specific tasks and objectives in the development and utilization of geothermal systems. The purpose of the matrix is to help those using the manual to determine the scope of analytic programs that meet specific needs without including unnecessary analyses. Reviewers of the "Comment Issue" suggested new references, corrected errors and inconsistencies, and proposed alternate ways to arrange or emphasize the material presented. Responding to specific requests for suggestions on sampling and on the conduct of round robin comparison of analytic methods, the reviewers were in general

agreement that it was perhaps too early to standardize sampling methods, particularly the hardware and methodology necessary to representatively sample wells producing two phase flow. They felt that premature attempts to standardize might slow rather than contribute to progress in this difficult area of methods development.

Favorable reactions to the proposed evaluation of analytic methods through a round robin program came from reviewers and others contacted during visits to several laboratories. To implement this program, a workshop was conducted at the Battelle Seattle Research Center in Seattle, WA on May 24-25, 1977. Fourteen laboratories representing industry, commercial analytic services, and government agreed to an ambitious summer schedule for sampling and analyzing two brines. Two subsequent discussions were scheduled to review results and refine procedures and ground rules. Battelle coordinated the effort, preparing control samples to accompany the brines, collecting and shipping the brines and compiling results. The USGS monitored and assisted in obtaining samples from East Mesa 6-2 in July and the more complex brine from Woolsey #1 near the Salton Sea in August. Additional laboratories became involved with nineteen participating in the first round robin and twenty-two in the second. Otto Vetter of Vetter Associates, Costa Mesa, CA, served as a consultant throughout the program and assisted in the arrangements and conduct of field work.

An "Interim Manual"(b) was issued in January 1978 as a result of the above program. In this manual we attempted to establish the format of the

final manual. The content reflected input from over twenty-five sources, including a productive exchange of information and data generated by twenty laboratories participating in round robin analyses of two geothermal brines. The sampling section was written with the aid of Otto Vetter and included sampling methods reported from literature sources. Copies of the interim manual were sent to participants of the round robin program and others for comment on content and modifications of format.

A field evaluation conducted by PNL personnel of some of the methods contained in the sampling section was conducted during March and April of 1978. Otto Vetter served as a consultant and assisted in arrangement of the field tests. These tests were performed at the Republic Geothermal, Inc., East Mesa, CA, site. Sampling methods were evaluated utilizing two producing geothermal wells, Republic wells 56-30 and 16-29. Comments from this field evaluation of the sampling methods have been included in a rewritten sampling section contained in this manual. The sampling field test report (Appendix 1) is currently being written and will be available shortly. The analysis section has also been corrected to incorporate the comments of reviewers of the interim manual. Additional features of this manual include a statistical evaluation of the round robin data generated during 1977 and the addition of some sampling methods which have recently been reported.

The input from the contributing organizations as well as the comments of reviewers will hopefully make this document beneficial to those involved in geothermal endeavors.
MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES

The complexities of geothermal sources, the phases included in samples, and the varying applications for analytic results in exploration, development, and utilization all influence the scope of an analytic program. The inter-relationships of these variables are presented here in matrix form as an aid to defining the scope and capabilities of an analytic program. References cited are the basis for the matrix in its present form and typically place greater emphasis on the evaluation and application of analytic results than on the methods used to obtain data.

Because the matrix emphasizes chemical aspects, it obviously cannot be regarded as a basis for complete sample characterization. Obvious omissions essential to full characterization include: temperature, pressure, flow rate at time of sample, flow history, documentation of sampling and storage methods. Categories related to the operational phase of energy recovery have been included though entries are few. The intent here is to provide users a format for making their own entries and establish a basis for later revision as the industry and its needs develop.
### Legend

<table>
<thead>
<tr>
<th>Sample Form</th>
<th>Property of Interest</th>
<th>Sampling Procedure</th>
<th>Established</th>
<th>Developed but not universally applied</th>
<th>Under Development</th>
<th>None discovered by authors or other results</th>
<th>Other Analytic Methods May Satisfy Requirements</th>
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</tbody>
</table>

### Property of Interest

- **F**: Field Analysis
- **L**: Laboratory Analysis
- **R**: Ratio with other constituent
- **M**: Constituent modifies interpretation
- **b**: Isotopic composition

### Dissolved Solids

- **F**: Field Analysis
- **L**: Laboratory Analysis

### Matrix of Geothermal Tasks and Related Chemical Analyses

<table>
<thead>
<tr>
<th>Task or Objective</th>
<th>Property of Interest</th>
<th>Sampling Procedure</th>
<th>Established</th>
<th>Developed but not universally applied</th>
<th>Under Development</th>
<th>None discovered by authors or other results</th>
<th>Other Analytic Methods May Satisfy Requirements</th>
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<td>N</td>
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</tr>
</tbody>
</table>

### Notes

- [More detailed explanation or context of the matrix and its purpose]
REFERENCES FOR MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES


Sampling Procedures
for Geothermal Fluids and Gases

I. The sampling methods contained in this section are taken from literature sources and also communicated by those people currently involved in geothermal sampling.

II. Some of the sampling methods were evaluated during a field test at the Republic Geothermal Inc. Facility, East Mesa Site, CA during February - April 1978. Comments relevant to this field test are contained on the pages describing the appropriate method.

III. A format of the presentation for each method is given on the following page.

IV. The sequence of methods in this section is:
   a) Sampling hot springs, fumaroles, etc.
   b) Sampling condensed brine and entrained gases.
   c) Sampling steam-lines.
   d) Low pressure separator systems.
   e) High pressure separator systems.
   f) Two phase sampling.
   g) Downhole samplers.
   h) Miscellaneous methods.

V. Illustrations and descriptions of some of the sample methods contained in this section are under copyright 1977, by Academic Press, Inc. These sections were reproduced with the permission of Academic Press, Inc., 111 Fifth Ave., New York, NY 10003.
**METHOD TITLE:**

Descriptive statement of method

<table>
<thead>
<tr>
<th>NO.</th>
<th>Sampling Reference Number</th>
</tr>
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</table>

**SAMPLE TYPE:**

Gas or liquids

<table>
<thead>
<tr>
<th>SAMPLE POINT:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipeline, wellbore, fumarole, etc.</td>
</tr>
</tbody>
</table>

**APPLICATION:**

Sampling operation to be performed.

**REFERENCES:**

Literature source of sampling method.

**DESCRIPTION**

Summary of sampling procedure and special equipment required.

**COMMENTS:**

Limitations of method including field experience with method.
**METHOD TITLE:**
Immersible bottle method for collecting air-free water.

<table>
<thead>
<tr>
<th>NO.</th>
<th>1-S</th>
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<tr>
<td>SAMPLE TYPE:</td>
<td>Liquid</td>
</tr>
<tr>
<td>SAMPLE POINT:</td>
<td>Hot springs or weir box</td>
</tr>
</tbody>
</table>

**APPLICATION:**
Sampling hot springs or weir boxes (from silencers).

**REFERENCES:**

**DESCRIPTION**
Two glass, or polyethylene, sample bottles with 15-cm lengths of wide-bore butyl rubber tubing over their necks and with a screw clip placed halfway up the tube are used. Rubber stoppers fitted with stainless steel tubing are placed in the ends of the wide-bore tubing. The assembly is submerged so that the shorter tube is under the surface and the long tube is exposed. Both bottles fill, with one bottle being purged with an extra 500 ml of water. The screw clamp on the tube is closed, allowing the water in the purged bottle to cool in the absence of air.

**COMMENTS:**
Sample bottle contains water that has not been exposed to the atmosphere (as would happen if a bottle were placed directly within the hot spring).
ILLUSTRATION:

APPARATUS FOR COLLECTING AIR-FREE WATER SAMPLES FROM A WEIR BOX OR HOT SPRINGS
METHOD TITLE:  Water displacement method for collecting gases from hot springs.

SAMPLE TYPE:  Gas
SAMPLE POINT:  Hot springs

APPLICATION:  Sampling gases from hot springs.


DESCRIPTION
1. Glass or polyethylene funnel is attached to the top of a glass bottle with rubber tubing (Figure 1). The bottle and funnel, attached to a pole if necessary, are immersed in the hot spring and filled with water. The assembly is then positioned with the funnel over the most active bubbling area of the spring. The lip of the funnel must be kept beneath the water surface at all times to prevent air contamination; a lead ring around the funnel lip will help keep it submerged. A clamp on the rubber tubing joining the funnel with the bottle seals the bottle when it has filled with gas.

2. A polyethylene funnel fitted into a butyl rubber hose attached to the flask is placed below water level above a stream of gas bubbles (Figure 2). Carbon dioxide and hydrogen sulfide are the predominant gases in hot springs and may be absorbed into solution by the addition of a caustic soda solution to the flask. This allows the collection of larger volumes of nonacidic gases.

COMMENTS:
ILLUSTRATION:

FIG 1. GAS COLLECTION FROM A BUBBLING SPRING BY WATER DISPLACEMENT

FIG 2. APPARATUS FOR COLLECTING GAS SAMPLES FROM SPRINGS
METHOD TITLE:
Seep (from hot springs) sampling method.

SAMPLE TYPE:
Liquid

SAMPLE POINT:
Hot springs seep

APPLICATION:
Sampling of seeps from hot springs where limited amount of liquid is available.

REFERENCES:

DESCRIPTION
1. For sampling seeps from hot springs where only a limited amount of fluid is available, a 1/4" diameter tygon tube is inserted directly into the flow, and water is drawn with a hand-operated vacuum pump. Instead of passing directly into the collection bottle, the water can also be drawn directly through a 0.45 μm cellulose acetate filter.

2. 500 ml Nalgene bottles were used for collecting bottles. Nalge also manufactures the hand operated vacuum pump.

COMMENTS:
ILLUSTRATION:

PORTABLE FILTERING APPARATUS WITH HAND-OPERATED VACUUM PUMP.
METHOD TITLE:
Round bottom flask method for collecting volcanic gases.

APPLICATION:
Sampling volcanic gases.

REFERENCES:

DESCRIPTION
1. The apparatus in Figure 1 of the illustration has been used to sample volcanic gases. The use of a right angle bend in the intake tube ca. 10 cm from the end allows for convenient connection of the sample bottles for any fumarolic outlet configuration encountered. The sample bottles are 300 ml cylindrical round-bottomed flasks, equipped with a Rotaflo teflon stopcock and containing 50 ml 4N NaOH.

2. A variation (Figure 2) consists of 2 flasks joined on the bottom by a two-way teflon stopcock. One flask contains 25 ml 0.1 N As$_2$O$_3$ solution in 1 N HClO$_4$, the other contains 50 ml 4 N NaOH. Both bottles are evacuated and weighed. In the field, the collection tubes are connected to the arsenic-containing bottle, the flask is tilted to allow passage of the gas through the absorbent. After pressure equalization due to accumulation of unabsorbed CO$_2$, the connecting stopcock is opened carefully and the acid gases are rapidly absorbed by the alkaline solution. The first bottle is used primarily for trapping sulfur containing gases while the second is primarily for trapping CO$_2$.

COMMENTS:
In Figure 1, the use of titanium intake tubes prevents reaction of the tubes with volcanic gases.
**ILLUSTRATION:**

Figure 1. Apparatus for collection of volcanic gas samples.

Figure 2. Collection bottles for volcanic gas samples.
METHOD TITLE: Evacuated flask method for fumarole sampling.

APPLICATION: Sampling steam and gas from volcanic fumaroles.

REFERENCES:

DESCRIPTION

1) The gas and steam emanating from a fumarole is collected in an evacuated collecting flask containing 100-200 ml 50-70 Vol. % NaOH or KOH solution. The flask capacity is 0.5-10 liters. A stainless steel dome is placed over the vent of the steam fumarole. The base of the dome is covered for insulation and to prevent air infiltration through cracks between the lip of the dome and the edge of the vent. A vertical pipe, lagged to reduce condensation, leaks excess discharge to the atmosphere and sample discharge through a tee-joint near its base to an air condenser. When the dome and condenser have been purged of air by the fumarole discharge, the flask is attached to the condenser and opened, gradually, to avoid drawing in air through the pipe in the dome.

2) The alkaline condensates are analyzed as soon as possible after collection, if necessary in the field. Alkaline sodium sulfide oxidizes rapidly in the presence of small amounts of air. Aliquots of the sample are withdrawn from the flask by means of a probe similar to that shown in Figure 3. The probe is evacuated by a hand vacuum pump or filled with distilled water before use. Sodium carbonate solutions are stable, and may be retained for long periods before analysis.

The partial pressure of residual gases can be measured in a simple field laboratory and the gases transferred to small glass ampoules for storage, using the apparatus shown in Figure 3. All connections are made of thick-walled (OD 22 mm; ID 7 mm) butyl rubber, which is impervious to gases. The pressure of residual gas in the storage ampoule is kept as near atmospheric pressure as possible. The residual gases are analyzed in the laboratory using standard PVT techniques or gas chromatography. The composition of the steam discharged from a fumarole is assessed from the analyses of carbon dioxide and hydrogen sulfide, the partial pressure and analysis of the residual gases, the temperature of the flask during residual gas pressure measurement, and the known volumes of the flask, condensate, and sodium hydroxide.

COMMENTS:

1. The flow of vapor through the sampling outlet can be controlled with a gravity flap valve on top of the stainless steel tube in the fumarole (Figure 4). The flap valve can be weight adjusted according to the velocity of the discharge.

2. Flask is cooled by water or by air when water is not available.

3. Collection in KOH or NaOH traps CO₂ and H₂S. Separate collections for NH₃, F, B, and SiO₂ are made in evacuated flasks containing no alkali.

4. The residual gases N₂, CH₄, H₂, etc. remain undissolved in caustic. The pressure of the residual gases is initially low and a pressure gradient is maintained between the steam inlet and the flask. Collection ceases when the residual gas pressure equals the steam inlet pressure. Additional collection for H₂S and CO₂ can be achieved by attaching a vacuum pump to the flask outlet and removing the residual gases.
ILLUSTRATION:

FIG 1. METHOD OF SAMPLING FUMAROLIC GAS & STEAM BY CONDENSATION IN EVACUATED FLASKS

FIGS 2 & 3. APPARATUS FOR TRANSFERRING STEAM CONDENSATE AND GAS SAMPLES IN THE FIELD

FIG 4. APPARATUS FOR SAMPLING LARGE FUMAROLES
METHOD TITLE:
Naughton tube method for sampling volcanic fumaroles.

SAMPLE TYPE: Gas
SAMPLE POINT: Fumarole

APPLICATION:
Sampling of gases from fumaroles.

REFERENCES:

DESCRIPTION
1. The Naughton tube shown in the illustration consists of a one meter length of Pyrex glass tube (10 mm OD) with an enlarged section near one end and break-seals at each end (one for sampling and one for analysis).
2. Silica gel, for adsorption of the acid gases and water vapor, fills the narrow section and is activated by heating to 350°C during evaucation of the tube.
3. The break-seal at the sampling end is hook-shaped to facilitate opening of the tube with a wire pull-off.
4. A constriction between the silica gel section and the sampling tip allows the tube to be sealed with a portable gas-oxy torch while the tip remains in the vent.
5. For analysis, the gases are released through the enclosed break-seal to a pressure measuring and gas transfer system. The gases adsorbed on the silica gel are desorbed by gradually bringing the temperature of the adsorbent up to 300°C.

COMMENTS:
Reactions between collected gases (especially H₂S and SO₂) are prevented in the Naughton tubes by adsorption and separation of the acid gases on activated silica gel, which acts in the same manner as a chromatographic column.
ILLUSTRATION:

Silica gel gas sampling tube.

Method of sampling volcanic gases from a fumarole with the silica gel sampling tube.
### Method Title:
Air displacement method for sampling fumaroles.

<table>
<thead>
<tr>
<th>No.</th>
<th>7-S</th>
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<tbody>
<tr>
<td>Sample Type:</td>
<td>Gas</td>
</tr>
<tr>
<td>Sample Point:</td>
<td>Fumarole</td>
</tr>
</tbody>
</table>

### Application:
Sample fumarole gases

### References:

### Description
Apparatus consists of an intake tube attached to one end of a sample flask. A sample is collected by inserting the intake tube into the gas vent. When the sampling train is judged to be swept free of air, the sample flask is sealed.

A condenser, usually a glass bottle or tube cooled by ice water or air circulation is often placed between the intake tube and the sample flask to separate and collect the steam fraction of the discharge.

A water aspirator or pump is often used to pull the sample through the collecting train if insufficient pressure is present.

### Comments:
Copper, iron, and stainless steel intake tubes tend to react with volcanic gases and may contaminate the sample. Pyrex glass or, for high temperature vents, silica tubing, are preferable, although strength is sacrificed. This might be overcome by placing the intake tube inside a stainless steel tube.
Gas collection from a fumarole by air displacement.
METHOD TITLE: Syringe method for sampling entrained gases.

APPLICATION: Sampling dissolved and entrained gases in fumaroles, hot springs, or steam wells.


DESCRIPTION:
Two 60 ml polypropylene syringes (Monoject) and an evacuated 50 ml pyrex gas sample bottle with an o-ring seal (constructed using Ace glass adapter 5027 modified by the addition of a second o-ring so that the exit tube can be evacuated) are connected by 1/8" ID Tygon tubing and four 3-way polypropylene stopcocks (Pharmaseal) with short pieces of tubing used to seal the joints.

At the start of each collection, 10 or 20 ml of 3 m NaOH (prepared from low carbonate reagent) is drawn into syringe B through stopcock 4. Dissolved air in the solution is reduced by closing the stopcock to the syringe (the stopcock handle indicates the closed direction; see detail in illustration), pulling the plunger to produce a partial vacuum over the solution, shaking to join the air bubbles and releasing the accumulated air through the stopcock. An inverted funnel connected to the apparatus with 1/8" Tygon tubing is dipped in the hot spring and filled with water. With stopcock 1 closed to the side tube, syringe A and stopcock 2 are used to pump water through the tubing and out of the sidearm of stopcock 4 which is closed toward the gas bottle. When this part of the tubing is water filled, the inverted funnel is moved over the gas vent and gas is allowed to accumulate. Further pumping with syringe A displaces the water in the tube with gas from the vent. When the tubing is flushed with gas, stopcock 4 is closed by moving it 45° to an intermediate position. Syringe A is then filled with 50 ml of gas which is allowed to cool to near air temperature. The cooled gas, its volume noted, is then transferred into syringe B through stopcocks 2 and 3. With stopcock 2 closed to the sidearm the apparatus is shaken and the CO₂ and H₂S are rapidly absorbed into the NaOH solution. The volume of the non-absorbable or residual gas may be measured from the change in the position of the plunger of syringe B. This procedure is repeated until approximately 25 ml of residual gas has accumulated in syringe B. The tubing from stopcock 2 to the glass sample bottle is then partially evacuated by closing stopcock 4 to the vent, stopcock 3 to the NaOH solution, and stopcock 2 to the funnel and pulling the plunger of syringe A out as far as possible without breaking the seal while the plunger is out. Stopcock 2 is then closed toward the gas bottle and the evacuated air and gas is released through stopcock 1. This procedure is repeated twice more.

The evacuated gas sample bottle is then opened by unscrewing its threaded bushing slightly.

COMMENTS:
1. In collecting from high temperature springs, some condensate will accumulate in the syringe and this may be either discarded or collected through stopcock 1.
2. For volume measurements in the syringe, it is not accurate to note the position of the meniscus because the ends of the syringe and plunger are conical. The plunger is usually slightly sticky and an accurate volume measurement requires manipulation and bracketing by feel.

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PAGE: B-10
Apparatus for gas sampling of fumaroles, hot springs or steam wells.

and pushing the closure tube into the bottle until the small hole in the tube is within the bottle. Now, with syringe B held upright, gentle opening of stopcock 3 to connect the glass bottle to syringe B allows the residual gas to flow into the bottle. When 4 ml residual gas remains in syringe B, stopcock 3 is closed, the gas bottle is closed by gently pulling its closure tube out of the bottle until its side hole is no longer connected to the bottle interior, and the bushing is tightened. The 4 ml of remaining gas is then pushed into the tubing to reduce the possibility of air contamination.
METHOD TITLE: Sealable bottle method for sampling weir boxes.

SAMPLE TYPE: Liquid

SAMPLE POINT: Weir box

APPLICATION: Sampling silencer weir boxes for liquid.


DESCRIPTION
The apparatus consists of a bottle holder, into which a different bottle is fitted for each sampling, attached to a long handle. Connected to the handle is a spring-operated rubber block which covers the top of the bottle during its immersion and withdrawal from the weir box. This prevents evaporation of the sample.
ILLUSTRATION:

SAMPLER FOR COLLECTING WATER SAMPLES FROM THE WEIR BOX OF A GEOTHERMAL WELL
### METHOD TITLE:
Naughton tube method for sampling volcanic gases.

<table>
<thead>
<tr>
<th>NO.</th>
<th>SAMPLE TYPE</th>
<th>SAMPLE POINT</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-S</td>
<td>Gas</td>
<td>Drill hole</td>
</tr>
</tbody>
</table>

### APPLICATION:
Sampling volcanic gases.

### REFERENCES:

### DESCRIPTION

1. Naughton tubes containing a silica gel absorbent are thermally insulated by placing them in a silica jacket with the annular space filled with crushed fire brick.

2. Stainless steel wire cable is used to lower the tubes into the drill holes and a wire pull-off is used to open the tip at the desired depth.

3. Thermal inertia of the insulation is such that heat is supplied to the inner sampling tube for a short time after withdrawal. The collected gas expands and will be "blowing out" as the tube is sealed. The tube is closed with a portable gas-oxy torch.

### COMMENTS:

1. Insulated tubes can be exposed to 1000°C for periods up to one minute without the temperature of the silica gel exceeding 100°C.

2. Collections were reported to be made within one minute time limit (at maximum depth of 15 meters) with the tubes being sealed immediately on withdrawal from the drill hole. During closing the flow of gas through the tube opening does not prevent the flow of air in the opposite direction. The flow rate of each gas through the opening depends primarily on the difference in the partial pressure of the gas on each side of the opening and on the size of the opening.
Method of sampling gases in holes drilled through the crust of a lava lake.
METHOD TITLE: Cooling coils

SAMPLE TYPE: Liquid

SAMPLE POINT: Pipeline, separator or other

APPLICATION: Sampling condensed brine

REFERENCES: Appendix 1: Field Test 1978.

DESCRIPTION

1. Cooling coils are made of stainless steel with total length 20 - 24 ft., ID 0.25 - 0.50 in. and OD 0.25 - 0.50 in. Wall thickness not less than 0.02 in. fulfills most requirements for sample cooling.

2. Varying diameters of tubing are used because of variability in sampling requirements.

3. Coil diameter is normally 8 - 10 in. to fit into container that acts as cooling bath. Five gallon buckets are most frequently used for this purpose.

4. Two coils commonly used; first is immersed in a water bath to cool sample to boiling point of water, second coil is immersed in an ice bath. This saves usage of large amounts of ice.

5. Flow of brine through coils must be carefully watched to avoid flashing of the sample in the coils.

6. Alternatively, a water cooled condenser can be used if a sufficient supply of cooling water is available.

COMMENTS:

1. During field test Whitey or equivalent shutoff or regulating needle valves were used for maintaining proper flow rates through the coils. Gate or ball valves are not suitable for regulating flow.

2. Flexible armored lines equipped with quick disconnect fittings were used upstream of coils to connect to 1" ball valves on pipelines, etc. This allowed for portability of cooling coils for various sample locations.

3. Coils of 1/4" ID or larger normally used for condensing brine. Smaller (1/8" ID) lines may be used to sample steam lines.

4. During field test, brine surging in pipelines resulted in pulsating effects while collecting through coils. It is not advisable to attempt to correct this effect with the flow regulating needle valves as steam can be emitted at

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SAMPLING CONDENSED BRINE USING COOLING COILS

WELL

PIPELINE

WATER COOLING BATH

ICE-WATER COOLING BATH

0.45 μ FILTER

CARBOY

COOLING WATER OUT

SAMPLING CONDENSED BRINE USING JACKETED CONDENSER

WELL

PIPELINE

CONDENSER

CARBOY

COOLING WATER IN

high velocity through the coils resulting in a potentially dangerous burn situation for the operator.
METHOD TITLE:
Sparging method for trapping gases.

SAMPLE TYPE: Gas
SAMPLE POINT: Pipeline

APPLICATION:
Sampling of dissolved and entrained gases in brine.

REFERENCES:
Appendix 1: Field Test 1978.

DESCRIPTION
1. Condensed brine is allowed to flow into a series of tubes or carboys containing absorbing solutions. The entrained gas is dispersed through fritted glass to allow for more complete absorption. (Figure 1)

2. Examples of absorbing solutions include sodium hydroxide solution for trapping H_2S and CO_2, ammonium hydroxide solution saturated with SrCl_2 for trapping CO_2, zinc acetate or cadmium chloride solution for trapping H_2S, etc.

3. Efficiency of absorption can be improved by the addition of more absorbing tubes in series (Figure 2) to allow the head space gas to be dispersed through additional absorbing solutions. During a field test of this arrangement the first sample tube on the left was filled with 750-1000 ml 2N NaOH sol'n for collecting CO_2. The second tube was filled with 100 ml 2N NaOH. Brine + gas entered the first tube through the sparger and mixed with the 2N NaOH until the final volume (in first tube) was 1000-1500 ml. Blanks were also taken by filling the 1st tube (on left) with 2N NaOH and pouring this into linear polyethylene sample bottles.

4. Fisher-Milligan bottles were also used in series during the field test to collect entrained gas (Figure 3). The long path length due to the spiral inner coil allows for long contact with the trapping solution.

COMMENTS:
1. During field test the apparatus in Figure 2 proved to be cumbersome to employ after sampling due to its large size. Some redesign is contemplated.

2. It was also found during the field test that it was unnecessary to fill the second (smaller) tube with trapping solution (2N NaOH) and that the larger tube was sufficient for trapping. This was based on the concentration levels of CO_2 encountered.

3. Fisher-Milligan bottles were found to be easy to operate and minimize contact of the operator with the NaOH sol'n. A contemplated modification to the bottles is an addition of a sparger stone to the bottom brine inlet tube.
ILLUSTRATION:

**FIG 1.** Carboy containing absorbing solution to trap entrained gas.

**FIG 2.** Sparger arrangement used in field test for trapping entrained gases.

**FIG 3.** Fisher-Milligan bottle system used in field test for trapping noncondensable gases.
METHOD TITLE:
Cerro Prieto method for sampling non-condensables and CO₂.

SAMPLE TYPE: Gas and Liquid
SAMPLE POINT: Pipeline from separator

APPLICATION:
Sampling noncondensable gases and CO₂.

REFERENCES:

DESCRIPTION
1. The steam and noncondensable gases pass from the separator through a cooling coil immersed in an ice-water bath (Figure 1). The condensed steam and noncondensables pass into a 5-liter preweighed evacuated sampling vessel. While the vessel is still partially evacuated a predetermined amount of 10% NaOH solution is allowed to enter. This reacts with the CO₂ allowing more sample to be withdrawn from the separator. Following collection for a specified period of time, the 5-liter vessel is removed and reweighed to determine the amount of condensed steam phase. The liquid phase is analyzed for CO₂ while the gas phase is analyzed for residual gases (CH₄, N₂, H₂, etc.).

2. During a field test of this method (Figure 2) the 5-liter flask was initially filled with 500 ml 2 N NaOH and weighed. The flask was attached to a vacuum pump and evacuated for 1/2 hr. Steam and noncondensables were removed from the steam line through a 1/2" ID insertable sample probe. The flow then proceeded through a water cooling bath followed by an ice water cooling bath. The flask was connected to the outlet side of the second condensing coil. Steam condensate and gas were allowed to fill the flask until the flask pressure had equilibrated with the steam line pressure. The flask was then removed and reweighed.

COMMENTS:
1. The liquid phase is removed from the flask in the lab by using a suction flask and using care so that gas is not removed. The liquid is subsequently analyzed for CO₂.
2. The gas phase is removed in the lab by attaching an evacuated gas sampling bulb to the flask and drawing off a sample or alternatively by allowing a synthetic brine solution to enter through the bottom of the flask and displace the gas through the top stopcock. This has the disadvantage of allowing the gas to dissolve in the synthetic brine thus leading to some error. (See Figures 2 and 3 under evacuated flask method for fumarole sampling.)
3. The fragile nature of the collecting flasks does not allow for easy transport of the sample without the risk of breakage.

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ILLUSTRATION:

FIG 1. CERRO PRIETO METHOD FOR COLLECTING NON-CONDENSABLES & CO₂

FIG 2. CERRO PRIETO METHOD USED IN FIELD TEST
METHOD TITLE:
Hypodermic syringe method for sampling noncondensables.

SAMPLE TYPE:
Liquid and gas

SAMPLE POINT:
Steam line from separator

APPLICATION:
Sampling noncondensable gases in steam line.

REFERENCES:

DESCRIPTION
1. Steam and noncondensables flow from the steam line through an insertable sample probe into cooling coils in an ice bath. A line from a tee after the insertable probe goes to a manometer which is used to measure the inlet pressure. The flow from the cooling coils goes into the calibrated hypodermic syringe after passing through a short section of Tygon tubing. The steam line pressure is used to fill the syringe. A predetermined volume is collected in the syringe. Equilibration is achieved when bubble movement is no longer observed in the Tygon tube. The equation below is used to calculate % CO2:

\[
\% CO_2 = K P_{T1} \left( \frac{V_{G1}}{V_{L1}} \right) \left( 1 + \frac{M_C V_{L1}}{V_{G1}} \right) \left[ 1 - \left( \frac{V_{G2}}{V_{G1}} \right) \left( \frac{V_{L1}}{V_{L2}} - \frac{V_{NaOH}}{V_{G2}} \right) \left( 1 + \frac{M_n V_{L2}}{V_{G2}} \right) \right]
\]

where a) \( K = 0.00256 \) (involves formula weight \( CO_2 \), gas constant, temperature, and fluid density appropriate for press. measured in cm Hg, vol. in ml and density in grams per ml).

b) \( V \) and \( P \) refer to vol. and press., \( L \) and \( G \) refer to liq. and gas phase and 1 and 2 refer to the collections, specifically 2 refers to that involving NaOH.

c) Subscript \( T \) on pressure refers to total pressure inside syringe (barometric + manometer pressure).

d) \( F_1 \) represents fraction of \( P_{T1} \), due to non-CO2 gases.

e) Factor \( M_n \) represents mol.wt. nitrogen in equation above assuming nitrogen (over

COMMENTS:
1. This method should be used for low pressure lines only.
2. Six to eight field determinators per hour can be made using this method.
3. Absolute pressure (barometric) must be known to make accurate calculations.
f) $F_2$ represents virtual pressure fraction for CO$_2$.

The non-CO$_2$ fraction is given by: \[ \text{non-CO}_2 \text{ fraction} = \frac{F_1}{F_1 + F_2} \]

2. Two syringe collections are necessary for samples containing CO$_2$ mixed with other gases. One syringe contains NaOH solution to trap the CO$_2$. 

Illustration: System for sampling & measuring non-condensable gas in steam
METHOD TITLE:
Tedlar bag method for sampling steam condensate and noncondensable gases

SAMPLE TYPE:
Gas and condensate

APPLICATION:
Sampling of steam condensate and noncondensable gases.

DESCRIPTION
The arrangement of the sampling apparatus is shown in the illustration. The total volume of the tubing is approximately 1 liter. The stainless steel probe is inserted into the flow stream in such a way that only steam passes through the collection train; the high steam flow rates make this simple to achieve. Two condensers are used; the first being water cooled, and the second ice-water cooled. The system is purged and equilibrated without a collection bag attached for approximately 10 min. or until 10 to 20 cm$^3$ of condensate has passed through the system. Collection is then initiated and continued until 1 to 2 liter of non-condensable gas has been collected in a Tedlar bag. The gas contents are analyzed later in the laboratory. The condensate is collected in a trapping bottle upstream of the tedlar bag.

COMMENTS:
1. Sulfur-containing species are unstable in plastic bags and should be analyzed on site.
2. Diffusional losses of hydrogen are appreciable.
3. Use of plastic bags should be limited to collection of chemically stable and higher molecular weight gases.

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REFERENCES:
ILLUSTRATION:

STEAM SAMPLING SYSTEM USING TEDLAR BAG

FLEXIBLE HOSE

PROBE AND TIP

CONDENSER COILS

WATER COOLING BATH

ICE-WATER COOLING BATH

TEDLAR GAS COLLECTION BAG
METHOD TITLE: Wet test meter method.

SAMPLE TYPE: Gas
SAMPLE POINT: Steam line from separator.

APPLICATION: Sampling steam for noncondensable gases.

REFERENCES:

DESCRIPTION
1. The condenser coil in an ice water bath is connected to the steam line via a by-pass valve by means of a 25-foot flexible, stainless steel tubing using appropriate fittings at both ends (Figure 1). The by-pass valve is positioned to vent with no flow to the condenser and the sample port valve on the steam line is fully opened. After flowing steam through the connecting tubing for sufficient time (usually 10 to 15 minutes) for the tubing to come to temperature, steam is valved to the disconnected condenser until a condensate flow rate of about 50 ml/min is obtained. Approximately one liter of condensate is purged through the condenser. This allows the condenser system to come to an equilibrated condition and also cleans the tubing of any possible residue or contamination from prior samplings.

The wet test meter is equilibrated by attaching the equilibrated condenser to the sample train and passing the noncondensable gases through the wet test meter for 10 to 15 minutes. The condenser is disconnected from the sample train. The collection bottle is replaced by a tared one-quart bottle and the wet test meter reading is noted. The condenser is quickly attached to the sample train by means of rubber tubing and actual sampling begins. Sampling continues until the collection bottle is filled or 3 to 4 liters of noncondensible gas volume is reached. The condenser is then disconnected from the train and the noncondensible gas content of the steam determined from the weight of water collected and the volume of gas measured after appropriate corrections for temperature and barometric pressure.

2. The system shown in Figure 2 was used to evaluate the method under field conditions. The steam and noncondensable gas flow passed from the steam line through an insertable sample probe (inserted to the center of the steam line) into a flexible armored line. Flow then continued to a cooling bath filled with water followed by a second cooling bath filled with ice water. The flow then passed into the glass separator with the condensed steam being removed from the bottom for analysis or alternatively the rate could be measured with a graduated cylinder. Noncondensables from the top of the glass separator passed through the wet test meter or alternatively were (cont.)

COMMENTS:
1. Wet test meters must be properly equilibrated to prevent absorption of gases such as carbon dioxide for accurate volume measurements.
2. Glass separator should only be used under low pressure conditions (for field test the steam line inlet pressure was 7-9 psig).
3. Field test showed improved collection results are obtained and more controllable flow regulation using 1/2" ID insertable probes instead of smaller ID probes (1/4" ID) due to better collection rates from the steam line.
4. Filling the gas collection bulb initially with water (in field test) and allowing the gas to displace the water proved to be a useful way to determine if air was excluded. Collection is continued for 3-4 volume displacements.
ILLUSTRATION:

EXCESS STEAM VENT TO MISPHERE
STEAM SOURCE
FLEXIBLE LINE
CONTROL VALVES
CONDENSER
COLLECTORS CONTAINING REAGENTS
NON-CONDENSIBLE GAS COLLECTOR
TO ATMOSPHERE
WET TEST METER

FIG 1. STEAM SAMPLING APPARATUS

FIG 2. WET TEST METER METHOD USED IN FIELD TEST TO SAMPLE NONCONDENSABLES IN STEAM LINE

collected in gas sampling bulbs. The noncondensible gas flow rate can be checked using the graduated cylinder water displacement method.
### METHOD TITLE:
Radon Gas Collection and Measurement

### APPLICATION:
Measurement of radon gas concentrations in geothermal gases.

### SAMPLE TYPE:
Noncondensable gas

### SAMPLE POINT:
Noncondensable gas line

### REFERENCES:
- J. D. Ludwick, Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

### DESCRIPTION
Radon concentrations in most geothermal gases are sufficiently high to measure directly in filled Lucas tubes. A Lucas tube is a glass sphere with a flat quartz window on one end and a stopcock on the other. The inside surfaces of the Lucas tube, except for the quartz window, are coated with activated zinc sulfide/silver scintillator. Prior to sampling the tubes are evacuated with a vacuum pump. The gas sample is then taken by connecting the Lucas tube to the noncondensable gas line, opening the stopcock and allowing the Lucas tube to pressurize slightly. Before entering the Lucas tube the gas is filtered through a 2μm membrane filter to remove any radon daughters. The tube is then disconnected, the stopcock opened briefly to allow the tube to equilibrate to atmospheric pressure and the stopcock is then closed. After a period of about 4 hours to allow buildup of the radon daughter products the Lucas tube is optically coupled to a multiplier phototube. The alpha decay of the radon and its daughters produces scintillation of the zinc sulfide layer and the light pulses are amplified and counted. Each Lucas tube is of known volume and individually calibrated.

### COMMENTS:
ILLUSTRATION:

LUCAS TUBE RADON COUNTER

GROWTH AND DECAY OF RADON DAUGHTERS

COUNTS (1000/10MIN) vs TIME (MINUTES)

* USING LAC-2 COUNTER
THEORETICAL CURVE
METHOD TITLE:
Determination of the Chemical Forms of Gaseous Mercury.

APPLICATION:
Determining the concentrations and chemical forms of mercury in geothermal noncondensable gases and in ambient air.

REFERENCES:

DESCRIPTION
Geothermal noncondensable gases contain highly elevated levels of mercury compared to ambient air, and a sampling technique has been developed which simultaneously quantifies and determines the chemical species of mercury in the gas or air phase. The sampling technique is based on the selective adsorption of various mercury forms on adsorption tubes connected in series. The gas or air is first flowed through a fiberglass filter to remove any microparticulate mercury and then through a quartz tube containing chromasorb-W which has been pretreated with 3% SE-30 silicone and HCl gas. This tube selectively removes Hg\textsuperscript{2+} compounds and passes all other forms. The gas or air then flows through a tube containing chromasorb-W which has been pretreated with NaOH. This adsorbent selectively removes methyl mercury and passes all other forms. The gas or air then flows through a tube containing silver coated glass beads to selectively remove elemental Hg\textsuperscript{0} vapor. The final tube is filled with gold coated glass beads and removes dimethyl mercury or any other form which passes through the first three tubes. The tubes are then disconnected and heated in resistance coils to drive the mercury off in a stream of nitrogen into a mercury analyzer for quantification.

COMMENTS:
SELECTIVE ABSORPTION TUBES FOR MERCURY FORMS IN GASES
METHOD TITLE:
Evacuated bottle method for collecting residual, dissolved and entrained gases.

APPLICATION:
Sampling dissolved gases in equilibrium with water.

REFERENCES:

DESCRIPTION
1. Brine is collected in an evacuated pre-weighed 300 - 500 ml bottle by attaching vinyl tubing from the condenser to the bottle.
2. Gases in equilibrium with the water (in head space) are analyzed by gas chromatography or other means.
3. Dissolved gases such as CO₂ are determined in the liquid phase. For steam condensate and gas samples, the bottle is filled with 50 - 100 ml 4N NaOH (as carbonate free as possible). This traps both CO₂ and H₂S. Flow from the condenser should be reduced by regulating the valve on the separator or steam bypass. Pressure relief valve may be used to prevent overpressuring the gas bottle.

COMMENTS:
These bottles may also be used to sample the top of the gas water separator (gas only sample without condensate). A larger quantity of caustic is needed (100 - 150 ml). Since flow into the bottle may exceed flow into the gas water separator, the bottle flow should be restricted by pinching the vinyl tubing until a balance is achieved.
ILLUSTRATION:

Exploded view of gas sample bottle. The bottle is opened by sliding the hole inside the o-ring. The tube may be evacuated with the bottle closed by clamping a second o-ring and washer to the top of the adapter. Gas bottles with NaOH solution are evacuated by a water aspirator with gentle boiling of the solution.
METHOD TITLE:
Glass separator method for determining liquid and gas.

APPLICATION:
Separating two phase flow from low pressure source.

DESCRIPTION
1. Two phase flow enters tangentially into the glass separator through a flexible armored line (Figure 1). This armored line is connected to the pipeline through a 1" Whitey (or equivalent) ball valve equipped with a quick disconnect attachment. The steam noncondensable phase pressure is measured and the flow passes through a cooling coil immersed in an ice bath. The steam gas-flow then proceeds to a second glass separator. The flow rate of noncondensable gas can be measured using an inverted graduated cylinder and the water displacement technique. Alternatively, the gas can be collected in gas sampling bulbs for later analysis. Another modification shown in Figure 2 allows for the introduction of a carbon dioxide sparger trap to remove CO₂ and H₂S prior to collecting the residual gases (CH₄, H₂, N₂, etc.) in the glass sampling bulbs (500 cc). Liquid from the first separator passes through a cooling coil immersed in an ice bath and is collected for analysis. Flow rates of liquid from the first separator and steam condensate from the second separator are measured with graduated cylinders.

2. A second arrangement using a glass separator is shown in Figure 3. This setup was used to sample the steam line coming from the large site separator. Steam and gas were removed from the pipeline through an insertable probe. The flow next went through an ice water cooling bath and then into the 1st glass separator. Condensate was removed from the bottom of the first glass separator or alternatively the rate of condensate production could be measured. The second glass separator was used as a liquid (steam condensate) level controller. Noncondensable gas was taken from the top of the first glass separator and collected in a glass sampling bulb. Alternatively, the gas flow rate can be measured by displacing the water in an inverted graduated cylinder.

COMMENTS:
1. During field evaluation of this method the steam noncondensable phase pressure (from the 1st separator) was maintained at 5 psig.

2. Field test showed that difficulty was encountered regulating flow rates when 1500 cc 2M NaOH was used in the sparger (back pressure was created). Reduction to 750 cc NaOH sol'n in the sparger remedied this problem. During field test gas collection in the gas sampling bulbs proceeded until the equivalent of 5 bulb volumes of gas had passed through (to remove air contamination).

3. This system should be used for low pressure sources only.
5. Vortex formation (in the glass separator) should be minimized by adjusting inlet and outlet pressure and liquid level in the glass separator.

6. Filling the gas collection bulb initially with water (in field test) and allowing the gas to displace the water proved to be a useful way to determine if air was excluded, (Figure 3). Collection is continued for 3-4 volume displacements.
METHOD TITLE:
Non-metallic Steam Condenser

APPLICATION:
Condensing steam for analyses of condensate and noncondensable gases, and for determining steam/gas ratios. Especially applicable for sampling for trace metal analyses.

REFERENCES:
D. E. Robertson and J. D. Ludwick, Battelle, Pacific Northwest Labs. Richland, WA 99352.

DESCRIPTION
Incoming steam from a steam-brine separator or from a dry steam well-head enters the 20-liter Pyrex glass sphere which is cooled by a spray of circulating cold water. The steam swirls around in the sphere and condenses on the walls. A final Pyrex glass condenser coil assures complete steam condensation, and only noncondensable gases exit via the sidearm tube of the final condenser. Fresh condensate can be withdrawn from a tap at the bottom of the sphere for analyses without disturbing the condensing process. The noncondensable gases are normally of a sufficient flow rate and pressure to monitor the flow with a rotameter during gas sampling. The temperature of the cooling water is recorded for correcting gas data to STP. This condenser is quite efficient and approximately 500 gm of steam per minute can be condensed.

COMMENTS:
This condenser can be used for obtaining accurate steam/gas ratios by simultaneously measuring the volume of noncondensable gases and the weight of steam condensed. The gas volume is measured with a wet test meter and the condensate is measured volumetrically.

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ILLUSTRATION:

NON-METALLIC STEAM CONDENSER
METHOD TITLE: Low pressure separator method.

APPLICATION: Separation of steam-gas phase from liquid phase for low pressure source.

REFERENCES:

DESCRIPTION
1. In Figure 1, a simple separator operating at atmospheric pressure is used for sampling low pressure (30-40 psig) two phase flow. The source enters tangentially with the liquid phase being removed at the bottom and steam-gas phase removed from the top. Enthalpy of the discharge is measured by a calorimeter so separate results from steam and water analyses can be related to concentrations in the total flow.

2. The separator in Figure 2 is a modification of the above separator to allow for more efficient separation of CO₂ from the liquid phase. The baffles prevent liquid droplets from being carried over into the steam sample. Brine and steam enter near the middle of the miniflasher. Water droplets containing entrained carbon dioxide are condensed on the series of baffles and fall to the bottom. Liquid sample is removed from the bottom and the steam sample is taken from the top.

COMMENTS:
1. The separator, calorimeter, and piping must be heavily insulated to prevent heat losses, otherwise diluted water samples and concentrated steam samples will result. Before taking samples the separator is allowed to warm up for 15 minutes.

2. At sampling pressures of a few tens of pounds, the errors due to steam and water being sampled in incorrect proportions are often small, but the proportions of steam and water entering the separator should be checked by a simple water calorimeter and corrections to concentrations made (see section on steam loss corrections). A discharge of almost pure steam or water is sometimes obtained from low-pressure sample points, in which case extreme dilution of the small quantity of water by condensed steam will occur, or of the steam by flashing of the excess water.
ILLUSTRATION:

**FIG 1. LOW PRESSURE SEPARATOR SAMPLING APPARATUS**

- 1" STEAM PIPE AND 1" VALVE TO CONTROL OUTLET
- HEAVY LAGGING ON SEPARATOR CALORIMETER AND PIPework
- 16" DIA. SEPARATOR
- SIGHT GLASS
- 3/8" S. S. TUBE TO CONTROL WATER
- CLIP TO CONTROL WATER
- WATER OUTLET
- 3/4" COPPER TUBE SPIRAL
- CONTAINER WITH WATER TO ACT AS CALORIMETER FOR MEASURING ENTHALPY OF DISCHARGE

**FIG 2. BRINE SAMPLING SYSTEM USED TO MINIMIZE READSORPTION OF NONCONDENSABLE GASES IN FLUID SAMPLES**

- STEAM SAMPLE
- BARRIES
- LIQUID LEVEL
- BRINE
- CONDENSER
- COOLING WATER
- LIQUID SAMPLE
METHOD TITLE:
Steam-gas separator using modified graduated cylinder.

SAMPLE TYPE:
Condensate and Gas

SAMPLE POINT:
Condenser or separator

APPLICATION:
Separation of steam condensate from gas.

REFERENCES:

DESCRIPTION
This steam condensate-gas separator is constructed from a graduated cylinder by attaching two tubulations at the top and one at the bottom. Flow from the condenser enters at the top (vinyl tubing is used for all connections) and the flow of condensate from the bottom is restricted with a clamp so that gas alone issues from the remaining top tubulation. Tubing at bottom is inserted in a large bottle of steam condensate to prevent backflow of air into the separator.

COMMENTS:
1. This apparatus allows for checking incomplete steam separation in the separator.
2. Use of 1/4" vinyl tubing provides for small, relatively uniform slugs from the separator. The average composition of issuing fluid is uniform over the period of collection.
- Steam-gas separator modified from a 100 ml graduated cylinder.
METHOD TITLE: Portable gas-liquid separator.

SAMPLE TYPE: Liquid and gas
SAMPLE POINT: Pipeline

APPLICATION: Separating two-phase flow into liquid and gas.


DESCRIPTION
A simple gas-liquid separator which can be used in situations where a larger separator is not available is shown in the illustration. The volume of noncondensable gases is measured by water displacement in a graduated cylinder. Noncondensable gases are trapped in gas collectors for later laboratory analysis.

COMMENTS:
Collection of air free gas sample.
METHOD TITLE:
Webre separator method

SAMPLE TYPE: Liquid and gas
SAMPLE POINT: Two phase source

APPLICATION:
Separation of steam noncondensable gas phase from liquid phase in high pressure two phase sources.

REFERENCES:

DESCRIPTION
1. High pressure (>100 psig) samples are taken using small Webre separators which have very small pressure drops (Figure 1). The Webre separator consists of a vertical drum with a tangential inlet at the center, an outlet for water at the bottom, and a central outlet tube open at the top which collects the steam. The two-phase fluid enters tangentially at the center, spins rapidly around the outer wall of the drum with the water collecting on the outside and falling to the bottom and the steam moving to the inside and flowing down the central tube. Steam samples are condensed in evacuated glass flasks cooled by water. The flasks may be partly prefilled with alkaline solution to absorb CO₂ and H₂S for laboratory analysis by titrations. Water samples are collected after passing the hot pressurized water through a cold-water jacketed pipe.

2. A field arrangement using a Webre separator is shown in Figure 2. The separator is equipped with a sight glass for viewing the liquid level. Two phase flow tangentially enters the separator through a flexible armored line. The armored line is connected to the pipeline through a 1" White ball valve equipped with a quick disconnect fitting. Steam and gas exit the separator through the central standpipe. The steam-gas flow then goes through a series of condensing coils (first one water cooled and second one ice water cooled) then into a glass separator. Noncondensable gases are removed from the top of the glass separator while condensate is removed from the bottom. Flow rates are measured with graduated cylinders (water displacement method for gas flow). The main liquid flow from the Webre separator is from an outlet on the side of the separator. The liquid sample line comes from the bottom of the separator below the main liquid line (to avoid steam contamination). The liquid sample line is cooled through the series of cooling baths. Flow rates are measured with graduated cylinders.

COMMENTS:
1. Water samples should be taken, if possible, from a separate tap below the water outlet of the separator where the water is less likely to be contaminated with steam.
2. See comments under dual Webre separator method.
3. During the field test, to operate the separator as a gas separator the separator pressure was maintained above the steam flash point but below the CO₂ flash point. A gas bubble was allowed to build up in the top of the separator by adjusting the liquid outlet (from separator) line.

4. Under operating conditions it was found to be difficult to maintain liquid level and operating pressure in the Webre separator. Careful constant adjustment of the brine inlet and liquid outlet lines is required.

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5. Vortex formation (which cannot be seen) inside the separator can lead to steam and gas emanating from the liquid outlet. Careful control of the separator pressure and liquid level is therefore necessary.

6. Filling the gas collection bulb initially with water (in field test) and allowing the gas to displace the water proved to be a useful way to determine if air was excluded, (Figure 2). Collection is continued for 3-4 volume displacements.
METHOD TITLE: Dual Webre separator method.

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SAMPLE TYPE: | Gas and Liquid
SAMPLE POINT: | High pressure two-phase source

APPLICATION: Separation of steam-gas phase from liquid phase while sampling a high pressure source.

REFERENCES:

DESCRIPTION
1. When the equipment in Figure 1 is used, the discharge from the sampling point enters the first unit at 1 and valves 2 and 3 are adjusted to obtain dry steam from outlet 4. The second separator is adjusted with the valves at 3 and 9 to operate slightly flooded, a condition which is recognized by the presence of water in the steam discharged from the steam outlet 5. This ensures that water entering the cooling coils in cylinder 6 contains no condensed steam. The unit must be operated with a minimum pressure drop (0.2 bar) through the separators, the gauge at 7 ensuring that this condition can be controlled through the sampling period. The unit is heavily insulated to prevent heat losses and to reduce the possibility of water samples being diluted with condensed steam.
2. The apparatus in Figure 2 is a similar type of dual separator used by the U.S. Geological Survey.
3. Figure 3 shows a sampling arrangement on a pipeline using a dual Webre separator.

COMMENTS:
1. In Figure 1, the unit operates effectively over a sampling pressure range of 1.5-30 bars and a discharge enthalpy range of 190-475 cal/g. At lower or higher enthalpies, there is difficulty in obtaining both dry steam and undiluted water samples at the same valve settings. In these cases the valves are adjusted to collect either steam or water. The presence of condensed steam in a water sample is recognized from gas bubbles in the water emerging from the water cooler. The occurrence of boiling within the separators is more difficult to recognize. Some indication may be obtained if large fluctuations in pressure (±0.3 bar) are recorded on the pressure gauge.
2. If minimum pressure drop through the separators is not maintained, the steam sample is diluted by extraneous steam formed from water boiling as it enters lower-pressure zones in the separators.

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ILLUSTRATION:

FIG 1. WEBRE CYCLONE SEPARATOR FOR COLLECTING STEAM & WATER SAMPLES UNDER PRESSURE FROM A DISCHARGING GEOTHERMAL WELL

FIG 2. MINI CYCLONE SEPARATOR OF NEW ZEALAND DESIGN

FIG 3. FIELD ARRANGEMENT FOR DUAL WEBRE SEPARATOR SYSTEM
METHOD TITLE: Steam-Water Separator

SAMPLE TYPE: Steam and liquid

SAMPLE POINT: Pipeline

APPLICATION: Separation of Flashd Steam from Hot Water, and for Determining Steam/Brine Ratios.

REFERENCES: J. D. Ludwick and D. E. Robertson, Battelle, Pacific Northwest Labs., Richland, WA 99352

DESCRIPTION

Incoming steam and hot water (or unflashed brine) enter through the top of a 4-liter teflon-coated stainless steel cylinder from a pipe extending about one-third of the way into the cylinder. Flashed steam is removed from a sidearm at the top of the cylinder and the brine is withdrawn through a tap at the bottom. The water level in the cylinder is kept constant by equilibrating the rate of incoming fluid and outgoing brine. A sightglass is used to keep the cylinder about one-half full. Pressure gauges are installed at the point of incoming fluid and at the steam exit. If necessary, the separated brine can be passed through a cooling coil to collect the brine without a further loss of steam. The separated steam can then be passed into a condenser. This separator can be used for obtaining accurate steam/brine ratios by simultaneously measuring the weight of brine and condensed steam passing through the separator.

COMMENTS:

Great emphasis should be placed on obtaining representative fluids from the pipeline, and isoenthalpic sampling ports are desirable. Faulty steam/brine ratios can be obtained when unrepresentative samples of partially flashed fluids are withdrawn for phase separation and measurement.
ILLUSTRATION:

INCOMING STEAM AND HOT WATER

PRESSURE GAGE

UNION

BALL VALVE

RELIEF VENT

4 LITER TEFLOM COATED SS CYLINDER

INSULATED JACKET

BRINE

STEAM

PRESSURE GAGE

STEAM FLOW TO CONDENSER

SIGHT GLASS

HIGH PRESSURE STEAM-WATER SEPARATOR

SEPARATED BRINE
METHOD TITLE: Insertable sample probe method.

APPLICATION: Sampling two phase systems for liquid and gas.

REFERENCES:

DESCRIPTION
1. The probe in Figure 1 can be inserted through a one-inch valve on the top of the pipeline. For the six inch line sampled, the probe was positioned 3/4" below the top of the pipe to obtain top ("vapor" phase) samples and 3/4" above the bottom of the pipe to obtain bottom ("liquid" phase) samples. Samples were collected in stainless steel bottles with inner Teflon coating after passing through the probe. Bombs were flushed with nitrogen prior to collection.

2. The insertable probe shown in Figure 2 was fabricated for field test use. It consists of Inconel 600 1/4" and 1/8" OD tubing with a 45° bevel at one end. A 1" handle is welded 3" from the opposite end (on same side as bevel) to aid in determining the orientation of the bevel when the probe is inserted in the pipe. The probe is attached to 1" Whitey (or equivalent) ball valves on the pipeline by means of a Conax fitting. This fitting allows the operator to move the probe and thereby traverse the pipe diameter by loosening the Conax fitting.

COMMENTS:
1. These probes as demonstrated by the field test allow the operator to traverse the pipe diameter. A horizontal and vertical traverse is useful in profiling the flow pattern in the pipe.

2. Larger diameter (1/2" ID) probes were found during field testing to be more useful for sampling separator steam lines due to the lower pressures involved in these lines.

3. Care must be exercised when inserting probes through the ball valves (on pipeline). The probe is inserted into the closed valve until resistance is felt, and the Conax fitting loosely tightened on the ball valve. The ball valve is then opened slowly while pushing carefully on the probe to push it through the valve. The Conax fitting is then fully secured and tightened.

4. See also "porcupine" arrangement method.
FIG 1. INSERTABLE SAMPLING PROBE ILLUSTRATION

FIG 2. INSERTABLE SAMPLING PROBE USED IN FIELD TEST
METHOD TITLE: "Porcupine" arrangement.

SAMPLE TYPE: Liquid and gas
SAMPLE POINT: Pipeline

APPLICATION: Sampling multiphase systems.

REFERENCES: Appendix 1: Field Test 1978.

DESCRIPTION

1. Sample points are arranged around the circumference of a pipe. The sample points may be fixed or of the insertable probe type. Fixed sample points have tubes inserted to various depths in the pipe to enable the operator to sample the various phases present in the pipe. Insertable probes accomplish the same purpose with the additional advantage that they can be moved to sample various pipe depths.

2. This configuration called a "porcupine" arrangement allows for sampling various flow regimes inside the pipe.

3. Samples coming from these sample points can be condensed with cooling coils, introduced directly into bombs or collected in other sampling arrangements.

4. The illustration shows an arrangement used in a field test. The valves on the pipeline are 1" Whitey ball valves mounted on welded sockets which are on the pipeline. In this illustration the two ball valves are mounted in the vertical and horizontal positions. An insertable sampling probe is shown in the horizontal position connected to the ball valve through a Conax fitting. This arrangement allows for traversing the pipe diameter (see insertable probes method). The brine-gas sample is cooled in an ice-water bath downstream of the probe.

COMMENTS:

1. Using this arrangement it is possible to study the flow profile of the pipe using insertable probes.

2. By using the "porcupine" arrangement and evacuated cylinders (see evacuated cylinder method) it was possible to show during a field test that primarily gas was removed from the vertical sample port and primarily liquid was removed from the horizontal sample port (inlet brine sample).

3. During actual field use it is a simple matter to mount another ball valve on top of a leaking valve if this situation develops.
CROSS SECTION OF PIPE SHOWING "PORCUPINE" ARRANGEMENT OF BALL VALVES WITH INSERTABLE TRAVERSING PROBE PRESENT (USED IN FIELD TEST)
METHOD TITLE: Evacuated cylinders

SAMPLE TYPE: Gas and Liquid

SAMPLE POINT: Wellhead, pipeline, etc.

APPLICATION: Sampling of gas and liquid from wellheads, pipelines, etc.

REFERENCES:
2) Appendix 1: Field Test 1978.

DESCRIPTION
1. Evacuated cylinders can be used for sampling total discharge (Figure 1). An evacuated pressure cylinder can be connected directly to a tap on the wellhead or delivery line. A "T" fitting with a valve and bleed line permits purging of air from the connecting line and fittings.

2. Corrosive gases, e.g., H$_2$S, react with the container walls and fittings. Measurement of concentrations of these types of components from the cylinder contents should be regarded with caution.

3. Alternatively, the evacuated cylinder can be used to sample downstream of a cooling coil, for sampling steam phase from a separator, etc.

4. The arrangement in Figure 2 was used to evaluate the method in a field test. Double valving (Whitey shutoff valves) of the S.S. bombs was necessary to prevent air contamination while shipping. Results show that for this test primarily gas was collected in the vertically mounted cylinder while primarily liquid was obtained from the horizontal collection port.

COMMENTS:
1. Field evaluation showed that gross metals contamination of the liquid phase occurs inside the cylinder after collection. In particular iron, nickel, and chromium concentrations showed dramatic increases. Results for these metals should be regarded with caution.

2. Evaluation of CO$_2$ and H$_2$S should be regarded with caution due to the reactive metal environment of the cylinder.
ILLUSTRATION:

**FIG 1.** EVACUATED CYLINDER SAMPLING APPARATUS

**FIG 2.** EVACUATED CYLINDER ARRANGEMENT USED IN FIELD TEST
METHOD TITLE: Evacuated cylinder-storage oven method.

SAMPLE TYPE: Liquid
SAMPLE POINT: Pipeline

APPLICATION: Sampling hot pressurized fluid systems.

REFERENCES:

DESCRIPTION
The sampling system consists of three parts; the sample vessels, the storage oven, and the desampler. The sampler is a 304 stainless steel sample cylinder equipped with stainless steel valves and purge line, as shown in Figure 1. Some samplers are equipped with a stainless steel in-line filter holder. This unit used a 25mm diameter, 5-micron Teflon filter. Gas samples are collected in these samplers, but are not kept at well temperature. The oven is constructed for rugged use, as shown in Figure 2. It is a stainless steel box with three inches of Marinite insulation, a stainless steel liner, and a 1100-watt heater. The desampler is used to cool and dilute hot pressurized geothermal fluid while keeping it at a pressure that will not allow phase separation. A nonreactive gas, such as helium or nitrogen, is used to pressurize the system. It can also be used to purge air or other reactive gases from the sample.

COMMENTS:
1. Storage oven used to maintain sampling conditions during transport of the sample to the laboratory.
2. See comments under evacuated cylinder method based on 1978 Field Test results.
FIG 1. GEOTHERMAL HIGH PRESSURE SAMPLER

FIG 2. SAMPLE STORAGE OVEN
METHOD TITLE: Klyen downhole sampler

APPLICATION: Downhole sampling of liquid and gas.

REFERENCES:
2. Literature from Kuster Co., P.O. Box 7038, Long Beach, CA 90807.

DESCRIPTION

The loaded sampler is shackled to the suspension wire of a suitable winch which must be fitted with a depthometer. It is then lowered into a recovery tube on the top of the borehole, the suspension wire passing over a pulley wheel and through a threaded gland, which is screwed on to the top of the recovery tube to ensure effective sealing against borehole pressure.

At the sampling station, the suspension wire is jerked such that the activated inertia mechanism (A) breaks the tube (C). The non-return valve (E) is opened by the external downhole fluid pressure allowing the fluids to flow into the sample chamber (F). When the interior pressure together with the spring pressure equal the exterior pressure, the non-return valve closes. The vessel is then withdrawn from the borehole and if necessary cooled, to prevent the pressurized sample from boiling off when the sample release valve is opened.

COMMENTS:
An important additional feature is the vessel's capability to hold a vacuum in the loaded position, thereby enabling collection of air-free gas and water samples.
ILLUSTRATION:

- WIRE SUSPENSION
- INERTIA MECHANISM (A)
- BREAK-OFF TUBE STRIKER (B)
- BREAK-OFF TUBE (C)
- BREAK-OFF TUBE SEAL GLAND (D)
- FILTER

NON-RETURN VALVE (E)
NB: VALVE STEM IS OF TRIANGULAR CROSS SECTION ALLOWING TRANSFER OF SAMPLE FLUIDS

- SAMPLE VESSEL (F)
- SAMPLE RELEASE VALVE (G)

Klyen Subsurface Sampler
METHOD TITLE:
Down-hole water and gas sampling in geothermal wells using a down-hole sampler

NO. | 33-S
---|---

SAMPLE TYPE: | Liquid and Gas
SAMPLE POINT: | Wellbore

APPLICATION:
Down-hole sampling

REFERENCES:

DESCRIPTION
Sampler in open position is lowered using a long flexible stainless steel tube into the wellbore and fluid flows through it during descent. Closure is accomplished by nitrogen gas pressure applied from the surface through the flexible tube to a piston and plunger within the sample chamber. Continued application of nitrogen gas pressure during withdrawal of the device prevents leakage caused by changing conditions of temperature and pressure.

COMMENTS:
1. All materials are stainless steel except for one teflon o-ring, two viton o-rings, and several other teflon parts.
2. A modification of the lower end of the sampler using a special gas extraction fitting allows the sampler to be used for gas sampling.
3. Sample device can be used at temperatures up to 280°C.
Equipment for down-hole sampling: a, reel with flexible stainless steel tube, b, wound upon it, c, precision pressure gage, d, high-pressure valve, e, flexible high-pressure connecting tubing, f, gas-regulating valve, g, cylinder of nitrogen gas, h, gate valve, i, short length of pipe, j, 5-pound lead weight, k, check valve, m, coupling that serves as support ring for sheave, n, reducer, r, plug, s, packing gland, t, sheave with automatic counter to tally the number of revolutions, u, pressure gage for wellhead pressures.
METHOD TITLE:
Evacuated flask method for silencer sampling.

APPLICATION:
Sampling of reactive gases (CO₂ and H₂S) from silencers.

REFERENCES:

DESCRIPTION
A stainless steel or aluminum cone is suspended over the top of the silencer, or alternatively, a stainless steel probe is inserted through the silencer wall near the top of the structure. Steam and gas entering the cone (or probe) pass to a water condenser by stainless steel tube or butyl rubber hose. An evacuated double-ended thin-walled glass flask partially filled with a solution of sodium hydroxide is attached to the condenser.

Air entering the steam at the silencer inlet is collected in the flask with the geothermal gases. Air rapidly fills the flask, and must be removed to allow carbon dioxide and hydrogen sulfide to be collected in sufficient quantities for analysis. Removal is by a hand vacuum pump, or by a simple pump operated by steam or water discharged from a convenient tapping on the horizontal discharge pipe. A capsule filled with sand saturated with lead acetate is fitted between the flask and pump to detect hydrogen sulfide escaping through the alkaline solution.

COMMENTS:
The method is not applicable for collecting residual gas (CH₄, N₂, H₂, etc.) samples.
ILLUSTRATION:

APPRARATUS INSTALLED ON TYPICAL WELL

APPRARATUS FOR COLLECTING STEAM AND GAS SAMPLES FROM THE SILENCER OF A GEOTHERMAL WELL
METHOD TITLE:
Liquid sampling from unsilenced discharge pipes.

APPLICATION:
Sampling of liquid from discharge pipes.

REFERENCES:

DESCRIPTION
The sampling apparatus is welded to the discharge pipe or held in the hand if the discharge is small. If held in the hand, the sampler should be inserted very slowly into the discharge, preferably toward the bottom of the pipe. Evaporative heat losses are generally small and samples at close to boiling temperature are obtained.

COMMENTS:
Extreme caution should be exercised sampling total discharge. If held by hand the apparatus can easily be pulled into the discharge and then violently out of the hand by the force of the flowing fluid.
ILLUSTRATION:

APPARATUS FOR COLLECTING WATER SAMPLES FROM THE END OF THE HORIZONTAL DISCHARGE PIPE OF A GEOTHERMAL WELL
METHOD TITLE:
Gas concentration measurement method.

APPLICATION:
Measurement of the gas concentration in a steam or steam-water discharge.

SAMPLE TYPE:
Gas

SAMPLE POINT:
Pipeline

REFERENCES:

DESCRIPTION
The apparatus is shown in the illustration (Figures 1 and 2). A mixture of steam, water, and gas, discharged from a standard sampling point on the horizontal or vertical discharge pipe of a well, is passed into the heavily lagged, heat-insulated vessel B. A small stainless steel capsule C, which is partially filled with degassed distilled water during measurements, is sealed into the center of B. The interiors of B and C are connected to a standard mercury manometer or differential pressure gauge capable of accurately recording pressure differences down to 0.006 bar. The temperature of the water in C rapidly attains the temperature of the discharge, and a pressure equivalent to the vapor pressure of water at the temperature is exerted on one leg of the manometer or gauge. The pressure in B, which is equal to the vapor pressure of water plus the sum of the partial pressures of the gases in the discharge, is exerted on the second leg of the gauge, and a reading of the total gas pressure is obtained.

The percentage by volume of gas in the discharge is readily obtained by assuming ideal gas behavior. To obtain the percentage by weight of gas in steam, the gas composition is required. For a large number of geothermal systems only a small error is introduced by assuming that CO₂ is the only gas present.

Convenient formulas for converting the measured partial pressure of gas into pounds of gas per pound of steam or kilograms of gas per kilogram of steam are

\[ W(\text{lb}) = \frac{M144P_{Vs}}{1545T} \quad \text{and} \quad W(\text{kg}) = \frac{MP_{Vs}}{83.13T} \]

where \( W \) is pounds of gas per pound of steam or kilograms of gas per kilogram of steam; \( P_{Vg} \) partial pressure of gas in pounds per square inch or bars; \( V_{s} \) specific volume of steam at the vapor pressure of the water discharged in cubic feet per pound or cubic centimeters per gram (vapor pressure = total pressure - partial pressure of gas); \( T \) absolute temperature in °F or degrees Kelvin and \( M \) is the mol. wt. of the gas.

COMMENTS:
FIG 1. APPARATUS FOR MEASURING THE GAS CONTENT OF THE DISCHARGE FROM A GEOTHERMAL WELL

FIG 2. SCHEMATIC ARRANGEMENT OF GAS PROBE IN USE
METHOD TITLE:
Gas sample inlet system for gas chromatograph.

SAMPLE TYPE:
Gas

SAMPLE POINT:
Gas sample inlet system.

APPLICATION:
Injecting gas samples into gas chromatograph system.

REFERENCES:

DESCRIPTION
1. This system allows the operator to introduce a gas sample from a sample bomb into a gas chromatograph without air contamination. Figure 1 of the illustration shows the arrangement of the system. All tubing and valves are 1/16" stainless steel to minimize volume. The sample bomb is first connected at the sample inlet. With the valve to the bomb closed, valves 1-4 are opened with valves 5 and 6 closed and the system evacuated with a vacuum pump. After evacuation valves 2, 3, and 4 are closed, the sample valve on the bomb is opened and the pressure read. If the pressure is high enough, the sample may be directly introduced into the chromatograph sample loop. If the pressure is not high enough, the pressure may be increased by using the mechanical syringe. The syringe will have to be withdrawn and evacuated prior to sample introduction. After the sample is introduced and the pressure read, valves 1 and 2 are closed and the gas compressed with the syringe. Valve 2 is then opened to allow the sample to be introduced into the sampling loop. A standard gas mixture may also be introduced by evacuating the system, introducing the standard mix through valve 5 and proceeding as before.

2. Details of the syringe are given in Figure 2. Additional detail of the piston inside the syringe is given in Figure 3.

COMMENTS:
Figure 1

GC INLET SYSTEM

Figure 2

DETAIL OF SYRINGE

Figure 3

DETAIL OF PISTON
Recommended Analytical Methods for Geothermal Liquids

I. Purpose: The analytical methods compiled herein were included by virtue of being used to analyze two types of geothermal brines (0.5% and 22% dissolved solids) in round robin testing. They are presented here to solicit further refinement of analytical methods for the geothermal industry.

II. Scope: The methods in this manual cover the following general properties of geothermal brines:

- Physical properties: pH, conductivity, alkalinity, etc.
- Dissolved solids: both metallic and non-metallic species.
- Dissolved and entrained gases: \( \text{H}_2\text{S} \) and \( \text{CO}_2 \).

The methods do not cover analysis of gaseous or solid phase components associated with geothermal brines.

III. The sequence of methods listed for each parameter is:

a) Wet chemical.
b) Gravimetric.
c) Colorimetric.
d) Electrode.
e) Atomic absorption.
f) Flame emission.
g) X-ray fluorescence.
h) Inductively coupled plasma-atomic emission spectroscopy.
i) Ion exchange chromatography.
j) Spark source mass spectrometry.
k) Neutron activation analysis.
l) Emission spectrometry.
Format of an Individual Analysis:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Method Name</th>
<th>Parameter symbol and/or name</th>
<th>No.</th>
<th>Analysis Reference Number</th>
</tr>
</thead>
</table>

**Method:** Brief description of fundamental theory of analysis and manipulations required.

**Sample Handling:** Type of sample used in this analysis and any extra necessary treatment of sample before analysis.

**Range:** Useful range of method for geothermal brine. **Precision:** **Accuracy:** Based upon round robin test results: Precision in terms of % RSD and accuracy in terms of % relative error.

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>References, appendices, other sampling numbers, and analyses numbers in this manual</td>
<td>References literature outside this manual - see bibliography for details.</td>
<td>Required equipment, instrumentation and special apparatus for this method.</td>
</tr>
</tbody>
</table>

**Reagents:** Chemicals used in this method

**Remarks:** Includes interferences, special observations about this method, and other miscellaneous information.
Sampling and Sample Stabilization Procedures Used in Collecting Round Robin Samples:

A. Preparation of Sample Bottles and Containers Used to Collect Geothermal Round Robin Samples:

1. **Bottles and Containers:**
   Brine samples were collected in virgin linear polyethylene bottles and carboys with polypropylene caps. No glass containers were used for collection.

2. **Preparation of Containers:**
   All bottles and carboys were washed prior to sample collection using the following sequence:
   a) Distilled water rinse,
   b) Nitric acid rinse (nitric acid suitable for Hg determination),
   c) Two more distilled water rinses.

B. Methods Used to Collect Brine Samples for Analyses:

1. **Raw Untreated (RU)** brine was collected through two stainless steel cooling coils. The first coil was cooled by a water bath and the second was cooled in an ice bath; pH was determined on this sample in the field.

2. **Filtered Untreated (FU)** brine was collected through the two previously mentioned cooling coils followed by passing the brine through a 0.45 μm membrane filter. Parameters determined using this FU sample included alkalinity, bicarbonate-carbonate, chloride, fluoride, bromide, iodide, phosphate, sulfate, and total dissolved solids.

3. **Raw Acidified (RA)** brine was collected through the cooling coils and acidified with 10 mls of high purity concentrated HCl per liter of unfiltered brine. Parameters determined using the RA sample included hardness, aluminum, ammonia, antimony, arsenic, barium, boron, calcium, cesium, copper, iron, lead, lithium, magnesium, manganese, mercury, potassium, rubidium, silver, sodium, strontium, zinc, and silicon.
4. **Filtered Acidified** (FA) brine was acidified with 10 mls of high purity concentrated HCl per liter of brine. This brine was collected by passing the brine through the previously mentioned cooling coils and through a 0.45 μm membrane filter. Parameters determined using the FA sample were the same as for the RA sample.

5. A 20:1 dilution for silica (SiO₂) using cooled filtered brine and distilled, deionized water for the dilution.

6. A sample was collected for entrained H₂S by passing cooled filtered brine through a sintered glass frit immersed in a solution of 0.5 N zinc acetate; the sample collected represents a 1:1 dilution of the brine.

7. A sample was collected for entrained CO₂ by passing cooled filtered brine through a sintered glass frit immersed in a solution of 2 N NaOH; the sample collected represents a 1:1 dilution of the brine.
ALKALINITY

Analysis: Acid Titration

Method: The sample is titrated with a strong acid (H₂SO₄ or HCl) to separate equivalence points for OH⁻, CO₃²⁻, and HCO₃⁻. Equivalence points are determined either potentiometrically or with visual indicators.

Sample Handling: Use RU brine, determine as quickly as possible after sampling to avoid CO₂ losses.

Range: >20 mg/l CaCO₃  Precision: ±3%  Accuracy: ±10%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
- Standard HCl or H₂SO₄
- Phenolphthalein indicator
- Mixed methyl red-bromocresol green indicator or methyl orange indicator
- Standard pH buffers

Literature Reference:
- API 2.21-2.22 (68)
- USGS Book 5 Chapter A1 (1974) EPA 00710 (76)
- APHA 403 (75)
- ASTM 1067-70 (77)

Equipment:
- Buret, pH meter and electrodes

Remarks:
1. Interferences: determinations of OH⁻, CO₃²⁻, and HCO₃⁻ contributions to total alkalinity possible only with absence of other weak bases; residual Cl⁻, color, and turbidity affect visual indicator titrations; loss or gain of atm. CO₂ affects results; erratic results obtained when oxidizing or reducing species are present; some constituents may cause buffering at endpoint.
2. Field determination recommended.

Edition: 7/78
Analysis: Atomic Absorption (Direct)  
Method: The sample containing aluminum is aspirated directly into a nitrous oxide-acetylene flame of an atomic absorption instrument, the absorbance is measured at 309.3 nm and compared with a standard curve.

Sample Handling: Use RA or FA brine.

Range: (linear) 0.7-60 mg/l  
Precision: ±5%  
Accuracy: ±10%

Cross Reference:
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 3-A, 4-A, 5-A

Literature Reference:
APHA 301 IV (75)  
EPA 01105 (76)  
Instrument Manufacturer's Standard Methods Manual

Reagents:
Al standard solutions  
Nitrous oxide gas cylinder  
Potassium chloride

Equipment:
Atomic Absorption Spectrophotometer  
N₂O burner head

Remarks: 1. High Fe, PO₄³⁻, and Cl may interfere.
2. Careful matrix matching between sample and standards of the more predominant alkali and alkali earth metals and interferents required to ensure accurate measurement. Use of standard additions and background correction recommended.
3. To minimize ionization interference; sample, standards and blanks should contain 2000 mg/l K.

Edition: 7/78  
(cont. on back)
4. If sample shows Tyndall effect, filter through 0.45 µ membrane filter.
Analysis: Atomic Absorption (Graphite Furnace)  

Method: Aluminum is determined using a graphite furnace and the following atomization conditions:  
- Dry: 20 sec at 200°C  
- Ash: 40 sec at 1080°C  
- Atomize: 10 sec at 2500°C  
- Wave length: 309.3 nm

Sample Handling: Use RA or FA brine.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision: ±4%</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 2-A, 4-A, 5-A

Reagents:  
- Aluminum standards  
- Argon gas

Literature Reference:  
Instrument Manufacturer's Methods Manual

Equipment:  
- Atomic absorption spectrophotometer  
- Graphite furnace  
- Plastic tip pipets

Remarks: Matrix matching between sample and standards, standard additions and background correction recommended.
**Analysis:** Atomic Absorption (Extraction)  

**Method:** Al is complexed in the aqueous sample with 8-quinolinol, then extracted from the aqueous phase with chloroform or methyl isobutyl ketone. The organic solution is then aspirated directly into an N₂O-acetylene burner and the absorption measured at 309.3 nm.

**Sample Handling:** Use RA or FA brine; extraction in field may be desirable.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision: ±15%</th>
<th>Accuracy: ±6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appendix 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis Methods: 2-A, 3-A, 5-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Literature Reference: | | |
|----------------------|-----------------|
| APHA 301 V (75) | APHA 301 V (75) |
| Presser and Barnes, USGS WRI-22-74 | Presser and Barnes, USGS WRI-22-74 |

<table>
<thead>
<tr>
<th>Reagents:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl isobutyl ketone or chloroform</td>
<td>Atomic Absorption Spectrophotometer</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>N₂O burner head</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>Separatory funnels</td>
</tr>
<tr>
<td>8-Hydroxyquinoline (8-Quinolinol)</td>
<td></td>
</tr>
<tr>
<td>Aluminum standards</td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide gas cylinder</td>
<td></td>
</tr>
</tbody>
</table>

| Remarks: | |
|----------||
| 1. Interferences: Ionization of Al in flame reduces sensitivity. | |
| 2. Extraction technique measures only "extractable aluminum polymeric aluminum will not be extracted. | |
| 3. Extraction enhances detection limit of aluminum by flame AA. | |
| 4. Use of background correction recommended. | |
| 5. High iron and salt concentrations may interfere. | |

**Edition:** 7/78
**Analysis:** Flame Emission

**Method:** Aluminum is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 396.1 nm from aluminum is measured by a spectrophotometer.

**Sample Handling:** Use filtered acidified or raw acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter of sample.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0.05 mg/l</td>
<td>&lt;0.5 mg/l±25%</td>
<td>&lt;0.5 mg/l±25%</td>
</tr>
<tr>
<td></td>
<td>&gt;0.5 mg/l±5%</td>
<td>&gt;0.5 mg/l±5%</td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 2-A, 3-A, 4-A

**Reagents:**
- Aluminum atomic absorption standard solution or aluminum metal
- Hydrochloric acid if zinc metal is used
- Nitrous oxide gas cylinder
- Potassium chloride

**Literature Reference:**

**Equipment:**
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
- Nitrous oxide burner head.

**Remarks:**
1. High iron, phosphate, and chloride may interfere.
2. Careful matrix matching between sample and standards must be made (i.e. using some amounts of NaCl, other alkali metal and alkaline earth metal ions).
3. Use of standard additions and background correction recommended.
4. Severe spectral interference due to calcium must be corrected by preparing blank, when measuring low concentrations of aluminum.
5. In lab, dilute sample and add 2000 mg/l potassium chloride as an ionization buffer.
Analysis: X-Ray Fluorescence

Method: The sample containing aluminum is caused to fluoresce by X-ray bombardment. The fluorescent radiation is dispersed by a crystal and detected by a scintillation counter and/or a flow proportional counter.

Sample Handling: Use RA or FA brine; sample may be run as is or evaporated to dryness depending upon instrumentation.

Range: ~~~ ~~~ ~~~ ~~~ ~~~

Precision: ~~~ ~~~ ~~~ ~~~ ~~~

Accuracy: ~~~ ~~~ ~~~ ~~~ ~~~

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Aluminum standards

Equipment:
X-ray fluorescence spectrophotometer

Remarks: 1. Computer program usually required to interpret data.
2. Standardization of instrument required.
3. X-ray fluorescence provides simultaneous, multi-element determinations of selected metals and non-metals.

Edition: 7/78  C-10
**Analysis:** Inductively Coupled Plasma-Atomic Emission Spectroscopy

**Method:** The brine sample is aspirated into a radiofrequency generated, inductively coupled argon plasma and the intensity of the emission spectrum of aluminum is measured by the instrument and compared with standards. Intensity is measured at 308.22 nm or alternate wavelength.

**Sample Handling:** Use RA or FA brine.

<table>
<thead>
<tr>
<th>Range: single spectral line</th>
<th>Precision: ± 1-10%</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
- Aluminum standards

**Equipment:**
- Inductively coupled plasma-atomic emission spectrometer

**Remarks:***
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard additions recommended.
2. Inductively coupled plasma technique provides simultaneous, multi-element determinations of metals.

**Edition:** 7/78
4. Upper limit of concentration range may be extended by using alternate spectral lines.
**Analysis:** Spark Source Mass Spectrometry

**Method:** A dehydrated sample containing aluminum is vaporized and ionized by an arc source and enters the analytical chamber. Aluminum is separated and detected by its mass/charge ratio, and the quantitative determination is made by comparison to standard curves.

**Sample Handling:** Use RA or FA brine. Evaporate samples to dryness before analysis.

| Range: 0.1-1000 mg/l | Precision: ±25% | Accuracy: ±25% |

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
- Aluminum standards

**Equipment:**
- Spark Source Mass Spectrometer

**Remarks:**
1. Replicate determinations must be made for adequate accuracy and precision.
2. Spark source mass spectrometry provides simultaneous, multi-element analysis for selected metals and ion-metals.
**Analysis:** Neutron Activation

**Method:** Sample containing aluminum is exposed to a neutron source (e.g. nuclear reactor) and radioactive aluminum isotopes formed are identified by their beta and gamma spectra using a multi-channel analyzer. The amount of aluminum present is proportional to the measured activity.

**Sample Handling:** Use RA or FA brine. Evaporate samples to dryness before neutron irradiation.

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
</tr>
</tbody>
</table>

**Reagents:**

**Equipment:**

1. Neutron Source (nuclear reactor)
2. Multichannel analyzer.

**Remarks:**

1. Sufficient time must be allowed for decay of sodium species where sodium spectrum masks Al peaks.
2. Neutron activation provides simultaneous multi-element analysis for selected metals and non-metals.

**Edition:** 7/78
Analysis: Emission Spectrometry

Method: The sample containing aluminum in either solid or liquid state is vaporized using a flame, AC spark or DC arc and the intensity of the selected emission line is measured against standards.

Sample Handling: Use ⁷N or FA brine. Evaporation to dryness may be required.

Range: 0.3-2 mg/l

Precision: ±10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Aluminum standards
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Emission spectrometry provides simultaneous, multi-element determinations for metals.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
**Analysis:** Distillation Procedure

**Method:** Ammonia is distilled from the sample buffered with a borate buffer at pH 9.5. The distilled ammonia is captured in a solution of boric acid or sulfuric acid and then analyzed by desired procedure.

**Sample Handling:** Use RA or FA brine.

**Range:**

**Accuracy:**

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 12-A, 13-A, 14-A, 15-A

**Reagents:**
- Na$_3$B$_4$O$_7$
- NaOH
- Dechlorinating agent (any of the following):
  - Phenylarsine oxide
  - Sodium arsenite
  - Sodium sulfite
  - Sodium thiosulfate
  - Sulfuric acid
  - Ammonia-free H$_2$O

**Remarks:**
1. Procedure is necessary to get rid of most interferences, especially from the nesslerization and titration procedures; distillation may be desirable before any ammonia analysis.
2. Hydrolyzable and/or volatile amines and cyanide will interfere, but these are usually absent from geothermal fluids.

**Equipment:**
- 800-2000 ml pyrex flask
- Vertical condenser
- 500 ml receiving flask
- (Micro-distillation equipment may also be used)

**Literature Reference:**
- APHA 418A (75)
- ASTM 1426-74 (77)
- EPA 00610 (76)

**Edition:**
- 7/78
**NH₃**

Ammonia

**Analysis:** Titration

**Method:** Distillation of ammonia from alkaline solution and collection in known amount sulfuric acid and subsequent back titration with sodium hydroxide.

**Sample Handling:** Distill RA or FA brine per the distillation procedure for ammonia.

**Range:**

| Preciseion: ±2% | Accuracy: unknown |

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 11-A

**Reagents:**
- Standardized sodium hydroxide and sulfuric acid, and a solution of: 675 grams sodium hydroxide and 80 grams sodium thiosulfate/L, methyl red.

**Literature Reference:**

**Equipment:**
- KJELDAHL apparatus with flasks, burets.

**Remarks:** Distillation required before analysis.

**Edition:**
- 7/78

**C-16**
**NH₃**

**Ammonia**

**Analysis:** Nesslerization

**No.** 13-A

**Method:** A basic solution of HgI₂ + KI is added to the sample to form NH₂Hg₂I₃ which has a yellow to brown hue that is measured between 450 and 500 nm.

**Sample Handling:** Use RA or FA brine. Distillation recommended.

**Range:** 0.05-5 mg/l  
**Precision:** ±10%  
**Accuracy:** ±20%

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
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<tbody>
<tr>
<td>Appendix 2</td>
<td>APHA 418B (75)</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td>ASTM 1426-74A,B (77)</td>
</tr>
<tr>
<td>Analysis Methods: 11-A</td>
<td>EPA 00610 (76)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO₄·7H₂O</td>
<td>Spectrophotometer or filter photometer at 453-500 nm</td>
</tr>
<tr>
<td>EDTA or Rochelle salt solution</td>
<td>Matched absorbance cells or Nessler tubes</td>
</tr>
<tr>
<td>Nessler reagent (HgI₂ + KI)</td>
<td>pH meter</td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
</tr>
<tr>
<td>Ammonia standards</td>
<td></td>
</tr>
<tr>
<td>Ammonia free H₂O</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Remarks:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Interferences: many interferences eliminated by distillation; others (in nondistilled samples) eliminated by addition of basic ZnSO₄ to precipitate Ca²⁺, Fe, Mg²⁺, and H₂S; addition of EDTA or Rochelle salts prevents Ca²⁺ and Mg²⁺ from precipitating during determinations; S²⁻, hydrazine, urea, and other hydrolyzable organic amides and amino acids will interfere.</td>
</tr>
<tr>
<td>2. Ammonia standards must be prepared fresh daily.</td>
</tr>
</tbody>
</table>

**Edition:** 7/78  
**C-17**
NH₃

Ammonia

Analysis: Automated Colorimetric Phenate

Method: The blue indophenol species is formed when alkaline phenol, hypochlorite, and ammonia react together. The blue color is proportional to the ammonia concentration and is measured in a 15 or 50 mm flow cell at 630-660 nm.

Sample Handling: Use RA or FA brine. Distillation may be desirable.

Range: 0.01-10 mg/l  Precision: ±3%  Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 11-A

Reagents:
Ammonia free water
Sulfuric acid
Sodium phenolate
Sodium hypochlorite
Disodium EDTA
Sodium nitroprusside
Ammonia standards

Literature Reference:
EPA 00610 (76)
Technicon Auto Analyzer Industrial Method
98-70W Revised
Bolleter, W.T., Bushman, C.J. and Tidwell, P.H.,

Equipment:
Technicon Auto Analyzer with:
Sampler
Manifold (AAI) or Analytical Cartridge (AAII)
Proportioning pump
Heating bath w/ double delay coil (AAI)
Colorimeter w/ 15 mm or 50 mm tubular cell
630-660 nm color filter
Recorder or digital printer

Remarks:
1. Distillation may be desirable.
2. Interferences in non-distilled samples: Ca and Mg (eliminated by adding EDTA), large amounts of Hg²⁺, turbidity (removed by filtration), color absorbing from 630-660 nm.

Edition:
7/78
Analysis: Ammonia Selective Electrode

Method: Ammonia is determined with a pion or millivolt meter and an ammonia selective electrode after raising sample pH to 10-14.

Sample Handling: Use raw or filtered acidified brine. Distillation usually not required, but may be done if so desired.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision: ±3%</th>
<th>Accuracy: ±3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-17,000 mg NH₃/l</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 11-A

Literature Reference:
- Presser and Barnes USGS, WRI-22-74
- EPA 00610 (76)
- Electrode Manufacturer's Literature

Reagents:
- NaOH
- Ammonia standards
- Ammonia free water

Equipment:
- Ammonia gas electrode
- pion or millivolt meter with expanded scale
- Magnetic stirring apparatus

Remarks:
1. Interferences: volatile amines, S²⁻, Hg(II).
2. Fresh ammonia standards required daily.
3. Use of standard additions recommended to check accuracy of analysis, especially if distillation not performed.

Edition: 7/78
NH₃

Ammonia

Analysis: Ion-Exchange Chromatography

Method: Ionic components are separated on sulfonated polymer-based column. A dilute nitric acid solution is used as the eluting solvent. The separation column is followed by a suppressor column to remove highly concentrated background components, and ammonium ion is detected by a conductivity detector.

Sample Handling: Use RA or FA brine. Distillation not required.

Range: Precision: ±1.83% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Nitric acid
Ammonia standard solutions

Equipment:
Dionex ion chromatograph
72-120 psi air supply

Remarks:
1. Ammonia may be determined simultaneously with lithium by this method.

Edition: 7/78
Analysis: Atomic Absorption (Direct)

Method: Sample containing antimony is aspirated directly into an air-acetylene flame and the absorbance at 217.6 nm is compared to a standard curve.

Sample Handling: Use RA or FA brine.

Range: (linear) 0.2-30 mg/l  
Precision: ±5%  
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 18-A

Literature Reference:

Reagents:
Antimony standards  
(Potassium antimony tartrate  
Hemihydrate may be used)

Equipment:
Atomic Absorption Spectrophotometer  
Air-Acetylene burner head  
Antimony electrodeless discharge lamp (optional)

Remarks:
1. Spectral interferences from non-absorbing wavelengths may be compensated by using a narrow slit-width or a different wavelength.
2. Cu and Pb in significant amounts compared to antimony interfere: use 206.8 or 231.2 nm antimony resonance lines.
3. Acid concentration must be matched between standards and sample.
4. Use of the more intense antimony electrodeless discharge lamp will give better detection limits.
5. Background correction, matrix matching and standard additions recommended. (cont. on back)
6. Use of a graphite furnace will increase sensitivity.
Sb

Analysis: Atomic Absorption (Hydride Evolution)

Method: Sb is determined by atomic absorption at 217.6 nm in a nitrogen or argon-hydrogen flame after evolution as its hydride by addition of NaBH₄ to an acid solution of sample containing SnCl₂ and KI.

Sample Handling: Use raw or filtered acidified brine.

Range: >0.1 μg  
Precision: ±2%  
Accuracy:

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 17-A

Literature Reference:  
Instrument Manufacturer's Methods Manual

Reagents:  
KI solution  
SnCl₂ solution  
NaBH₄ solution  
HCl  
Nitrogen or argon bottled gas  
Hydrogen bottled gas

Equipment:  
Atomic absorption spectrophotometer  
Hydride evolution unit

Remarks: Use of matrix matching, standard additions and background correction recommended.

Edition:  
7/78
**Sb**

**Antimony**

**Analysis:** X-ray Fluorescence

**Method:** The sample containing antimony is caused to fluoresce by X-ray bombardment. The fluorescent radiation is dispersed by a crystal and detected by a scintillation counter and/or a flow proportional counter.

**Sample Handling:** Use RA or FA brine; sample may be run as is or evaporated to dryness depending upon instrumentation. Sample may be stabilized by adding 5 ml HNO₃ per liter.

**Range:** 10-100 mg/l

**Precision:** ±10 mg/l

**Accuracy:** ±10 mg/l

**Cross Reference:** Appendix 2

**Sampling Methods:** 11-S, 29-S

**Reagents:** Antimony standards

**Equipment:**

X-ray fluorescence spectrophotometer

**Literature Reference:**

**Remarks:**
1. Computer program usually required to interpret data.
2. Standardization of instrument with antimony standards required.
3. X-ray fluorescence provides simultaneous, mult-element determinations for selected metals and non-metals.
4. Use standard additions for quantification.
5. Detectability and accuracy limited by presence of antimony (as fire retardant?) in plastic films used to contain liquid sample.
Antimony

**Analysis:** Inductively Coupled Plasma - Atomic Emission Spectroscopy

**Method:** The brine sample is aspirated into a radiofrequency generated, inductively coupled argon plasma and the intensity of the emission spectrum of antimony is measured by the instrument and compared with standards. Intensity is measured at 217.59 nm or alternate wavelength.

**Sample Handling:** Use RA or FA brine.

**Range:** 3-5 orders of magnitude from a single spectral line

**Precision:** ± 1-10%

**Accuracy:**

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
Antimony standards

**Equipment:**
Inductively coupled plasma
Atomic emission spectrometer

**Remarks:**
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard additions recommended.
2. Inductively coupled plasma technique provides simultaneous multi-element analysis of metals.

**Edition:** 7/78
4. Probable spectral interference from manganese at antimony 217.59 nm line when analyzing concentrated brines.

5. Upper limit of concentration range may be extended by using alternate spectral lines.
Analysis: Spark Source Mass Spectrometry

Method: Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Antimony is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

Sample Handling: Use RA or FA brine, evaporate to dryness.

Range: 0.1-1000 mg/l
Precision: ±25%
Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Remarks: Spark source mass spectrometry provides simultaneous, multi-element determination for selected metals and non-metals.

Literature Reference:

Equipment:
Spark source mass spectrometer
Antimony

Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive antimony isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount isotope present.

Sample Handling: Use RA or FA brine and evaporate sample to dryness.

Range: 

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Precision:</th>
<th>Accuracy:</th>
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<tbody>
<tr>
<td>Appendix 2</td>
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<tr>
<td>Sampling Methods: 11-S, 29-S</td>
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Cross Reference:

<table>
<thead>
<tr>
<th>Literature Reference:</th>
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Reagents:

<table>
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<tr>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron source (nuclear reactor)</td>
</tr>
<tr>
<td>Multichannel analyzer</td>
</tr>
</tbody>
</table>

Remarks: 1. Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest. 2. Neutron activation provides simultaneous, multi-element determination for metals and non-metals.
Antimony

Analysis: Emission Spectrometry

Method: The sample containing antimony is either solid or liquid state is vaporized using a flame, AC spark or DC arc and the intensity of the selected emission line is measured against standards.

Sample Handling: Use RA or FA brine. Evaporation to dryness may be required. (Ash filter and mix with graphite.)

Range: 0-40 mg/l

Precision: ±20%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Antimony standards
HNO₃ or HClO₄
Graphite

Equipment:
Emission spectrometer
Muffle furnace
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Emission spectrometry provides simultaneous, multi-element determinations for metals.
3. Antimony precipitated along with SiO₂ in HNO₃ dehydration procedure.
4. Alternatively antimony may be precipitated with HClO₄ during dehydration procedure. This method is not applicable where high levels of alkali metals form difficultly dissolved perchlorate salts.

Edition: 7/78

C-27
5. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Arsenic Analysis: Silver Diethyldithiocarbamate

Method: Arsenic is reduced to arsine by zinc in an arsine generator. The arsine gas is passed through a glass plug impregnated with lead acetate and into a chamber containing silver diethyldithiocarbamate dissolved in pyridine where the gas forms a red solution which is measured spectrophotometrically at 535 nm.

Sample Handling: Use RA or FA brine. Nitric acid will give a negative interference if used for acidification.

Range: >0.005 mg/l  
Precision: ±0.002 mg  
Accuracy: ±0.002 mg

Cross Reference: Appendix 2  
Sampling Methods: 11-S, 29-S

Literature Reference:  
APHA 404 A(75)  
EPA 01002 (76)  
ASTM D2972-74 (77)

Reagents:  
Hydrochloric acid  
Potassium iodide  
Stannous chloride  
Lead acetate  
Silver diethyldithiocarbamate  
Pyridine  
Arsenic standards

Equipment:  
Arsine generator and absorption tube  
Spectrophotometer at 535 nm

Remarks:  
1. Interferences: Cr, Co, Cu, Hg, Mo, Ni, Pt, Ag interfer if in large enough concentrations. Antimony interferes by forming stibine. Sulfide is trapped in the lead acetate trap.

2. Standard additions should be used to establish recoveries.

3. Generator system must be tightly closed to avoid losses of arsine during analysis.

4. 1-Ephedrine in chloroform is a suitable solvent substitute for pyridine.

Edition: 7/78
**Analysis:** Atomic Absorption (Direct)

**Method:** Sample containing arsenic is aspirated into an air acetylene flame and the absorbance of the 193.7 arsenic resonance line is measured and compared to standards.

**Sample Handling:** Use RA or FA brine.

<table>
<thead>
<tr>
<th>Range: 0.7-20 mg/l</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 26-A

**Literature Reference:**

**Reagents:**
Arsenic standards

**Equipment:**
Atomic absorption spectrophotometer.
Arsenic electrodeless discharge lamp (optional)

**Remarks:**
1. Interferences: main interference is the absorption of the hollow cathode radiation by air-acetylene flame. In the direct air-acetylene flame method Al, Cr, Hg, Mn, Mo, Ni, Sn, Ti and nitrate ion interfere.
2. Matrix matching of samples and standards, standard additions and background correction recommended.
3. Use of an arsenic electrodeless discharge lamp gives lower detection limits.

**Edition:** 7/78 (cont. on back) C-29
4. Use of a graphite furnace will increase sensitivity.
As

Arsenic Analysis: Atomic Absorption (Hydride Evolution)

Method: Arsenic is determined as its hydride by atomic absorption at 193.7 nm in an argon or nitrogen-hydrogen flame after reduction with SnCl₂ – KI and conversion to its hydride by addition of Zn to the acid solution.

Sample Handling: Use RA or FA brine.

Range: 0.5-50 μg/l

Precision: ±10%

Accuracy: ±10%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 25-A

Literature Reference:
Instrument Manufacturer's Methods Manual
APHA 301A (1975)

Reagents:
KI
SnCl₂
Zn floury (200 mesh Zn)
HCl
Nitrogen or argon bottled gas
Hydrogen bottled gas
NaBH₄ pellets 10/32 in. (option)

Equipment:
Atomic absorption spectrophotometer
Hydride evolution unit

Remarks:
1. Use of matrix matching, standard additions and background correction recommended.
2. Use of an electrodeless discharge lamp will increase sensitivity.
3. Arsenic can also be generated by the action of NaBH₄ and hydrochloric acid on the sample. The arsenic may be stored in a balloon prior to AA analysis instead of being flushed directly into the burner.

Edition: 7/78
**Analysis:** Inductively Coupled Plasma-Atomic Emission Spectroscopy

**Method:** The brine sample is aspirated into a radiofrequency generated, inductively coupled argon plasma and the intensity of the emission spectrum of arsenic is measured by the instrument and compared with standards. Intensity is measured at 193.76 nm or alternate wavelengths.

**Sample Handling:** Use 1A or 1A brine.

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Remarks:**
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard additions recommended.

**Equipment:**
- Inductively coupled plasma
- Atomic emission spectrometer

**Literature Reference:**
3. Probable spectral interference from manganese and iron at arsenic 193.76 nm line when analyzing concentrated brines.

4. Upper limit of concentration range may be extended by using alternate spectral lines.
**As**

**Analysis:** Spark Source Mass Spectrometry

**Method:** Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Arsenic is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

**Sample Handling:** Use RA or FA brine.

**Range:** 0.1-1000 mg/l  
**Precision:** ±25%  
**Accuracy:** ±25%

**Cross Reference:**
Appendix 2  
Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
Arsenic standards  

**Equipment:**
Spark source mass spectrometer

**Remarks**
1. Spark source mass spectrometry provides simultaneous, multi-element determination for selected metals and non-metals.

2. Since arsenic is a volatile element, evaporation to complete dryness may volatilize arsenic (Rowe, Fournier, and Morey, 1973, USGS Bulletin #1303).

**Edition:** 7/78
Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive arsenic isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of isotope present.

Sample Handling: Use RA or FA brine and evaporate sample to dryness.

Range:  

Precision:  

Accuracy:  

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S

Literature Reference:  

Reagents:  

Equipment:  
Reactor  
Multichannel analyzer

Remarks:  
1. Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2. Neutron activation provides simultaneous, multi-element determination for selected metals and non-metals.

Edition:  
7/78  
3. Since arsenic is a volatile element, evaporation to complete dryness may volatilize arsenic (Rowe, Fournier, and Morey, 1973, USGS Bulletin #1303).
As

Arsenic

Analysis: Emission Spectrometry

Method: The sample containing arsenic in either solid or liquid state is vaporized using a flame, AC spark or DC arc and the intensity of the selected emission line is measured against standards.

Sample Handling: Use RA or FA brine. Evaporation to dryness may be required. (Ash filter and mix with graphite.)

Range: 0-40 mg/l

Precision: ±20%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Arsenic standards
Zinc oxide
Graphite

Equipment:
Emission Spectrometer
pH meter
Magnetic stirrer
Photo processor
Microphotometer
Muffle furnace

Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Emission spectrometry provides simultaneous, multi-element determination for metals.
3. Arsenic precipitated by ZnO addition to final pH of 5.3, using iron as the collector.
4. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78

C-34
### Analysis:

**Method:** Barium is measured turbidimetrically at 420 nm as its sulfate.

### Sample Handling:

Use filtered acidified brine.

### Range:

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
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<tbody>
<tr>
<td>Appendix 2</td>
<td>API 3.32 (1968).</td>
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<tr>
<td>Sampling Methods:</td>
<td></td>
</tr>
<tr>
<td>11-S, 29-S</td>
<td></td>
</tr>
<tr>
<td>Analysis Methods:</td>
<td></td>
</tr>
<tr>
<td>197-A, 198-A</td>
<td></td>
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</tbody>
</table>

### Reagents:

- Magnesium chloride
- Barium chloride
- Sodium citrate dihydrate
- Dioctyl ester of sodium sulfosuccinic acid (Aerosol OT)
- Hydrochloric acid
- Magnesium sulfate

### Equipment:

Spectrophotometer to measure at 420 nm.

### Remarks:

1. Calcium interferes when >100 mg/l CaCO₃.
2. Strontium interferes directly and is read as barium.
3. Polyphosphate >2 mg/l can inhibit the formation or turbidity. Boiling with concentrated hydrochloric acid and subsequent neutralization with sodium hydroxide can overcome this effect.
4. Interference can also be expected from high concentrations of organic acids or organic complexing agents.

Edition: 7/78
Analysis: Atomic Absorption

Method: The sample containing barium is aspirated directly into a \( \text{N}_2\text{O} \)-acetylene flame and the absorbance of the Ba resonance line at 553.6 nm is measured.

Sample Handling: Use RA or FA brine.

Range: 1-20 mg/l  
Precision: ±5%  
Accuracy: ±10%

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S

Reagents:  
Barium standards  
KCl  
Nitrous oxide gas cylinder

Equipment:  
Atomic absorption spectrophotometer  
Nitrous oxide burner head

Remarks:  
1. The ionization of barium in the nitrous oxide-acetylene flame is reduced by adding KCl until a 1000-2000 mg/l K background is obtained in both standards and samples.

2. Graphite furnace atomization may be used in the place of the nitrous oxide flame.

3. Use of standard additions and matrix matching of alkali and alkaline earth metals recommended.

Edition: 7/78

(cont. on back)

C-36
4. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.

5. Some high salinity brines generate spectral interference around the 553.6 nm line. A window of 40 μm is recommended.
**Ba**

**Barium**

**Analysis:** Flame Emission

**Method:** Barium is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 553.6 nm from barium is measured by a spectrophotometer.

**Sample Handling:** Use filtered acidified or raw acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and 5 ml HNO₃ per liter of sample.

| Range:  >0.05 mg/1 | Precision: <0.5 mg/1±25% | Accuracy: <0.5 mg/1±25% |

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 32-A

**Reagents:**
- Barium atomic absorption standard solution or barium chloride
- Nitrous oxide gas cylinder
- Potassium chloride or potassium nitrate

**Literature Reference:**

**Equipment:**
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
- Nitrous oxide burner head.

**Remarks:**
1. The ionization of barium in the nitrous oxide-acetylene flame is reduced by adding KCl or KNO₃ until a 1000-2000 mg/1 K background is obtained in both standards and samples.
2. Use of standard additions and matrix matching of alkali and alkaline earth metals recommended.
3. Precipitated BaSO₄ may be determined by filtration of brine through 0.45μ filter ashing paper dissolution of BaSO₄ with EDTA and ammonia and measurement via FAE.

**Edition:** 7/78
4. Some high salinity brines generate spectral interference around the 553.6 nm line. A window of 40 \(\mu\)m is recommended.
**Inductively Coupled Plasma - Atomic Emission Spectroscopy**

**Method:** The brine sample is aspirated into a radiofrequency generated, inductively coupled argon plasma and the intensity of the emission spectrum of barium is measured by the instrument and compared with standards. Intensity is measured at 233.53 nm or alternate wavelength.

**Sample Handling:** Use RA or FA brine.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5 orders of magnitude from a single spectral line</td>
<td>±1-10%</td>
<td></td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:** Barium standards

**Equipment:** Inductively coupled plasma-atomic emission spectrometer

**Remarks:**
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard additions recommended.
2. Inductively coupled plasma technique provides simultaneous, multi-element determination for metals.

**Edition:** 7/78

(cont. on back) C-38
4. Upper limit of concentration range may be extended by using alternate spectral lines.
Ba

Barium

Analysis: Spark Source Mass Spectrometry

Method: The dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber where barium is separated and detected by its mass to charge ratio; quantitative analysis require comparison to standard barium samples.

Sample Handling: Use RA or FA brine, evaporate to dryness.

Range: 0.1-1000 mg/l
Precision: ±5% (isotope dil.)
Accuracy: ±5% (isotope dil.)

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Barium standards

Equipment:
Spark source mass spectrometer

Remarks:
1. Spark source mass spectrometry provides simultaneous, multi-element determination for selected metals and non-metals.

Edition: 7/78

Literature Reference:
Barium

Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive barium isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of isotope present.

Sample Handling: Use RA or FA brine; evaporate sample to dryness.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td>Literature Reference:</td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reagents: Neutron source (e.g. nuclear reactor)

Equipment: Multichannel analyzer

Remarks: 1. Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2. Neutron activation provides simultaneous; multi-element determination of selected metals and non-metals.

Edition: 7/78
Analysis: Emission Spectrometry

Method: The sample containing barium in either solid or liquid state is vaporized using a flame, AC spark or DC arc and the intensity of the selected emission line is measured against standards.

Sample Handling: Use RA or FA brine. Evaporation to dryness may be required.

Range: 0.25-7.5 mg/l
Precision: ±10%
Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Barium standards
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Emission spectrometry provides simultaneous, multi-element determination for metals.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78

C-AI
HCO₃⁻, CO₃⁻
Bicarbonate, Carbonate

Analysis: Acid Titration  

Method: The bicarbonate and carbonate species concentrations are determined from the sample pH, and the titration of the sample to pH 8.3 (if the sample pH is > 8.3) then to a pH of 4.5 with standard HCl. Species concentrations are then calculated from the equilibrium reactions of carbonate and bicarbonate.

Sample Handling: Use RU or FU brine.

Range: >10 mg/l  
Precision: ±0.5%  
Accuracy: ±0.5%

Cross Reference: Appendix 2  
Sampling Methods: 11-S, 29-S  

Reagents: Standard HCl, Phenolphthalein indicator  
Methyl red - bromocresol green indicator or methyl orange indicator

Literature Reference: 
APHA 407 B(75)  
ASTM D513-71C (77)  

Equipment: pH meter

Remarks: 1. Interferences: Large deviations from 25°C (unless equilibrium constants are used that reflect the temperature of the sample); variable ionic strength of sample, (activity coefficients may be used to correct for sample ionic strength).

2. CO₃²⁻, HCO₃⁻, and H₂CO₃ concentrations may be determined by this method.

3. Determine bicarbonate and carbonate on site whenever possible on fresh raw unacidified brine.

Edition: 7/78

(cont. on back)
4. HCl may be standardized with Na₂CO₃. Dry Na₂CO₃ at 280°C and cool in dessicator before using.

5. Affected by suspended solids, salts of weak acids, and oily matter.

6. Air oxidation of iron and manganese cause drastic changes in alkalinity.
Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Analysis: Calcium Carbonate Saturation Calculation

Method: By determining the sample pH and calcium ion concentration and with the values of the solubility product of CaCO₃ (Kₛ) and the second proton dissociation constant of H₂CO₃ (K₂), bicarbonate may be determined from the equation: \( \log(\text{HCO}_3^-) = -\log(\text{Ca}^{2+}) - \log(K_2/K_S) - \text{pH} \) and carbonate from the equation: \( (\text{CO}_3^{2-}) = \frac{K_2(\text{HCO}_3^-)}{(\text{H}^+)^3} \)

Sample Handling: Use RU brine for pH measurement and RA or FA brine for Ca²⁺ determination.

Range: Precision: Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Remarks: 1. pH, Ca²⁺ concentration, and total dissolved solids (TDS) must be determined before using this method.
2. Interferences: differences in temperature and sample ionic strength may cause inaccuracies in results; use activity coefficients and equilibrium constants for temperature of measurement when possible.

Equipment:
Use equipment appropriate to pH, Ca²⁺, and TDS determinations.

Literature Reference:
APHA 203 (75)
### Analysis: Carmine Colorimetric

**Method:** Carmine in concentrated $\text{H}_2\text{SO}_4$ changes from bright red to bluish-red in the presence of boron. Color is measured at 585 nm.

---

**Sample Handling:** Use RA or FA brine.

<table>
<thead>
<tr>
<th>Range: 2-20 µg</th>
<th>Precision: $4 \mu\text{g} \pm 10%$ higher conc. $\pm 5%$</th>
<th>Accuracy: $4 \mu\text{g} \pm 10%$, higher conc. $\pm 5%$</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 41-A

**Literature Reference:**
- APHA 405B (1975)
- ASTM D3082-74A (77)
- USGS Book 5, Chapter Al (1976)

**Reagents:**
- Boron standards
- $\text{HCl}$
- $\text{H}_2\text{SO}_4$
- Carmine N.F. or carminic acid
- $\text{NaOH}$

**Equipment:**
- UV-Vis spectrophotometer at 585 nm.

**Remarks:**
1. Interferences: $\text{F}^-$, $\text{SiO}_2$ and $\text{PO}_4^{3-}$ create slight interference.
2. Range may be expanded by dilution or evaporation of sample.

**Edition:**
7/78
**Boron**

**Method:** An acidified sample containing boron is evaporated in the presence of curcumin to produce rosocyanine which is measured colorimetrically at 540 nm.

**Sample Handling:** Use RA or FA brine.

**Range:** 0.1 - 1 mg/l  
**Precision:** ±5%  
**Accuracy:** ±5%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 40-A

**Reagents:**  
- Boron standards  
- Curcumin reagent  
- Ethyl or isopropyl alcohol  
- HCl  
- Oxalic acid  
- NaOH or Na₂CO₃

**Literature Reference:**  
- APHA 405A (75)  
- EPA 01022 (76)

**Equipment:**  
- UV-Visible spectrophotometer to measure at 540 nm  
- Evaporation dishes  
- Heat source (e.g. hot water bath or infrared lamp)

**Remarks:**  
1. Interferences: >20 mg/l NO₃⁻; >100 mg/l Ca²⁺ and Mg²⁺ may be removed by precipitating with NaOH or Na₂CO₃ and filtering.  
2. Close control of evaporating times, volumes and other variables required.  
3. Range may be expanded by sample dilution or concentration.

**Edition:**  
7/78
**Boron**

**Analysis:** Flame Emission

**Method:** Boron is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 249.8 nm from boron is measured by a spectrophotometer.

**Sample Handling:** Use raw unacidified or filtered unacidified brine. Stabilization not necessary.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision: ±10-25%</th>
<th>Accuracy: ±10-25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;2 mg/l low brine</td>
<td>&gt;20 mg/l high brine</td>
<td></td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Reagents:**
- Boric acid or boron atomic absorption standard solution
- Nitrous oxide gas cylinder
- Hydrochloric acid
- Isopropanol

**Literature Reference:**

**Equipment:**
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
- Nitrous oxide burner head.

**Remarks:**
1. 1% (v/v) hydrochloric acid added to standards.
2. Use of standard additions and matrix matching of alkali and alkaline earth metals recommended.
3. Dilute samples with distilled water, acidify with 1% (v/v) HCl, add 10% (v/v) isopropanol.

**Edition:** 7/78
Analysis: Inductively Coupled Plasma - Atomic Emission Spectroscopy

Method: The brine sample is aspirated into the radiofrequency generated inductively coupled argon plasma and the intensity of the emission spectrum of boron is analyzed by the instrument and compared with standards. Intensity is measured at 249.68 nm or alternate wavelength.

Sample Handling: Use RA or FA brine.

Range: a single spectral line. Precision: ± 1-10% Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S


Reagents: Boron standards

Equipment: Inductively coupled plasma-atomic emission spectrometer

Remarks: 1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Use standard additions and background correction whenever possible.

2. Inductively coupled plasma technique provides simultaneous, multi-element determination for metals.


Edition: 7/78
(cont. on back) C-47
4. Upper limit of concentration range may be extended by using alternate spectral lines.
Boron

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Boron is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

Sample Handling: Use RA or FA brine. Evaporate to dryness for analysis.

Range: 0.1-1000 mg/l
Precision: ±5% (isotope dil.)
Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Boron standards

Literature Reference:

Equipment:
Spark source mass spectrometer

Remarks:
1. Spark source mass spectrometry provides simultaneous, multi-element determination for selected metals and non-metals.


3. Since boron is a volatile element, evaporation to complete dryness may volatilize boron (Rowe, Fournier, and Morey, 1973, USGS Bulletin #1303).
Analysis: Emission Spectrometry

Method: The sample containing boron in either solid or liquid state is vaporized using a flame, AC spark or DC arc and the intensity of the selected emission line is measured against standards.

Sample Handling: Use RA or FA brine. Evaporation to dryness may be required.

Range: 2-10 mg/l

Precision: ±10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Boron standards
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Emission spectrometry provides simultaneous, multi-element determination for selected metals.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78
Analysis: Hypochlorite Oxidation - Titration

Method: Iodide in a sample is oxidized with bromide to iodate; the excess bromide is then destroyed. Iodine is then formed by oxidizing iodide with the iodate and the resulting iodine is determined by titration with thiosulfate. Iodide and bromide are then determined together by oxidizing both with ClO⁻ to iodate and bromate. Excess ClO⁻ is destroyed; the iodine is liberated and determined with thiosulfate. The bromide content is taken as the difference between the iodide and bromide content and the iodide content.

Sample Handling: Use RU or FU brine.

Range: 2-20 mg/l

Precision: ±12%

Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 96-A

Literature Reference:
ASTM D 1246-77C (1977)
EPA 7187 (76)

Reagents:
Acetic acid
Bromine
Calcium Carbonate
Calcium oxide
Methyl red indicator
Potassium fluoride
Potassium hydroxide
Chlorine gas (bromine free)
Potassium Iodide
Sodium acetate

Sodium chloride
Sodium Formate
Sodium thiosulfate
phenyl arsine
oxide titrant
Starch indicator
Sulfuric acid

Equipment:
Hotplate
Magnetic stirrer
Common lab glassware (burets, pipets, etc.)

Remarks: Interferences: Fe, Mg and organic material (removed prior to determination with CaO).

Edition:
7/78
Bromide Analysis: Chromic Acid Oxidation - Extraction

Method: Bromide is oxidized by chromic acid to bromine, then extracted from the aqueous phase with CCl₄. The CCl₄ solution is then measured at 417 nm for bromine content.

Sample Handling: Use RU or FU brine.

Range: 8-400 mg/l  
Precision: ±4-5% @ 200-400 mg/l  
Accuracy: ±3-4% @ 200-400 mg/l

Cross Reference:
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 48-A, 49-A

Reagents:
Sulfuric acid  
Chromium trioxide  
Carbon tetrachloride

Remarks: 1. Chloride and iodide do not interfere in this method.  
2. Large precipitates may form upon addition of H₂SO₄ to high solids brine. Dilution with 1:1 water/sulfuric acid reduces the amount of precipitate prior to the extraction step.  
3. Longer gelling times for phase separation are required for high solids brines during the extraction step.

Edition: 7/78

Literature Reference:
API 3.14 (68)

Equipment:
UV-Vis spectrophotometer at 417 nm  
Separatory funnels  
Filtering apparatus
Analysis: Colorimetric (Iodine-Permanganate)

Method: Bromide catalyzes the oxidation of I\(_2\) to periodate by permanganate and hence affects the reaction rate. For a given time, pH, temperature and reactant concentrations, the concentration of bromide is inversely proportional to the unreacted I\(_2\). The I\(_2\) is extracted with CCl\(_4\) and measured colorimetrically at 515 nm.

Sample Handling: Use raw unacidified or filtered unacidified brine.

Range: 0.001-0.1 mg/l  
Precision: ±19%  
Accuracy: 

Cross Reference:
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 47-A, 49-A

Literature Reference:
ASTM D 1246-77B (1977)  

Reagents:
Carbon tetrachloride  
Potassium bromide  
Potassium iodide  
Sulfuric acid  
Potassium permanganate

Equipment:
Spectrophotometer to measure at 515 nm.  
Separatory funnels  
Water bath (0°C)  
Timer

Remarks:
1. Following ions interfere: I\(_2\) >10mg/l, Ag\(^+1\) >3mg/l, Zn\(^+2\) >3mg/l, Mn\(^+2\) >3mg/l, Fe\(^+3\) >3mg/l, NO\(_3^-\) >1mg/l, S\(_2\)O\(_3^-\) >3mg/l, Co\(^+2\) >3mg/l, Ni\(^+2\) >3mg/l. Dilution of sample will reduce these interferences.
2. Any substance that oxidizes iodine or reduces iodate or permanganate will interfere.
3. Free chlorine cannot be tolerated or nitrite.

Edition: 7/78
Analysis: Phenol Red - Colorimetric

Method: Bromide reacts with phenol red in the presence of chloramine T at pH 5.0-5.4 to form a reddish-violet complex which is measured colorimetrically at 590 nm.

Sample Handling: Use RU or FU brine.

Range: Precision: Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 47-A, 48-A

Reagents:
Acetic acid
Sodium acetate
Phenol red (sodium salt)
Chloramine T
Sodium thiosulfate
Bromide standards

Literature Reference:
APHA 406 (75)

Equipment:
UV-Vis spectrophotometer to measure at 590 nm.

Remarks:
1. Interferences: Cl₂ forms during reaction, may be removed by addition of Na₂S₂O₃.
2. Glassware must be cleaned using dilute HNO₃ to remove traces of bromide.
3. High salinity may affect consistency of results.

Edition: 7/78
Analysis: Bromide Specific Electrode

Method: Bromide activity is measured using a bromide specific electrode containing a silver bromide crystal which responds to bromide ion in solution. The potential response of the electrode is proportional to the log of the bromide activity.

Sample Handling: Use RU or FU brine.

Range: 0.1-100 mg/l

Accuracy: +2%

Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 74-A, 89-A, 101-A

Reagents:
- Ionic strength adjustor (NaNO₃)
- Bromide standards
- Electrode filling solutions

Equipment:
- pH or millivolt meter with expanded scale
- Bromide specific electrode
- Reference electrode (double junction Ag/AgCl recommended)

Remarks:
1. Chloride and iodide interfere severely with this method.
2. Ionic strength adjustor solution consisted of the addition of 2 ml 5 M NaNO₃ per 100 ml solution.

Edition:
7/78
Analysis: X-Ray Fluorescence

Method: The sample containing bromide is caused to fluoresce by X-ray bombardment. The fluorescent radiation is dispersed by a crystal and detected by a scintillation counter and/or a flow proportional counter.

Sample Handling: Use RA or FA brine; sample may be run as is or evaporated to dryness depending upon instrumentation.

Range: 2-100 mg/l
Precision: ±5 mg/l
Accuracy: ±5 mg/l

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Bromide standards

Equipment:
X-ray fluorescence spectrophotometer

Remarks:
1. Computer program usually required to interpret data.
2. Standardization of instrument required.
3. Bromide is usually determined with metal cations in this multi-element technique.
4. Use standard additions for quantification.

Edition: 7/78
Bromide

Analysis: Ion-Exchange Chromatography

Method: Anion components are separated on sulfonated cation exchange columns coated with finely ground anion resin. A dilute sodium carbonate/bicarbonate solution is used as the eluting solvent. The separation column is followed by a suppressor column to remove highly concentrated background components, and bromide is detected by a conductivity detector.

Sample Handling: Use RU or FU brine.

Range: Precision: ±2% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Na₂CO₃
NaHCO₃
Standard bromide solutions

Literature Reference:
Microchem. Jour. 22, (45-49) (1977)

Equipment:
Dionex Ion Chromatograph
75-120 psi air supply

Remarks:
1. Bromide may be determined simultaneously with fluoride, nitrate, and sulfate by this method.

Edition: 7/78
Bromide Analysis: Spark Source Mass Spectrometry

Method: The dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber where bromide is separated and detected by its mass to charge ratio; quantitative analysis requires comparison to standard bromide samples.

Sample Handling: Use RA or FA brine, evaporate to dryness.

Range: 0.1-1000 mg/l    Precision: ±25%    Accuracy: ±25%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents: Bromide standards

Remarks: 1. Acidified brine is recommended for this analysis because bromide is usually determined concurrently with the metal constituents of the brine.
2. Spark source mass spectrometry provides simultaneous, multi-element determination of selected metals and non-metals.

Edition: 7/78

C-57
Br

Bromide

Analysis: Neutron Activation

Method: A dehydrated brine sample is irradiated by neutron bombardment to form radioactive bromine isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of isotope present.

Sample Handling: Use RU or FU brine. Evaporate to dryness.

Range:        Precision:        Accuracy:

Cross Reference: | Literature Reference:
Appendix 2     Robertson & Carpenter, "Neutron Activation Techni- 
Sampling Methods; 11-S, 29-S  ques for the Measurement of Trace Metals in 

Reagents:      Equipment:
Neutron source (e.g. nuclear reactor) 
Multichannel analyzer

Remarks: 1. Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.

2. Neutron activation provides simultaneous, multi-element determination of selected metals and non-metals.

Edition: 7/78
**Calcium**

**Analysis:** EDTA Titrimetric

**Method:** Titrimetric using murexide and EDTA titrant. pH is adjusted to 12-13 with sodium hydroxide and approximately 0.2 gms murexide is added and titrated with EDTA.

**Sample Handling:** Use raw acidified or filtered acidified brine.

**Range:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td>±5%</td>
<td>±3%</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis Methods: 92-A, 93-A, 124-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Literature Reference:**
- ASTM D511-76B (1977)
- APHA 306C (1975)
- EPA 00910, 00916 (1976)
- API 2.4 (1968)

**Reagents:**
- Murexide
- Sodium hydroxide
- EDTA

**Equipment:**
- Buret

**Remarks:** Barium and strontium interfere when present in quantities greater than 30 mg/l.

Edition: 7/78
Ca

Calcium

Analysis: Atomic Absorption

Method: Samples containing calcium are aspirated into an air-acetylene or nitrous oxide-acetylene flame and determined by the absorption of the calcium resonance line at 422.7 nm.

Sample Handling: Use raw or filtered acidified brine.

Range: 0.01-3 mg/l

Precision: ±5%

Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 57-A

Literature Reference:
EPA 00916 (1976)

Reagents:
Ca stock solution, 1000 ppm, may be prepared from CaCO₃ and HC1
Nitrous oxide gas cylinder
Lanthanum chloride or strontium nitrate
Potassium chloride or strontium nitrate

Equipment:
AA Spectrophotometer
Nitrous oxide burner head

Remarks:
1. Interferences occur from Al, Si, Fe, SO₄²⁻, et al., removed by using a nitrous oxide flame (use hottest section of flame, just above red crown). Ionization interferences must be depressed by addition of 2000 mg/l K⁺, or 1% (w/v) Sr.
2. When using an air-acetylene flame standards, samples, and blanks should contain 0.1-1% (w/v) La³⁺ or Sr⁺² to minimize interferences from Si, Al, PO₄, SO₄, Ti, and Zr.
3. If sample shows Tyndall effect, filter through a 0.45μ membrane filter.

Edition: 7/78

(cont. on back) C-60
4. Matrix matching (using equivalent amounts of alkali and alkaline earth metals) in standards important. Use of standard additions recommended.

5. Alternatively, the 239.9 nm line and $D_2$ background correction may be used.
Analysis: Flame Emission

Method: Calcium is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 422.7 nm from calcium is measured by a spectrophotometer.

Sample Handling: Use raw acidified or filtered acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HN03 per liter of sample.

Range: >0.05 mg/l

Precision: <0.5 mg/l±25%

Accuracy: >0.5 mg/l±5%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 56-A

Literature Reference:

Reagents:
- Calcium atomic absorption standard solution or calcium carbonate
- Hydrochloric acid (to dissolve calcium carbonate)
- Nitrous oxide gas cylinders
- Potassium chloride or potassium nitrate

Equipment:
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer
- Nitrous oxide burner head

Remarks:
1. Addition of potassium chloride or potassium nitrate to give a final concentration of 2000 mg/l K is necessary to suppress ionization.
2. Slightly higher height of observation in flame reduces potential chemical interferences.
3. Use of standard additions and matrix matching of alkali and alkaline earth metal ions recommended.

Edition: 7/78
Ca

Calcium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: A sample containing calcium is aspirated into a radiofrequency generated argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 315.89 nm or alternate wavelength.

Sample Handling: Use raw or filtered acidified brine.

Range: a single spectral line

Precision: ± 1-10%

Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Calcium standard solution; prepared from CaCO₃ and HCl

Literature Reference:

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks: 1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which affect vaporization characteristics. Background correction and standard additions method recommended. ICP-AES is a simultaneous multi-element technique for metal ions.


Edition: 7/78

(cont. on back)
3. Upper limit of concentration range may be extended by using alternate spectral lines.
Calcium

Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive calcium isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of calcium present.

Sample Handling: Filter brine on site. Evaporate sample and irradiated residue with neutron source.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Standards containing calcium

Equipment:
Reactor
Multichannel analyzer

Remarks: 1-Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2-Calcium may be measured simultaneously with other elements of interest.

Edition: 7/78
Calcium (Ca)

Analysis: Emission Spectrometry

Method:
The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use raw or filtered acidified brine. Evaporation to dryness may be required.

Range: 2-20 mg/l

Precision: ±10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Calium standards
Vanadium internal standard

Equipment:
Emission Spectrometer
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions and background corrections whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78

C-64
Carbon Dioxide

**Analysis:** Titrimetric

**Method:** The sample is titrated with a strong acid (H₂SO₄ or HCl) to separate equivalence points for CO₂⁻, HCO₃⁻, and OH⁻. Equivalence points are determined either potentiometrically or with visual indicators. The molar concentration of CO₂ is equal to the molar concentration of carbonate.

**Sample Handling:** Carbon dioxide is trapped by passing raw or filtered brine through a fritted glass bubbler which is submerged in sodium hydroxide solution (forming carbonate). The sodium hydroxide solution is diluted to a preselected concentration with brine (usually 1:1).

**Range:** Precision: ±2%  
Accuracy: ASTM D513-71 C,D,E (1977)

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td>The following procedure which applies to free CO₂ can be used for total CO₂: APHA 407B (1975)</td>
</tr>
<tr>
<td>Sampling Methods:</td>
<td></td>
</tr>
<tr>
<td>4-S, 5-S, 8-S, 11-S</td>
<td></td>
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<tr>
<td>Analysis Methods:</td>
<td></td>
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<tr>
<td>1-A, 38-A, 39-A, 62-A</td>
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<tr>
<td>63-A, 64-A, 66-A, 141-A</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric or sulfuric acid</td>
</tr>
<tr>
<td>Sodium carbonate or sodium hydroxide</td>
</tr>
<tr>
<td>Brom cresol green-methyl red indicator</td>
</tr>
<tr>
<td>Phenolphthalein indicator</td>
</tr>
<tr>
<td>Equipment:</td>
</tr>
<tr>
<td>Buret</td>
</tr>
<tr>
<td>pH meter</td>
</tr>
</tbody>
</table>

**Remarks:**  
1. Cations or anions which affect the carbonate equilibrium or precipitate or consume the reactant (NaOH) preferentially affect the accuracy, as do colors and turbidity which obscure colorimetric end points.
2. Aluminum, iron, chromium, and copper will affect precipitation.
3. Abnormal results also obtained in the presence of high concentrations of ammonia, amines, phosphate, borate, sulfide and nitrate.
4. Excessive dissolved solids introduce error.

(cont. on back)
5. The endpoints can be detected more easily by titrating the excess caustic first with strong acid followed by titration with weak acid to the precise endpoints.

6. Sharper endpoints are obtained if the titration is blanketed with nitrogen.
CO₂

Carbon Dioxide

Analysis: Strontium Gravimetric

Method:
Sample is pretreated with phosphoric acid in a glass bubbler apparatus using a nitrogen atmosphere and boiled to remove all the CO₂ from sample. The CO₂ is trapped in a sodium hydroxide solution and is then determined gravimetrically by adding strontium nitrate solution, filtering, ashing and weighing the SrCO₃ precipitate.

Sample Handling:
Carbon dioxide is trapped by passing raw or filtered brine through a fritted glass bubbler which is submerged in sodium hydroxide solution (forming carbonate). The sodium hydroxide solution is diluted to a preselected concentration with brine (usually 1:1).

Precision: ±10%
Accuracy:

Cross Reference: Appendix 2

Reagents:
Phosphoric acid
Sodium hydroxide
Strontium nitrate
Sodium carbonate
Nitrogen gas - CO₂ free

Equipment:
Hot plate
Gas bubbler with reflux condenser

Remarks:
1. Phosphoric acid treatment eliminates interferences due to compounds that react with strontium or the sodium hydroxide to produce a precipitate. Problem in this method is the availability of CO₂ free nitrogen gas. Other gases might be tried.
2. Alternatively, strontium chloride dissolved in ammonium hydroxide may be substituted as the trapping solution (USGS method).

Edition: 7/78

C-66
**Carbon Dioxide**

**Analysis:** Precise Evolution

**Method:** CO₂ is liberated by acidifying and boiling the sample in a closed system. The liberated CO₂ is trapped by bubbling into a Ba(OH)₂ solution; excess Ba(OH)₂ is then titrated with standard HCl and the CO₂ species content determined by calculation from the titration and the pH of the sample.

**Sample Handling:** Carbon dioxide is trapped by passing raw or filtered brine through a fritted glass bubbler which is submerged in sodium hydroxide solution (forming carbonate). The sodium hydroxide solution is diluted to a preselected concentration with brine (usually 1:1).

**Range:** >10 mg/l  
**Precision:** ±1%  
**Accuracy:** ±5%

**Cross Reference:** Appendix 2  
**Sampling Methods:** 4-S, 5-S, 8-S, 11-S, 12-S, 13-S, 14-S, 19-S, 20-S, 29-S, 34-S  

**Reagents:**  
- Barium hydroxide  
- Hydrochloric acid  
- Methyl orange indicator  
- Phenolphthalein indicator  
- Chromic acid  
- Sulfuric acid  
- Ascarite (option)  
- Anhydrone (option)

**Equipment:**  
- Evolution flask  
- Absorption flask  
- Pump  
- pH meter  
- Burets  
- Heating mantle

**Remarks:**  
1. Any volatile acid, base, or barium precipitant not removed by scrubbing solution will interfere.  
2. See remarks under "Carbon Dioxide - Titrmetric".  
3. Alternatively, the CO₂ gas may be passed through a scrubbing train, collected as ascarite and weighed. ("Determination of Carbon Dioxide in Carbonates", Scott's Standard Methods of Chemical Analysis, 6th ed., New York, 1962.)

**Edition:** 7/78
**Analysis:** Calculation

**Method:** By determining the sample pH and calcium ion concentration and with the values of the solubility product of CaCO₃ \((K_s)\) and the second proton dissociation constant of \(H_2CO_3\) \((K_a)\), bicarbonate may be determined from the equation: 
\[
\log([HCO_3^-]) = -\log([Ca^{2+}]) - \log(K_a/K_s) - \text{pH} \quad \text{and carbonate from}
\]
\[
\log([CO_3^{2-}]) = K_a^2 \left(\frac{[HCO_3^-]}{[H^+]}\right). 
\]
The amount of CO₂ is determined by the relation: 
\[
\text{mg/l total CO}_2 = \text{mg/l free CO}_2 + 0.88(A+B) \quad \text{where } A = \text{mg/l bicarbonate alkalinity and } B = 1/2(\text{mg/l carbonate alkalinity}). 
\]
Free CO₂ is determined titrimetrically or nomographically.

**Sample Handling:** Use RU or FU brine for pH and alkalinity measurements and RA or FA brine for Ca²⁺ determination.

**Range:**

**Precision:**

**Accuracy:**

**Cross Reference:** Sampling Methods:
- 4-S, 5-S, 8-S, 11-S, 12-S, 13-S, 14-S
- 19-S, 20-S, 29-S, 34-S
Analysis Methods:

**Literature Reference:**
- APHA 203 (1975)
- APHA 407 A, B, C (1975)

**Reagents:**
Use appropriate reagents for pH, alkalinity, and Ca²⁺ determinations.

**Equipment:**
Use equipment appropriate to pH, Ca²⁺, and titrimetric determinations.

**Remarks:**
1. pH, Ca²⁺, and alkalinity concentrations must be determined before using this method.
2. Interferences: differences in temperature and sample ionic strength may cause inaccuracies in results; use activity coefficients and equilibrium constants for temperature of measurement when possible.

**Edition:** 7/78
**Analysis:** Carbon Analyzer (Infrared)

**Method:** Sample containing carbonate is acidified to convert carbonate back to carbon dioxide. Carbon dioxide is measured by a carbon analyzer using an infrared detector.

**Sample Handling:** Carbon dioxide is trapped by passing raw or filtered brine through a fritted glass bubbler which is submerged in sodium hydroxide solution (forming carbonate). The sodium hydroxide solution is diluted to a preselected concentration with brine (usually 1:1).

**Range:**

**Precision:**

**Accuracy:**

**Cross Reference:**

Sampling Methods:
- 4-S, 5-S, 8-S, 11-S, 12-S, 13-S, 14-S,
- 19-S, 20-S, 29-S, 34-S

Analysis Methods:
- 1-A, 38-A, 39-A,
- 61-A, 62-A, 63-A, 64-A, 141-A

**Reagents:**
- Potassium hydrogen phthalate
- Sodium bicarbonate
- Sodium carbonate

**Equipment:**
- Total carbon analyzer
- Syringes

**Remarks:**

1. Procedure applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. Particles in the sample may block the opening of the syringe or pipette.

2. See remarks under "Carbon Dioxide - Titrmetric".

**Edition:** 7/78
Cs

Cesium

Analysis: Atomic Absorption

Method: Samples containing Cs are directly aspirated into an air-acetylene flame and determined by absorption of the Cs resonance line at 894.4 nm or 852.1 nm.

Sample Handling: Use raw or filtered acidified brine.

Range: 0.02-10 mg/l

Precision: ±5%

Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 67-A

Literature Reference:

Reagents:
Cs standard solution

Equipment:
AA Spectrophotometer
Red filter, required for some spectrometer models at high wavelengths

Remarks:
1. Interference due to ionization should be suppressed by addition of KCl to a final K⁺ concentration of 5000 mg/l. Standard additions technique and use of Deuterium background lamp recommended.
2. If sample shows Tyndall effect, filter through 0.45μ membrane filter.
3. Use of electrodeless discharge lamp increases sensitivity.
4. Matrix matching (equivalent amounts of alkali and alkaline earth metals) in standards important.

Edition: 7/73

(cont. on back) C-70
5. Some difficulties in balancing signals when using red filters and background correction simultaneously have been reported.
Cs
Cesium

Analysis: Flame Emission
Method: Cesium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 852.1 nm from cesium is measured by a spectrophotometer.

Sample Handling: Use raw acidified or filtered acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HNO₃ per liter of sample.

Range: >0.05 mg/l Precision: >0.5 mg/l±5% Accuracy: >0.5 mg/l±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 66-A

Literature Reference:

Reagents:
Cesium atomic absorption standard solution or cesium nitrate.
Potassium chloride or potassium nitrate.
Ammonium oxalate (optional)
Ammonium hydroxide (optional)

Equipment:
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
Red filter required for some spectrophotometers.

Remarks:
1. Ionization is suppressed by the addition of potassium chloride or potassium nitrate to give a potassium concentration of 5000 mg/l.
2. Use of standard additions and matrix matching of alkali and alkaline earth metal ions recommended.
3. Deuterium background correction system enhances response.
4. Use of an air-hydrogen flame has also been reported.

Edition: 7/78
(cont. on back)
5. Calcium interference may be removed by treating with ammonium oxalate, ammonium hydroxide and filtering.
Cs

Cesium

Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive cesium isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of cesium present.

Sample Handling: Filter brine on site. Evaporate sample and irradiated residue with neutron source.

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<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
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</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td>Literature Reference:</td>
<td></td>
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<tr>
<td>Sampling Methods: 11-S, 29-S</td>
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</tbody>
</table>

Reagents: Standards containing cesium

Equipment:
Reactor
Multichannel analyzer

Remarks:
1- Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2- Several elements may be measured simultaneously with this method.

Edition: 7/78

C-72
**Analysis:** Emission Spectrometry  
**No.:** 69-A

**Method:** Sample is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected cesium emission line is measured against standards.

**Sample Handling:** Use raw or filtered acidified brine. Evaporation to dryness may be required.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td>Literature Reference:</td>
<td>Equipment:</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td>Instrument Manufacturer's Literature.</td>
<td></td>
</tr>
</tbody>
</table>

**Reagents:** Cesium standards

**Remarks:**
1. Use matrix matching, standard additions and background correction whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Chloride

Analysis: Silver Nitrate Titration

Method: Silver chloride precipitates quantitatively as silver nitrate titrant is added to the sample. The endpoint is marked by the formation of red silver chromate. The pH range of the solution must be 7-10.

Sample Handling: Use unacidified brine

Range: >5 mg/l

Precision: ±4%

Accuracy: ±4%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 71-A, 72-A

Literature Reference:
Fischer and Peters, Quantitative Chemical Analysis, p. 375.

Reagents:
Potassium chromate indicator
Standardized NaCl solution
Standardized AgNO₃ titrant solution

Equipment:
Burette
Magnetic stirrer and teflon-coated stirbar

Remarks:
Possible interferences: 1. Bromide, iodide, CN⁻, and S²⁻ will interfere as equivalent chloride concentrations, 2. Iron greater than 10 mg/l will mask endpoint; may be removed with Al(OH)₃ suspension (see APHA ref.), 3. High Ca²⁺ and/or Mg²⁺ content samples may form ppt. when pH is raised to 8.3. Dilution or separation of Ca and/or Mg may be necessary.

Edition: 7/78

(cont. on back)
4. Alternatively, 2,4 dichlorofluorescein may be used as the indicator with the endpoint detected as a change from yellow to pink. Dextrin may have to be added to disperse AgCl crystals. A back titration with KCl (1000 ppm) is recommended. If only 1-2 drops are needed to reach yellow color, then end point is accurate.
**Cl**

**Chloride**

**Analysis:** Mercuric Nitrate Titration

**Method:** The chloride sample is titrated with mercuric nitrate titrant; the endpoint is detected by diphenylcarbazone which forms a purple complex with excess Hg(II).

**Sample Handling:** Use unacidified brine sample.

<table>
<thead>
<tr>
<th>Range:</th>
<th>0.2-100 mg/l</th>
<th>Precision:</th>
<th>±2%</th>
<th>Accuracy:</th>
<th>±5%</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 70-A, 72-A

**Reagents:**
- Sodium chloride standard solution
- Nitric acid, 1. N
- Sodium hydroxide, .1 N
  - Indicator reagent:
    - diphenyl carbazone powder
    - bromphenyl blue powder
    - 95% ethyl alcohol
- Mercuric nitrate titrant

**Literature Reference:**
- EPA 00940 (1976)
- APHA 408B (1975)
- ASTM D512-67A (1977)

**Equipment:**
- Burette
- Magnetic stirrer and teflon-coated stirbar

**Remarks:**
1. Ferric ion (Fe$^{3+}$) must be reduced if greater than 10 ppm. Highly colored or turbid samples not suitable unless color or turbidity eliminated.
2. Other halides are also titrated by this method.

Edition: 7/78

C-75
Chloride

Analysis: Titrmetric (Conductometric)  No. 72-A

Method: AgCl precipitates quantitatively as silver nitrate titrant is added; the endpoint is indicated by plotting conductance data versus volume increments of silver nitrate added. The intersection of the two lines on the plot indicates the endpoint.

Sample Handling: No preservatives.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2 Fischer and Peters, Quantitative Chemical Analysis; p. 742.
Sampling Methods: 11-S, 29-S
Analysis Methods: 70-A, 71-A, 73-A, 74-A

Reagents: Equipment:
Sodium chloride standard solution Conductivity cell
Silver nitrate standard solution

Remarks: 1. A variation of this procedure involves plotting volume of AgNO₃ added vs potential using an Ag electrode and reference electrode (U.S. Geological Survey Method).

Edition:
7/78
Analysis: Gravimetric

Method: The chloride content of a soluble chloride is determined gravimetrically by precipitation as silver chloride by the addition of an excess of silver nitrate solution to the chloride solution containing nitric acid. The precipitate is filtered, washed, dried, and weighed as AgCl.

Sample Handling: Use unacidified brine sample.

Range: >100 mg/l

Precision: ±1%

Accuracy: ±2%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 70-A, 72-A

Reagents:
AgNO₃ standard solution
Nitric acid
Hydrochloric acid

Literature Reference:
Fischer and Peters, Quantitative Chemical Analysis; p. 181.

Equipment:
Filtration apparatus
Drying oven
Analytical balance

Remarks:
1. Interferences: anions which form insoluble salts with Ag⁺, e.g., S²⁻, Br⁻, I⁻, S₂O₅²⁻, SCN⁻, CN⁻, precipitate may contain occluded materials from mother liquor; AgCl precipitate subject to photo-
decomposition (procedure must be done in darkened room with incandescent lamp); peptization of precipitate may occur during washing.

2. Presence of nitric acid prevents precipitation of silver salts insoluble in neutral media.

Edition: 7/78
**Analysis:** Chloride-Specific Electrode

**Method:** The chloride electrode is a selective ion sensor which allows free chloride ions in aqueous solutions to be measured. The chloride electrode consists of a silver chloride/silver sulfide membrane bonded into the tip of an epoxy electrode body. When the membrane is in contact with the chloride solution, silver ions dissolve from membrane surface and electrode develops potential due to silver ion concentration. Potential measurements of chloride standards vs concentration are plotted on four-cycle semilog paper.

**Sample Handling:** Analyses were made on filtered unacidified samples. Ionic strength adjustor solution was added to samples and standards in order to keep a constant background.

**Range:** 1-100 mg/l  
**Precision:** ±2%  
**Accuracy:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
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<tbody>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
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<tr>
<td>Analysis Methods: 50-A, 72-A, 89-A</td>
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<tr>
<td>101-A</td>
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</tbody>
</table>

**Reagents:**  
Standard chloride solutions, prepared from NaCl  
Reference electrode filling solution  
Sodium nitrate, reagent grade

**Equipment:**  
Silver chloride electrode, Orion model 94-17 or 96-17  
Magnetic stirrer  
Double-Junction reference electrode  
PpH meter with expanded mV scale or specific ion meter

**Remarks:**  
1. Bromide ratio above $2 \times 10^{-3}$ and iodide ratio above $5 \times 10^{-7}$ will interfere.  
2. The ionic strength adjustor solution consisted of the addition of 2 ml of 5 M NaNO₃ per 100 ml of solution.

Edition: 7/78
Chloride Analysis: X-Ray Fluorescence

Method: The sample containing chloride is caused to fluoresce by X-ray bombardment. The fluorescent radiation is dispersed by a crystal and detected by a scintillation counter and/or a flow proportional counter.

Sample Handling: Use raw or filtered acidified brine; sample may be run as is or evaporated to dryness depending upon instrumentation.

Range: 1000-50,000 mg/l
Precision: ±3% @ 95% level
Accuracy: ±3%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Chloride standards
Cadmium nitrate

Reagents:
Cadmium nitrate

Equipment:
X-ray fluorescence spectrophotometer

Remarks:
1. Computer program usually required to interpret data.
2. Standardization of instrument required.
3. Several elements may be measured simultaneously with this method.
4. Cadmium nitrate added, CDLα radiation used as internal standard for matrix compensation.
5. For liquid samples, CdNO₃ solution added: sample first freed of any free H₂S by bubbling argon through liquid. Sample may be diluted to extend range.

Edition: 7/78
Analysis: Ion-Exchange Chromatography

Method: Anion components are separated on sulfonated cation exchange columns coated with finely ground anion resin. Sodium carbonate/sodium bicarbonate solution is used as the eluting solvent. The separation column is followed by a suppressor column to remove highly concentrated background components, and chloride is detected by a conductivity detector.

Sample Handling: Use unacidified brine.

Range: 

Precision: 

Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Standard chloride solutions
Sodium carbonate/sodium bicarbonate eluent

Literature Reference:
Dionex Corp., Sunnyvale, CA, Literature
Anal. Chem. 47, 11 (1975)
Microchem. Jour. 22, (45-49) (1977)
Anal. Chem. 49, 2, 3, 401 (1977)

Equipment:
Dionex Ion Chromatograph, Model 10 or 14
75-120 psi air supply
Anion separator column, 3mm x 500mm
Anion precolumn, 3mm x 150mm
Anion suppressor column, 6mm x 250mm

Remarks:
1. Due to typically high Cl⁻ concentrations in brines, this anion generally cannot be analyzed simultaneously with other anions.

Edition: 7/78
Chloride

**Analysis:** Neutron Activation

**Method:** Dehydrated sample is irradiated by neutron bombardment to form radioactive chloride isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of chloride present.

**Sample Handling:** Filter brine on site. Evaporate sample and irradiated residue with neutron source.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
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<tbody>
<tr>
<td><strong>Cross Reference:</strong></td>
<td><strong>Literature Reference:</strong></td>
<td><strong>Equipment:</strong></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
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</tbody>
</table>

**Reagents:** Standards containing chloride

**Remarks:**
1. Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2. Several elements may be measured simultaneously with this method.

**Edition:** 7/78
**CONDUCTIVITY**

**Conductivity**

**Analysis:** Conductivity Meter

**Method:** Conductivity is measured with a platinum electrode cell of known cell constant and a conductivity bridge.

**Sample Handling:** Use RU brine stored in plastic, determine < 6 hours after collecting. Record sample temperature at time of conductivity measurement.

**Range:** 10-500,000 μmhos/cm  
**Precision:** ±3%  
**Accuracy:** ±5%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S

**Literature Reference:**  
API 2.91 (68)  
EPA 00095 (76)  
APHA 205 (75)  

**Reagents:**  
Standard KCl solutions

**Equipment:**  
Conductivity meter, conductivity cell

**Remarks:**  
1. Interferences: temp. dependent, oil and residue foul electrodes.  
2. Cell constant at different temp. must be determined with standard KCl solutions or samples must be measured at constant temp. (e.g., 25°C).  
3. Cell constant should be measured with standard KCl solutions.  
4. Field analysis on fresh raw brine strongly recommended; commercial field conductivity meters available.  
5. Record sample temperature at time of conductivity measurement.  

**Edition:** 7/78
6. Specific conductivity will change as sample ages according to CO$_2$ concentration and oxidation of ion's (iron and manganese) and H$_2$S occurs.
Copper

Analysis: Atomic Absorption

Method: Samples containing Cu are directly aspirated into an air-acetylene flame and determined by absorption of the Cu resonance line at 324.7 nm.

Sample Handling: Use raw or filtered acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter at sample.

Range: 0.01-4 mg/l
Precision: ±5%
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 80-A

Reagents:
Cu stock solution, (purchased or prepared from metallic copper in 1:1 HNO₃)

Equipment:
Atomic absorption
Spectrophotometer

Remarks:
1. Standards should be matched to brine for major cations, so that physical properties such as viscosity are similar. Deuterium arc background lamp may be used for matrix background correction at a nearby wavelength. Graphite furnace has also been used in place of flame for atomization.
2. If samples show Tyndall effect, filter through 0.45μ membrane filter.
3. With high Zn/Cu ratios use a lean air-acetylene flame.
4. Spectral interferences due to Na and Ca in high brine samples at low copper concentration must be corrected.

Edition: 7/78
5. Use of standard additions recommended.
Copper

**Analysis:** Atomic Absorption (MIBK Extraction)  
**No:** 80-A

**Method:** Copper is extracted from the aqueous phase with ammonium pyrrolidine dithiocarbamate in MIBK. The extraction is then aspirated into an air-acetylene flame and the absorbance of the resonance line at 324.7 nm.

**Sample Handling:** Use raw or filtered acidified brine.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision: ±10%</th>
<th>Accuracy: ±5%</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 79-A

**Reagents:**
- Ammonium pyrrolidine dithiocarbamate
- Methyl isobutyl ketone
- Copper standard solutions, prepared from metallic copper and nitric acid

**Equipment:**
- AA spectrophotometer
- Separatory funnels

**Remarks:**
1. Extraction is useful for increased sensitivity.
2. Alternatively, chloroform can be used as the extraction solvent (ASTM D1688-77E (1977)).

**Edition:** 7/78
**Cu**

Copper

### Analysis:

**X-ray Fluorescence**

### Method:

Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

### Sample Handling:

Use filtered acidified, raw unacidified or filtered unacidified brine.

### Range: 

<table>
<thead>
<tr>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cross Reference:

- Appendix 2
- Sampling Methods: 11-S, 29-S

### Reagents:

- Copper metal or other copper standard
- Nitric acid (to dissolve copper)

### Literature Reference:


### Equipment:

- X-ray fluorescence spectrophotometer

### Remarks:

Edition: 7/78

C-85
Cu

Copper

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 324.75 nm or alternate wavelength.

Sample Handling: Use filtered acidified or raw acidified brine.

3-5 orders of magnitude from

Range: a single spectral line

Precision: ± 1-10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Copper atomic absorption standard solutions or copper metal
Nitric acid (to dissolve copper metal)

Literature Reference:

Equipment:
Inductively coupled plasma-atomic emission spectrometer.

Remarks:
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.
2. Additional references:

Edition: 7/78 (cont. on back)
3. Use of standard additions and background correction recommended.
4. Upper limit of concentration range may be extended by using alternate spectral lines.
Cu

Copper

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Copper is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

Sample Handling: Use raw or filtered acidified brine.

Range: 0.1-1000 mg/l  Precision: ±25%  Accuracy: ±25%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Solid copper
standard sample

Equipment:
Spark source mass spectrometer

Remarks: May be analyzed simultaneously with other elements of interest.

Edition: 7/78
Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive copper isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of copper present.

Sample Handling: Filter brine on site. Evaporate sample and irradiated residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents: Standards containing copper

Equipment:

Remarks: 1-Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2-Copper may be measured simultaneously with other elements of interest.

Edition: 7/78
## Cu

**Copper**

**Analysis:** Emission Spectrometry  |  **No.:** 85-A

**Method:** The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected copper emission line is measured against standards.

**Sample Handling:** Use raw or filtered acidified brine. Evaporation to dryness may be required.

**Range:** 0.04-0.2 mg/l  |  **Precision:** ±10%  |  **Accuracy:**

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**
- Instrument Manufacturer's Literature

**Reagents:**
- Copper standards
- Vanadium internal standard

**Equipment:**
- Emission spectrometer
- Photo processor
- Microphotometer

**Remarks:**
1. Use matrix matching, standard additions, and background correction whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

**Edition:** 7/78  |  C-89
Analysis: Alizarin (Pre-distillation)

Method: Fluoride is distilled away from chemical interferences in the sample by acidifying the sample with concentrated sulfuric acid and distilling off the volatile HF which is formed at 180°C. Silver sulfate is added to samples of high chloride content during distillation. 3-alizarinsulfuric acid, a yellow dye, is added to sample containing fluoride, to form a colorless zirconium hexafluoride species. Increasing fluoride concentration yields lighter sample color. Sample is matched visually to standards.

Sample Handling: Use unacidified brine sample.

Range: 0.05-1.4 mg/l  \( \text{Precision: } \pm 15\% \)  \( \text{Accuracy: } \pm 5\% \)

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 87-A, 88-A, 89-A

Reagents:
Sulfuric acid; cone
Hydrochloric acid; cone
Fluoride standard solutions; prepared from KF
Zirconyl-alizarin reagent; Zirconyl chloride (ZrOCl₂·8H₂O)
3-alizarinsulfuric acid (alizarin red S)
Sodium arsenite

Remarks: Interferences from Al(III), Cl⁻, Fe(III), hexametaphosphate, PO₄³⁻, SO₄²⁻, color and turbidity removed by distillation, which is quantitatively within the accuracy and precision of the Alizarin method. Procedure is time consuming. The still must be flushed by distilling with pure H₂O before and after distilling HF. One hour is required for development of zirconium hexafluoride species.

Edition: 7/78

Literature Reference:
Distillation: APHA 414A (1975)
Alizarin method: APHA 414D (1975)

Equipment:
Nessler tubes for visual comparison
**Fluoride**

**Analysis:** Colorimetric (Spadns)  

**Method:** Fluoride reacts with zirconium dye lake to produce a colorless zirconium hexafluoride species. The dye becomes lighter in color with the increasing concentration of fluoride. The color is measured at 570 nm.

**Sample Handling:** Use unacidified brine.

<table>
<thead>
<tr>
<th>Range</th>
<th>25-200 mg/l</th>
<th>Precision: ±16%</th>
<th>Accuracy: ±20%</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 86-A, 88-A

**Reagents:**
- Standard fluoride solutions
- Spadns solution
- Sodium arsenite
- Zirconyl chloride octahydrate
- Hydrochloric acid, conc.

**Literature Reference:**
- APHA 414 C. (1975)
- ASTM D1179-72 A (1977)
- EPA C0950, 00951 (1976)

**Equipment:**
- Spectrophotometer to measure at 570 nm.

**Remarks:** 1. No known interferences.

**Edition:** 7/78
Analysis: Amadac F Colorimetric

Method: Amadac F, followed by distillation; sample is distilled using excess silver sulfate in sulfuric acid media. Distillation is stopped at 180°C. The distillate is neutralized with sodium hydroxide and diluted to known volume. A portion of the distillate is reacted with 5 ml Amadac F solution in a 25 ml volumetric flask and read on spectrophotometer.

Sample Handling: Use raw unacidified or filtered unacidified brine.

Range: 

Precision: ±15%

Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 86-A, 87-A

Literature Reference: Burdick and Jackson Labs, Inc. Muskegon, MI Literature

Reagents: Amadac F, (trade mark of a mixture of chelated lanthanum and organic dyes), Isopropyl Alcohol, Silver Sulfate, Sulfuric Acid, Reagent Sodium Hydroxide.

Equipment: Distillation apparatus
Spectrophotometer to measure at 620 nm

Remarks: In concentrated brines, interferences have been observed.

Edition: 7/78
Fluoride

Analysis: Fluoride Specific Electrode

Method: Fluoride concentration is measured with a fluoride specific electrode containing a lanthanum fluoride crystal and an electrometer or pH meter.

Sample Handling: Use unacidified brine sample.

Range: 0.1-1000 mg/l

Precision: ±5%

Accuracy: ±15%

Cross Reference: Appendix 2

Sampling Methods: 11-S, 29-S

Analysis Methods: 50-A, 74-A, 101-A

Reagents:
Stock fluoride solution
Fluoride standards: 1-10 μg/ml
Total ionic strength adjustment buffer (TISAB)

Equipment:
Fluoride electrode
Calamol reference electrode
Magnetic stirrer and teflon stirbar
Specific ion meter or pH meter with millivolt scale

Remarks:
1. Aluminum interference (up to 2 mg/l) removed by complexation with citrate in TISAB solution.
2. Fluoride also forms complexes with Si, Fe²⁺, and other polyvalent cations as well as hydrogen. Extent of complexation depends on the concentrations, pH of the solution, and total ionic strength of the solution. TISAB also compensates for these effects.

Edition: 7/78

(cont. on back)
3. Recovery values from spiked samples may be high.
Fluoride

Analysis: Ion-Exchange Chromatography

Method: Anion components are separated on sulfonated cation exchange columns coated with finely ground anion resin. A sodium bicarbonate/carbonate solution is used as the eluting solvent. The separation column is followed by a suppressor column to remove highly concentrated background components, and fluoride is detected by a conductivity detector.

Sample Handling: Use unacidified brine

Range: Precision: ±0.55% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Standard fluoride solution
Sodium carbonate/sodium bicarbonate eluent

Literature Reference:
Dionex Corp., Sunnyvale, CA, Literature
Anal. Chem. 47, 11 (1975)
Anal. Chem. 49, 2, 3, 401 (1977)

Equipment:
Dionex Ion Chromatograph
75-120 psi air supply

Remarks: 1. May be analyzed simultaneously with bromide, nitrate, and sulfate.

Edition: 7/78
### Fluoride

**Analysis:** Spark Source Mass Spectrometry

**Method:** Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Fluoride is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

**Sample Handling:** Use filtered unacidified or raw unacidified brine. Evaporate samples and analyze residue.

<table>
<thead>
<tr>
<th>Range: 0.1-1000 mg/l</th>
<th>Precision: ±25%</th>
<th>Accuracy: ±25%</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Reagents:**
- Sodium fluoride or other fluoride std.

**Equipment:**
- Spark source mass spectrometer

**Remarks:**

**Edition:** 7/78

**No.:** 91-A

**Literature Reference:**
D. L. Donohue, J. A. Carter and J. C. Franklin
HARDNESS

Analysis: EDTA Titration

Method: A buffered aliquot of the sample is titrated with a standard solution of disodium - EDTA. Magnesium and calcium react with the EDTA to form chelated complexes. In the presence of a dye such as Eriochrome Black T the solution changes from wine red to blue at the end point.

Sample Handling: Use raw acidified or filtered acidified brine.

Range: 1-1200 mg/l
Precision: ±3%
Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 55-A, 93-A, 124-A

Literature Reference:
APHA 309B (1975)
ASTM D 1126-67B (1977)
EPA 00900 (1976)

Reagents:
- Hydrochloric acid
- Ammonium chloride
- Ammonium hydroxide
- EDTA-Mg salt or EDTA-dissodium salt
- Sodium cyanide
- Sodium sulfide
- Hydroxylamine hydrochloride
- Ethanol or isopropanol
- Eriochrome Black T dye
- Calcium carbonate

Equipment:
- Burets

Remarks:
1. Highly colored and strong brines interfere (Al >20 ppm, CO₂ >1000 ppm, Cl >10,000 ppm, SO₄ >10,000 ppm, Fe >30 ppm). Inhibitors can usually be used to overcome these effects.
2. In high calcium solution, addition of ammonium hydroxide can cause precipitation.
3. Maintain Mg²⁺ and Na₂-EDTA in approximate equivalence for best results.

Edition: 7/78
**HARDNESS**

**Analysis:** Calculation

**Method:** Hardness is determined as mg/l CaCO₃ by determining the concentrations of Ca, Mg, Sr, Fe, Al, Zn, and Mn, multiplying the mg/l concentrations of these metals by the appropriate factors and summing the products to obtain hardness in mg/l as CaCO₃.

---

**Sample Handling:** Use RA or FA brine for the metal determinations.

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<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 55-A, 92-A, 105-A, 124-A

**Reagents:**
- Use reagents required for metals determinations

**Literature Reference:**
- APHA 309 (75)

**Equipment:**
- Use equipment required for metals determinations

**Remarks:**
1. This method considered more accurate than hardness by EDTA.
2. Method requires those metals in highest concentration be determined.

**Edition:**
- 7/78
- C-97
Analysis: Titrimetric (Iodine)  

Method: Hydrogen sulfide is collected in zinc acetate solution. Excess iodine in water is added. The solution is acidified to allow sulfide to react with the iodine to form sulfur. Excess iodine is titrated with thiosulfate.

Sample Handling: Sulfide from Hydrogen Sulfide is precipitated as zinc sulfide by passing raw or filtered brine through a fritted glass bubbler which is submerged in a zinc acetate solution. The zinc acetate solution is diluted to a preselected concentration with brine (usually 1:1).

Range: >1 mg/l  
Precision: ±5% on S²  
Accuracy: ±5% on S²

Cross Reference: Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S  
Analysis Methods: 202-A

Reagents:  
- Zinc acetate  
- Sodium thiosulfate  
- Starch  
- Iodine  
- Hydrochloric acid

Literature Reference:  
- APHA 428 D (1975)  
- API 3.10.1 (1968)  
- EPA 00746 (1976)

Equipment:  
- Burets

Remarks:  
1. Reducing substances such as heavy metal ions, sulfite, thiosulfate and hydrosulfite will use up iodine and contribute positive errors.  
2. Oxygen and other oxidants react with hydriodic acid and contribute negative errors.  
3. Field analysis for sulfide is advised.

Edition: 7/78  
(cont. on back)
4. $\text{H}_2\text{S}$ may be evolved from sample by boiling with phosphoric acid and recapturing in a glass bubbler apparatus containing zinc acetate solution. This procedure frees sulfide from heavy metals. Use $\text{N}_2$ gas free of $\text{H}_2\text{S}$ for purging $\text{H}_2\text{S}$ out of original trapping solution.
Analysis: Colorimetric (Methylene Blue)  
Method: Methylene blue is formed when sulfide is reacted with 4-amino-N, N-dimethylaniline in the presence of ferric chloride. Ammonium phosphate is then added to destroy excess Fe(III). The color is measured at 600 nm.

Sample Handling: Sulfide from Hydrogen Sulfide is precipitated as zinc sulfide by passing raw or filtered brine through a fritted glass bubbler which is submerged in a zinc acetate solution. The zinc acetate solution is diluted to a preselected concentration with brine (usually 1:1).

Range: 0.01-1.0 mg/l  
Precision:  
Accuracy: ±10%

Cross Reference: Appendix 2  
Sampling Methods:  
4-S, 11-S, 12-S, 29-S, 34-S  
Analysis Methods: 204-A

Reagents:  
Zinc acetate  
Sodium carbonate  
N,N-dimethyl-phenylene-diamine oxalate (also called p-amino-dimethylaniline oxalate)  
Sulfuric acid  
Ferric chloride  
Diammonium hydrogen phosphate  
Sodium sulfide  
Sodium Hydroxide  
Iodine  
Potassium Iodide  
Sodium Thiosulfate  
Hydrochloric acid

Equipment:  
Spectrophotometer to measure at 600 nm  
Burets

Remarks:  
1. Reducing substances such as heavy metal ions, sulfite, thiosulfate and hydrosulfite inhibit color formation.  
2. Field analysis for sulfide is advised.  
3. A modification of this method using Lauth's violet dye instead of methylene blue gives more consistent color development with brine samples (Strickland and Parsons, "A Practical Handbook of Seawater Analysis", Fisheries Research Board of Canada, Ottawa, 1968, p. 41-44).
4. Field samples should be collected with all air space excluded from bottle.

5. Interferences due to sulfite, thiosulfate, iodide, and many other soluble substances, but not ferrocyanide may be removed by first precipitating sulfide as ZnS, decanting, and washing the precipitate with distilled water. The ZnS is then treated using the standard procedure [APHA 428B (1975)].
Analysis: Titrimetric (For Bromide and Iodide)

Method: Iodide in a sample is oxidized with bromine to iodate; the excess bromine is then destroyed. Iodine is then formed by oxidizing iodide in KI with the iodate and the resulting iodine is determined by titration with thiosulfate.

Sample Handling: Acidified or unacidified brine may be used.

Range: >50 mg/l

Precision: ±10%

Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 46-A

Literature Reference:
EPA 71865 (1976)
ASTM D1246-77C (1977)
API 3.16 (1968)

Reagents:
Acetic acid
Bromine water
Calcium carbonate
Calcium oxide
Hydrochloric acid
Methyl red indicator
Potassium fluoride
Potassium iodide
Sodium acetate
Sodium formate
Sodium chloride
Sodium molybdate
Sodium thiosulfate
standard solution
Sulfuric acid

Equipment:
Iodide flasks, 250 ml
Burette

Remarks:
1. Bromide and iodide are determined together similarly, by oxidation with hypochlorite ion. Bromide may then be determined by difference. (See Bromide, Titrimetric).
2. Iron, magnesium, and organic matter interfere, but are removed prior to determination with CaO.

Edition: 7/78
**Analysis:** Colorimetric (Arsenious-Ceric-Ferric thiocyanate)  

**Method:** Procedure is similar to the arslenous-ceric colorimetric method, except the reaction of Ce(IV) with the arslenous ion is quenched with ferric alum and thiocyanate to form the red Fe(III) thiocyanate complex which is measured at 510 or 525 nm.

**Sample Handling:** Use raw unacidified or filtered unacidified brine.

**Range:**

**Precision:**

**Accuracy:**

**Cross Reference:****

Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 98-A, 99-A, 100-A

**Literature Reference:**

APHA 415B (1975).

**Reagents:**

Sodium chloride  
Arsenious acid  
Sulfuric acid  
Ceric ammonium sulfate  
Ferrous ammonium sulfate  
Potassium thiocyanate  
Potassium iodide

**Equipment:**

Water bath  
Spectrophotometer to measure at 510 or 525 nm  
Timer

**Remarks:** 1. Excess of sodium chloride added to sample eliminates interference from chloride already present by attaining a stable maximum chloride concentration that sensitizes the reaction. Formation of noncatalytic forms of iodine and inhibitory effects of silver and mercury are reduced by NaCl addition.
Iodide Analysis: Leuco Crystal Violet Method

Method: Iodide is selectively oxidized to iodine which then reacts with leuco crystal violet to form the highly colored leuco crystal violet dye. The color is measured spectrophotometrically.

Sample Handling: Use raw unacidified or filter unacidified brine. Determine within 1 day after collection.

Range: >0.6 mg/l

Precision: ±10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 97-A, 99-A, 100-A

Reagents:
Potassium iodide
Citric acid
Ammonium hydroxide
Ammonium dihydrogen phosphate
Leuco crystal violet indicator
Mercuric chloride
Sulfuric acid
Potassium peroxymonosulfate
Sodium thiosulfate
Oxone

Literature Reference:
APHA 415A (1975)

Equipment:
Spectrophotometer to measure at 592 nm.

Remarks:
1. Chloride above 200 mg/l causes inhibition of the color formation.
2. Oxidized forms of manganese cause apparent high iodide results.
3. Color development time must be carefully watched.
4. Calcium oxide used to pretreat sample to remove various metal interferences. This treatment is followed by sulfuric acid neutralization.
Iodide

Analysis: Colorimetric (Arsenious-Ceric)

Method: The iodide concentration affects the first order reaction rate of AsO₃⁻ with Ce(IV) in acid solutions. Samples and standards are reacted in a constant temperature bath at 30°C for 30 minutes and the remaining yellow Ce(IV) ion is measured at 450 nm.

Sample Handling: Use unacidified brine.

Range: 0.001-0.1 mg/l  Precision: ±5%  Accuracy:  

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 97-A, 98-A, 100-A

Literature Reference:
ASTM D1246-77A (1977)

Reagents:
Arsenious acid solution
Ceric sulfate solution
Silver nitrate solution
Sulfuric acid

Equipment:
Spectrophotometer to measure at 450 nm
Timer
Water bath 30 ± .5°C

Remarks: 1. Reducing agents that react rapidly with ceric ion cause positive errors, but are removed by a preliminary treatment with dilute permanganate solution.

2. Oxidizing agents cause negative results by lowering the concentration of arsenious acid. The magnitude of the error is proportional to the iodide concentration.

Edition: 7/78
**Iodide**

**Analysis:** Photometric

**Method:** Iodide is oxidized to iodine by nitrous acid and extracted into carbon tetrachloride. The purple color of iodide is measured versus standards at 517 nm.

**Sample Handling:** Use unacidified or acidified brine.

| Range: 2-120 mg/l | Precision: ±1-2% at 10-50 mg/l | Accuracy: ±1-2% at 10-50 mg/l |

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 97-A, 98-A, 99-A

**Reagents:**
- Bromophenol blue
- Sulfuric acid
- Carbon tetrachloride
- Potassium iodide
- Potassium nitrate

**Remarks:** Hydrogen sulfide can interfere. May be removed by boiling acidified brine.

**Literature Reference:**
- API 3.15 (1968)

**Equipment:**
- Spectrophotometer to measure at 517 nm

Edition: 7/78  C-104
### Analysis

**Method:** Iodide concentration is measured directly using a silver iodide electrode and an electrometer.

### Sample Handling:

Use unacidified brine sample.

### Range

<table>
<thead>
<tr>
<th></th>
<th>0.1-100 mg/l</th>
<th>Precision:</th>
<th>±2%</th>
</tr>
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### Cross Reference

<table>
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<tr>
<th></th>
<th>Appendix 2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Sampling Methods: 11-S, 29-S</td>
</tr>
<tr>
<td></td>
<td>Analysis Methods: 50-A, 74-A, 89-A</td>
</tr>
</tbody>
</table>

### Literature Reference


### Equipment

- Silver iodide electrode, Orion model 94-53
- Specific ion meter or pH meter with millivolt scale
- Magnetic stirrer and stirbar
- Reference electrode

### Reagents

- Iodide standard solutions; prepared from potassium iodide
- Sodium nitrate, reagent grade

### Remarks

1. Sulfide interference at $10^{-6}$ ratio level.
2. Ionic strength adjuster solution added to samples and standards in order to keep constant background. Ionic strength adjuster consists of addition of 2 ml of 5 M NaNO₃ per 100 ml of solution.

Edition: 1Manufacturer's specifications.  
7/78
Iodide

Analysis: X-Ray Fluorescence

Method: The sample containing iodide is caused to fluoresce by X-ray bombardment. The fluorescent radiation is dispersed by a crystal and detected by a scintillation counter and/or a flow proportional counter.

Sample Handling: Use raw or filtered acidified brine; sample may be run as is or evaporated to dryness depending upon instrumentation.

Range: 10-100 mg/l

Precision: ±10 mg/l

Accuracy: ±10 mg/l

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Iodide standards

Equipment:
X-ray fluorescence spectrophotometer

Remarks:
1. Computer program usually required to interpret data.
2. Standardization of instrument required.
3. Iodide may be determined simultaneously with other elements of interest.
4. Use standard additions for quantification.

Edition: 7/78

C-106
Iodide

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Iodide is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

Sample Handling: Use filtered or raw unacidified brine.

Range: 0.1-1000 mg/l  Precision: ±25%  Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Solid iodide standard sample

Equipment:
Spark source mass spectrometer

Remarks: Other elements may be determined simultaneously with iodide.

Edition: 7/78  C-107
Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive iodide isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of iodide present.

Sample Handling: Filter brine on site. Evaporate sample and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Sampling Methods: 11-S, 29-S

Reagents: Equipment:
Standards containing iodide Reactor

Remarks: Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest. Iodine may be analyzed simultaneously with other elements of interest.

Edition: 7/78
Fe
Iron

Analysis: Phenanthroline Colorimetric

Method: Iron is reduced to Fe(II) with hydroxylamine hydrochloride and complexed with 1,10-phenanthroline between pH 2.9-3.5 to give an orange-red complex which is measured at 510 nm.

Sample Handling: Use raw acidified or filtered acidified brine.

<table>
<thead>
<tr>
<th>Range: 0.05-3 mg/l</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
- Hydrochloric acid
- Hydroxylamine hydrochloride
- Ammonium acetate
- Sodium acetate
- 1,10-phenanthroline monohydrate
- Iron standard
- Diisopropyl or isopropyl ether

Equipment:
Spectrophotometer to measure at 510 nm.

Literature Reference:
- APHA 310A (1975)
- ASTM D1068-77A (1977)

Remarks:
1. Interferences include strong oxidizing agents; cyanide; nitrite; phosphates; chromium and zinc > 10 times concentration of iron; cobalt and copper > 5 mg/l; and nickel > 2 mg/l.
2. Bismuth, cadmium, mercury, molybdate and silver precipitate phenanthroline.
3. In the presence of interfering metal ions an excess of phenanthroline is required to complex metal ions.
4. Extraction step may be necessary if large amounts of interfering metals are present.

Edition: 7/78

(cont. on back) C-109
5. If noticeable color is present evaporate sample, gently ash residue and redissolve in acid.
**Iron**

**Analysis:** Atomic Absorption  
**Method:** Aqueous samples of iron are aspirated directly into an air-acetylene flame and the absorbance of the Fe resonance line at 248.3 nm is measured.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:** 0.01-5 mg/l  
**Precision:** ±5%  
**Accuracy:** ±10%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 107-A, 108-A

**Reagents:**  
Iron stock solution, prepared from iron wire and 1:1 HCl  
Nitrous oxide gas cylinder (option)  
Potassium chloride (option)

**Literature Reference:**  
EPA 01045 (1976)  
Flame Emission and Atomic Absorption Spectrometry; Dean and Rains; 1975 Vol. III  
ASTM 2576-70F, D1088-77C (1977)

**Equipment:**  
AA spectrophotometer  
Nitrous oxide burner head (option)

**Remarks:**  
1. Major cations and acidity of brine should be simulated in standards, to liken physical properties such as viscosity. Interferences observed in air-acetylene flame (ref. 2) include aluminum, silica, sulfate, phosphate, et al. Standard additions technique is therefore recommended. Significant ionization occurs if a nitrous oxide/acetylene flame is used, and 1000 µg/ml total K⁺ should be added to solution for this flame.  
2. If samples show Tyndall effect, filter through 0.45 µ membrane filter.  
3. Background correction at 247.2 nm has been observed to be advantageous (N₂ lamp).
4. A reduction in sensitivity has been observed when iron is determined in the presence of nitric acid and nickel. This effect can be minimized by using a very lean flame. The use of a nitrous oxide/acetylene flame has been found to remove all interferences.
Analysis: Atomic Absorption (MIBK Extraction)

Method: Iron is extracted from the aqueous phase with ammonium pyrrolidine dithiocarbamate in MIBK. The extraction is then aspirated into an air-acetylene flame and the absorbance of the resonance line at 248.3 nm measured.

Sample Handling: Use raw or filtered acidified brine.

Range: Precision: ±14% Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 106-A, 108-A

Reagents:
Ammonium pyrrolidine dithiocarbamate
Methyl isobutyl ketone
Iron standard solutions, prepared from iron and hydrochloric acid

Literature Reference:
APHA 301-A-III (1975)

Equipment:
AA spectrophotometer
Separatory funnels

Remarks:
1. Improved sensitivity; useful for sub-ppm levels of iron.
2. Use of standard additions recommended.
3. Alternatively, chloroform may be used as the extraction solvent (ASTM D1068-77D (1977)).
Fe
Iron

Analysis: Flame Emission

Method: Iron is determined by aspirating the sample into a nitrous oxide acetylene flame and the emission intensity at 372.0 nm from iron is measured by a spectrophotometer.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter of sample.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0.05 mg/l low brine</td>
<td>&lt;0.5 mg/l ±25%</td>
<td>&lt;0.5 mg/l ±25%</td>
</tr>
<tr>
<td>&gt;0.5 mg/l high brine</td>
<td>&gt;0.5 mg/l ±5%</td>
<td>&gt;0.5 mg/l ±5%</td>
</tr>
</tbody>
</table>

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 106-A, 107-A

Literature Reference:

Reagents:
Iron atomic absorption standard solution or iron metal
Hydrochloric acid (to dissolve iron metal)
Nitrous oxide gas cylinder

Equipment:
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer
Nitrous oxide burner head

Remarks:
1. Iron often coprecipitates with silica and must be recovered by acid digestion of brine residue.
2. Careful matrix matching (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions) between sample and standards must be made.
3. Use of standard additions recommended.

Edition:
7/78
C-112
Analysis: X-ray Fluorescence

Method: Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

Sample Handling: Use filtered acidified, raw unacidified or filtered unacidified brine.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2 Nuc. Inst. and Methods, Vol. 106, pp. 525-538

Reagents: Equipment:
Iron standards X-ray fluorescence spectrophotometer

Remarks:

Edition: 7/78
Fe

Iron

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: The brine sample is aspirated into a radiofrequency generated argon plasma and the intensity of the emission spectrum of iron is analyzed by the instrument and compared with standards. Intensity is measured at 261.19 nm or alternate wavelengths.

Sample Handling: Use raw or filtered acidified brine.

Range: a single spectral line

Precision: ± 1-10%

Accuracy:

3-5 orders of magnitude from

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Iron standard solution, prepared from iron wire and hydrochloric acid

Equipment:
Inductively coupled plasma-Atomic emission spectrometer

Remarks:
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard additions method recommended.

2. ICP-AES is a simultaneous multi-element technique for metal ions.

3. Upper limit of concentration range may be extended by using alternate spectral lines.

Edition: 7/78 (cont. on back)

C-114
**Fe**

Iron

**Analysis:** Spark Source Mass Spectrometry

**Method:** Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Iron is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

**Sample Handling:** Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate samples and analyze residue.

<table>
<thead>
<tr>
<th>Range: 0.1-1000 mg/l</th>
<th>Precision: ±5% (isotope Dil.)</th>
<th>Accuracy: ±25%</th>
</tr>
</thead>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
- Iron standards

**Equipment:**
- Spark source mass spectrometer

**Remarks:**
1. Additional References:

**Edition:** 7/78
Fe

Iron

Analysis: Neutron Activation

Method: Sample is exposed to neutron source (reactor) and radioactive iron isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of iron is proportional to the measured activity.

Sample Handling: Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Sampling Methods: 11-S, 29-S

Reagents: Equipment:

Remarks: Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

Edition:
7/78
### Analysis:

**Emission Spectrometry**

**Method:**
The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected iron emission line is measured against standards.

### Sample Handling:
Use raw or filtered acidified brine. Evaporation to dryness may be required.

<table>
<thead>
<tr>
<th>Range: 0.5-2 mg/l</th>
<th>Precision: +10%</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

### Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S

### Reagents:
- Iron standards
- Vanadium internal standard

### Equipment:
- Emission spectrometer
- Photo processor
- Microphotometer

### Remarks:
1. Use matrix matching, standard additions and background correction whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spar, or DC arc).

**Edition:** 7/78
Pb

Lead

Analysis: Atomic Absorption

No. 114-A

Method: Aqueous sample containing lead is aspirated directly into an air-acetylene flame and the absorption of the resonance line at 217.0 nm or 283.3 nm is analyzed.

Sample Handling: Use raw or filtered acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter of sample.

Range: 0.02-15 mg/l  Precision: ±5%  Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 115-A

Literature Reference:
EPA 01051 (1976)
APHA 301A II (1975)
ASTM D2576-70, D3559-77A (1977)

Reagents:
Lead standard solutions; prepared from metallic lead and nitric acid.
EDTA

Equipment:
AA spectrophotometer

Remarks:
1. Anions which precipitate with lead may interfere. Making solutions 0.1 M in EDTA will largely eliminate these interferences (ref. 2 above). (These anions include PO₄, CO₃, I, F, and acetate when present in concentrations ten times greater than Pb.)
2. Use of a graphite furnace will increase sensitivity.
3. If samples show Tyndall effect, filter through a 0.45 μ filter.
4. Spectral interferences from sodium and calcium must be corrected at low Pb concentrations.
(cont'd. on back)

Edition: 7/78
5. Matrix matching (use of equivalent concentrations of alkali and alkaline earth metals) recommended.

6. Use of standard additions recommended.

7. Matrix interference may be removed by using a non-absorbing line at 282.5 nm for background correction.

8. Background correction using the 282.0 nm line has been shown to be advantageous.
Analysis: Atomic Absorption (MIBK Extraction)

Method: Lead is extracted from the aqueous phase with ammonium pyrrolidine dithiocarbamate in MIBK. The extraction is then aspirated into an air-acetylene flame and the absorbance of the resonance line at 283.3 nm measured.

Sample Handling: Use raw or filtered acidified brine.

Range: Precision: ±10% Accuracy: ±10%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 114-A

Reagents:
- Ammonium pyrrolidine dithiocarbamate solution
- Methyl isobutyl ketone
- Lead standard solutions, prepared from lead and dilute HNO₃

Literature Reference:
- APHA 301-A-III (1975)

Equipment:
- AA spectrophotometer
- Separatory funnels

Remarks:
1. Improves sensitivity, for very low concentrations of lead.
2. Use of standard additions recommended.
3. Alternatively, chloroform may be used as the extraction solvent (ASTM 3559-77B (1977)).

Edition: 7/78
**Pb**

**Inductively Coupled Plasma-Atomic Emission Spectroscopy**

**Method:** The brine sample is aspirated into a radiofrequency generated argon plasma and the intensity of the emission spectrum of lead is analyzed by the instrument and compared with standards. Intensity is measured at 220.35 nm or alternate wavelength.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:** 3-5 orders of magnitude from a single spectral line.

**Precision:** ± 1-10%

**Accuracy:**

**Cross Reference:** Appendix 2

**Sampling Methods:** 11-S, 29-S

**Reagents:** Lead standard solution, prepared from metallic lead and dilute nitric acid

**Equipment:** Inductively coupled plasma-atomic emission spectrometer

**Remarks:**

1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics. Background correction and standard addition recommended. Other metal ions may be measured simultaneously.

2. Upper limit of concentration range may be extended by using alternate spectral lines.

**Edition:** 7/78


**Literature Reference:** "Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System" EPA-600/4-77-032, June 1977.

**Additional References:**
**Pb**

**Lead**

**Analysis:** Spark Source Mass Spectrometry

**Method:** Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Lead is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:** 0.1-1000 mg/l  
**Precision:** ±25%  
**Accuracy:** ±25%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S

**Literature Reference:**  

**Reagents:**  
Solid lead standard sample

**Equipment:**  
Spark source mass spectrometer

**Remarks:**  
1. Other elements may be determined simultaneously with lead.  
2. Additional references:


**Edition:** 7/78
Analysis: Emission Spectrometry

Method: The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark, and the intensity of the selected lead emission line is measured against standards.

Sample Handling: Use raw or filtered acidified brine. Evaporation to dryness may be required.

Range:  

Precision:  

Accuracy:  

Cross Reference: Appendix 2  
Sampling Methods: 11-S, 29-S  

Literature Reference: Instrument Manufacturer's Literature  

Reagents: Lead standards  

Equipment: Emission spectrometer  

Remarks: 1. Use matrix matching, standard additions, and background correction whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78
Lithium

**Analysis:** Atomic Absorption

**Method:** Sample is aspirated directly into an air-acetylene flame and lithium is determined from the degree of absorption of the Li resonance line at 670.8 nm.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:** 0.05-2 mg/l

**Precision:** ±5%

**Accuracy:** ±10%

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 120-A

**Reagents:**
- Lithium standard solutions; prepared from Li₂CO₃ and hydrochloric acid
- Potassium chloride

**Literature Reference:**
- ASTM D3561-77 (1977)

**Equipment:**
- AA spectrophotometer

**Remarks:**
1. Interference by ionization of Li in flame can be suppressed by matching matrix of standards and samples for alkali and alkali earths metals. Addition of KCl to a final K⁺ concentration of 2000 μg/l recommended. Standard additions method also compensates for matrix effects.
2. If sample shows Tyndall effect, filter through a 0.45 μ membrane filter.
3. On same instruments a red filter is used.

**Edition:** 7/78
Analysis: Flame Emission

Method: Lithium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 670.8 nm from lithium is measured by a spectrophotometer.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by dilution with 9 parts distilled water and adding 5 ml HNO₃ per liter of sample.

Range: >0.05 mg/l  
Precision: <0.5 mg/l ±25%  
Accuracy: <0.5 mg/l ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 119-A

Reagents:
Lithium atomic absorption standard solutions or lithium carbonate
Hydrochloric acid (to dissolve lithium carbonate)
Potassium chloride or potassium nitrate

Remarks:
1. Lithium is partially ionized in an air-acetylene flame. This ionization may be suppressed by adding either potassium nitrate or potassium chloride to give a potassium concentration of 2000 ppm potassium.
2. Careful matrix matching between sample and standards must be made (i.e. use same amounts of alkali metal and alkaline earth metal ions).
3. High concentrations of sulfate interfere.
4. Use of standard additions recommended.

Edition: 7/78

Literature Reference:

Equipment:
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer
**Li**

**Lithium**

**Analysis:** Ion-Exchange Chromatography

**Method:** Ionic components are separated on sulfonated polymer-based column. Dilute nitric acid solution is used as the eluting solvent. The separation column is followed by a suppressor column to remove highly concentrated background components, and lithium is detected by a conductivity detector.

**Sample Handling:** Use raw or filtered acidified brine.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision: ±1.35%</th>
<th>Accuracy: ±5%</th>
</tr>
</thead>
</table>

**Cross Reference:**
Appendix 2
Sampling Methods: 11-S, 29-S

**Literature Reference:**
Dionex Corp., Sunnyvale, CA, Literature
Microchem. Jour. 22, (45-49) (1977)
Anal. Chem. 49, 2, 3, 401 (1977)

**Reagents:**
Standard lithium solution
Nitric acid solution; .003 M

**Equipment:**
Dionex ion chromatograph
75-120 psi air supply
Cation separator column; 6mm x 250mm
Cation suppressor column; 9mm x 250mm

**Remarks:**
1. May be determined simultaneously with potassium, sodium, and ammonium cations.

**Edition:**
7/78
Lithium

**Analysis:** Spark Source Mass Spectrometry

**Method:** Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Lithium is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:** 0.1-1000 mg/l  
**Precision:** ±25%  
**Accuracy:** ±25%

**Cross Reference:** Appendix 2  
Sampling Methods: 11-S, 29-S

**Reagents:**  
Solid lithium standard sample

**Literature Reference:**  

**Equipment:**  
Spark source mass spectrometer

**Remarks:**

**Edition:** 7/78

C-126
Lithium

Method: Sample is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected lithium emission line is measured against standards.

Sample Handling: Use raw or filtered acidified brine. Evaporation to dryness may be required.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Dilute to</th>
<th>≤ 1.0 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accuracy:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Lithium stock solution; may be prepared from Li₂CO₃ and HCl

Remarks:
1. Some flames (e.g. O₂-H₂-N₂) may not be hot enough to vaporize completely the aerosol from solutions with high solids contents.
2. Reference standards should contain as high a salt content as unknowns.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78
Mg

Magnesium

Analysis: EDTA Titrimetric

Method: Magnesium is determined volumetrically by titrating with EDTA in the presence of a compleximetric indicator dye at pH 10. A sample aliquot is first buffered and titrated with EDTA to a blue endpoint using Eriochrome indicator. This gives the Ca + Mg concentration. A second sample aliquot is treated with 4N NaOH and titrated with EDTA to a purple endpoint using murexide indicator. This gives the Ca concentration. The magnesium concentration is calculated by difference.

Sample Handling: Use raw acidified or filtered acidified brine.

Range:  
Precision:  
Accuracy:  

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 55-A, 92-A, 93-A

Reagents:  
Murexide (ammonium purpurate)  
Sodium hydroxide (4N)  
EDTA  
Ammonium chloride-ammonium hydroxide buffer  
Calcium standard  
Magnesium standard  
Eriochrome Black T  
Hydroxylamine hydrochloride

Remarks: Barium and strontium interfere when present in quantities greater than 30 mg/l.

Equipment:  
Buret

Edition: 7/78

C-128

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 55-A, 92-A, 93-A

Reagents:  
Murexide (ammonium purpurate)  
Sodium hydroxide (4N)  
EDTA  
Ammonium chloride-ammonium hydroxide buffer  
Calcium standard  
Magnesium standard  
Eriochrome Black T  
Hydroxylamine hydrochloride

Remarks: Barium and strontium interfere when present in quantities greater than 30 mg/l.

Equipment:  
Buret
Magnesium

Analysis: Atomic Absorption

Method: Solutions containing magnesium are aspirated directly into an air-acetylene flame and the absorbance of the resonance line at 285.2 nm is measured.

Sample Handling: Use raw or filtered acidified brine. Sample may be stabilized by dilution with 9 parts distilled water and adding 5 ml HNO₃ per liter of sample.

Range: 0.01-0.4 mg/l

Precision: ±5%

Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Magnesium stock solution, may be prepared by dissolving magnesium ribbon in 1:1 HCl
Potassium chloride
Nitrous oxide gas cylinder (option)
Lanthanum chloride

Literature Reference:
EPA 00927 (1976)
USGS Book 5, Chapter A1, APHA 301 A. II (1975)
ASTM D2576-70, D511-76C (1977)

Equipment:
Atomic Absorption spectrophotometer
Nitrous oxide burner head (option)

Remarks:
1. Aluminum and silicon interfere; effect may be largely removed by addition of 0.1-1%(w/v) La or use of nitrous oxide/acetylene flame. Ionization interference also occurs. Matrix of samples and standards should be matched for alkali salts and/or a final K⁺ concentration of 2000 mg/l should be added to all solutions. Standard additions technique recommended.
2. If sample shows a Tyndall effect, filter through a 0.45 µ membrane filter.

Edition: 7/78
Magnesium

Method: The brine sample is aspirated into a radiofrequency generated argon plasma and the intensity of the emission spectrum of magnesium is analyzed by the instrument and compared with standards. Intensity is measured at 279.55 nm or alternate wavelength.

Sample Handling: Use raw or filtered acidified brine.

Range: single spectral line. Precision: ± 1-10% Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Magnesium standard solution, prepared from magnesium ribbon and dilute HCl

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks:
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics.
2. This instrument allows simultaneous measurement of several metal cations.
3. Background correction and standard additions method recommended.
4. Upper limit of concentration range may be extended by using alternate spectral lines.

Edition: 7/78
## Mg

### Analysis:
Spark Source Mass Spectrometry

### Method:
Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Magnesium is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

### Sample Handling:
Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate samples and analyze residue.

### Range:
0.1-1000 mg/l

### Precision:
±25%

### Accuracy:
±25%

### Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

### Literature Reference:
D.L. Donohue, J.A. Carter and J.C. Franklin

### Reagents:
Magnesium standards

### Equipment:
Spark source mass spectrometer

### Remarks:

---

Edition: 7/78
**Analysis:** Neutron Activation

**Method:** Dehydrated sample is irradiated by neutron bombardment to form radioactive magnesium isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of magnesium present.

**Sample Handling:** Filter brine on site. Evaporate sample and irradiated residue with neutron source.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td>Literature Reference:</td>
<td>Equipment:</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Remarks:** Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest. Other elements may be analyzed simultaneously with magnesium.

**Edition:** 7/78
Magnesium

Analysis: Emission Spectrometry

Method: The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected magnesium emission line is measured against standards.

Sample Handling: Use raw or filtered acidified brine. Evaporation to dryness may be required.

Range: 0.1-1 mg/l
Precision: ±10%
Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Magnesium standards
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Use matrix matching, standard additions, and background correction whenever possible.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Manganese

Analysis: Atomic Absorption

Method: Manganese may be determined by aspirating the aqueous sample directly into an air-acetylene flame and measuring the absorbance of the resonance line at 279.4 nm.

Sample Handling: Use raw or filtered acidified brine. Sample may be stabilized with 5 ml HNO₃ per liter of sample.

Range: 0.07-3 mg/l
Precision: ±5%
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 131-A

Reagents:
Mn stock solution, 1000 ppm purchased or prepared from metallic manganese in 1:1 nitric acid
Nitrous oxide gas cylinder (option)

Remarks: 1. Interferences by silica, iron and phosphate, nickel, and cobalt have been reported in the literature, and the use of a nitrous oxide/acetylene flame or oxidizing air-acetylene flame suggested. Alkali salt content of samples and standard should be matched. Standard additions technique also recommended. Use of a background correction lamp at a nearby wavelength also suggested.

Equipment:
Atomic Absorption Spectrophotometer
Nitrous oxide burner head (option)

Literature Reference:
EPA 01055 (1976)
ASTM D2576-70, D858-77B (1977)
Dean and Rains, 1975, Vol. III.

Edition: 7/78

(cont. on back)
3. Manganese absorbance is also depressed in the presence of perchlorate, when using a reducing air/acetylene flame. In an oxidizing air/acetylene flame or a nitrous oxide/acetylene flame, this interference is not present.
Manganese

**Analysis:** Atomic Absorption (MIBK Extraction)

**Method:** Manganese is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl ketone (MIBK). The extraction is aspirated into an air-acetylene flame and the absorbance of the resonance line at 279.5 nm is measured.

**Sample Handling:** Use raw or filtered acidified brine.

**Range:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Precision: ±10%</th>
<th>Accuracy: ±10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis Methods: 130-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reagents:**

- Ammonium pyrrolidine dithiocarbamate solution
- Methyl isobutyl ketone
- Manganese standard solutions, prepared from manganese metal in dilute nitric acid

**Literature Reference:**

- ASTM 858-77C (1977)

**Equipment:**

- Atomic Absorption Spectrophotometer
- Separatory funnels

**Remarks:**

1. Extraction procedure improves sensitivity and helps to eliminate background interferences.
2. Use of standard additions recommended.
3. Alternatively, chloroform may be used as the extraction solvent, (ASTM D858-77C (1977)).

Edition: 7/78
**Mn**

**Manganese**

**Sample Handling:** Use filtered acidified, raw unacidified or filtered unacidified brine.

<table>
<thead>
<tr>
<th>Analysis:</th>
<th>X-ray Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.</td>
</tr>
</tbody>
</table>

**Range:**

**Precision:**

**Accuracy:**

**Cross Reference:**

Appendix 2

Sampling Methods: 11-S, 29-S

**Reagents:**

Manganese standards

**Equipment:**

X-ray fluorescence spectrophotometer

**Remarks:**

<table>
<thead>
<tr>
<th>Literature Reference:</th>
</tr>
</thead>
</table>

**Edition:**

7/78 C-136
Mn

Manganese

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: The brine sample is aspirated into a radiofrequency generated argon plasma and the intensity of the emission spectrum of manganese is analyzed by the instrument and compared with standards. Intensity is measured at 257.61 nm or alternate wavelength.

Sample Handling: Use raw or filtered acidified brine.

Range: 3-5 orders of magnitude from a single spectral line. Precision: ± 1-10% Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Manganese standard solution, prepared from metallic manganese and dilute nitric acid

Literature Reference:

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks:
1. NaCl matrix of samples and standards should be matched to minimize differences in solution properties which can affect vaporization characteristics.
2. This spectrometer allows simultaneous analysis of several metal cations.
3. Background correction and standard additions method recommended.
4. Upper limit of concentration range may be extended by using alternate spectral lines.

Edition: 7/78

(cont. on back) C-137
Manganese

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated brine sample is vaporized and ionized by an arc source and enters an evacuated chamber. Manganese is separated and detected by its mass/charge ratio and determined quantitatively by comparison with standards.

Sample Handling: Use raw or filtered acidified brine.

Range: 0.1-1000 mg/l  Precision: ±25%  Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Solid manganese standard sample

Remarks: Several elements of interest may be analyzed simultaneously with this instrumentation.

Edition: 7/78

No. 134-A

Manganese

Literature Reference:

Equipment:
Spark source mass spectrometer
Analysis: Neutron Activation

Method: Dehydrated sample is irradiated by neutron bombardment to form radioactive manganese isotopes. The beta and gamma spectra are analyzed by a multichannel analyzer; peak heights are proportional to the amount of manganese present.

Sample Handling: Filter brine on site. Evaporate sample and irradiated residue with neutron source.

Range:  

Precision:  

Accuracy:  

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S

Literature Reference:  

Reagents: Standards containing manganese

Equipment: Reactor  
Multichannel analyzer

Remarks: Sufficient time (several days) must be allowed for sodium decay if the sodium spectrum masks the element of interest. Other elements may be determined simultaneously with manganese.

Edition: 7/78
**Mn**

**Manganese**

<table>
<thead>
<tr>
<th>Analysis:</th>
<th><strong>Emission Spectrometry</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>The brine sample in either solid or liquid state is vaporized using a flame, d-c arc, or a-c spark and the intensity of the selected manganese emission line is measured against standards.</td>
</tr>
<tr>
<td>Cross Reference:</td>
<td></td>
</tr>
<tr>
<td>Sample Handling:</td>
<td>Use raw or filtered acidified brine. Evaporation to dryness may be required.</td>
</tr>
<tr>
<td>Range:</td>
<td>0.06-2 mg/l</td>
</tr>
<tr>
<td>Precision:</td>
<td>±10%</td>
</tr>
<tr>
<td>Accuracy:</td>
<td></td>
</tr>
<tr>
<td>Literature Reference:</td>
<td>Instrument Manufacturer's Literature</td>
</tr>
<tr>
<td>Reagents:</td>
<td>Manganese standards, Vanadium internal standard</td>
</tr>
<tr>
<td>Equipment:</td>
<td>Emission spectrometer, Photo processor, Microphotometer</td>
</tr>
<tr>
<td>Remarks:</td>
<td>1. Use matrix matching, standard additions, and background correction whenever possible.</td>
</tr>
<tr>
<td></td>
<td>2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).</td>
</tr>
</tbody>
</table>

Edition: 7/78
Analysis: Cold Vapor Atomic Absorption

Method: Mercury is oxidized to its Hg(II) state, then reduced to elemental mercury. The mercury vapor is circulated through a cell in an atomic absorption instrument and the absorption of the mercury resonance line at 253.7 nm is measured.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: 0.05-10 µg/l  
Precision: ±10%  
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 18-S, 29-S

Reagents:
Nitric acid
Hydrochloric acid
Potassium permanganate
Sodium chloride
Hydroxylamine sulfate
Stannous chloride
Mercuric chloride
Potassium persulfate
Sulfuric acid

Equipment:
Atomic absorption spectrophotometer or equivalent cold vapor mercury analyzer to measure at 253.7 nm.
Woodriff Furnace (option)

Remarks:
1. Certain volatile organic materials absorb at 253.7 nm. If this is suspected the sample should be analyzed without addition of stannous chloride (under oxidizing conditions). Obtain true value by difference between this value and reducing condition (with stannous chloride).
2. Additional permanganate (up to 25 ml) may be needed to overcome high chloride and sulfide values in brines.
3. High copper concentrations can cause interference.

Edition: 7/78
C-141
4. When using Woodriff Furnace an organic vapor trap apparatus is used due to high salt content. This allows for volatilization of any Hg in the sample without salt carryover to the graphite sample collection cup where the Hg is collected on a gold substrate.
Analysis: X-Ray Fluorescence  
Method: Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

Sample Handling: Use filtered acidified, raw unacidified, or filtered unacidified brine.

Range: 
Precision: 
Accuracy: 

Cross Reference: 
Appendix 2
Sampling Methods: 11-S, 18-S, 29-S

Literature Reference: 

Reagents: 
Mercuric chloride or other mercury standard.

Equipment: 
X-ray fluorescence spectrophotometer

Remarks: Detection limit 1-5 ppm not sensitive for water samples without much preconcentration, sample would have to be evaporated or ion exchanged.

Edition: 7/78
Analysis: Neutron Activation

Method: Sample is exposed to neutron source (reactor) and radioactive mercury isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of mercury present is proportional to the measured activity.

Sample Handling: Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 18-S, 29-S

Literature Reference:

Reagents:

Equipment:
Reactor (neutron source)
Multichannel analyzer

Remarks: 1. Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.
2. Since mercury is a volatile element, evaporation to complete dryness may volatilize mercury (Rowe, Fournier, and Morey, 1973, USGS Bulletin #1303).

Edition: 7/78
Analysis: Emission Spectrometry

Method: The sample containing mercury in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range:  

Precision:  

Accuracy:  

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 18-S, 29-S

Reagents:  
Mercury standards

Literature Reference:  
Instrument Manufacturer's Literature

Equipment:  
Emission spectrometer

Remarks: 1. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
pH

Analysis: pH meter

Method: The pH of a solution is determined by measuring the potential of the solution between glass and reference electrodes. The pH may be determined in batch form with dip type electrodes or flow-through form using flow-through cells.

Sample Handling: Use RU. Analyze within 6 hours of sampling. Record temperature of sample at time of pH measurement.

Range: 0-14 pH units
Precision: ±1%
Accuracy: ±1%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

APHA 424 (75)
ASTM D1293-65 (77)
API 2.1 (68)
EPA (76)

Remarks:
1. Interferences: temperature must be controlled, glass electrode suffers from Na ion interference at high pH and acid interference at low pH, poorly buffered sample difficult to analyze (unless flow-through is used), oil and grease coat electrodes, no interferences from color, turbidity, oxidants, reductants or colloidal matter.
2. Field analysis on fresh raw brine strongly recommended; commercial field pH meters available. Avoid loss or interchanges of gases.
3. Record sample temperature at time of pH measurement.

Reagents: Distilled water pH buffers

Equipment: pH meter
Glass electrode
Reference electrode

Edition: 7/78
4. Oxidation of various ions such as iron or manganese can influence pH.

5. The reaction $2\text{HCO}_3^- + \text{H}_2\text{O} + \text{CO}_2 + \text{CO}_3^{2-}$ increases pH.
Phosphate

Analysis: Colorimetric (Stannous Chloride)

Method: In acid solution molybdate is added to form molybdophosphoric acid which is reduced to the molybdenum blue complex by stannous chloride.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range: 2-25 mg/l  Precision: ±26%  Accuracy: ±29%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 143-A, 144-A

Literature Reference:
APHA 425 E (1975)

Reagents:
Sulfuric acid
Phenolphthalein indicator
Ammonium molybdate
Potassium dihydrogen phosphate
Nitric acid
Stannous chloride

Equipment:
Spectrophotometer to measure at 690 nm.

Remarks:
1. Increased sensitivity can be achieved or interferences can be overcome by benzene-isobutanol solvent - molybdate reagent extraction and further treatment as described in APHA 425 E (1975).
2. A preliminary digestion with ammonium persulfate allows for conversion of other phosphate forms to ortho phosphates which allows analyst to use this test for total phosphates (APHA 425 C (1975)). A precipitate may form during this digestion but it will not interfere with the analysis.

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(cont. on back) C-146
3. Alternatively the orthophosphate phosphorous is extracted selectively as phosphomolybdic acid into methyl isobutyl ketone from a 2 M HClO₄ medium. The yellow complex is then reduced to the molybdenum Blue complex and measured at 625 nm.

4. Arsenic can be a significant interference unless it is reduced first.
Analysis: Colorimetric (Ascorbic Acid Reduction)

Method: Orthophosphate reacts with ammonium molybdate and Sb-K tartrate to form an antimony phosphate tartrate complex which is reduced by ascorbic acid to a blue molybdenum complex. The complex is measured colorimetrically at 880 or 625-650 nm.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range: 0.03-40 mg/l
Precision: ±10%
Accuracy: ±10%

Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 142-A, 144-A

Reagents:
- Sulfuric acid
- Antimony potassium tartrate
- Ammonium molybdate
- Ascorbic acid
- Potassium dihydrogen phosphate

Equipment:
- Spectrophotometer or auto analyzer to measure at 880 nm or 625-650 nm.

Remarks:
1. A preliminary digestion with ammonium persulfate allows for conversion of other phosphate forms to ortho phosphates which allows analyst to use this test for total phosphates (APHA 425 C (1975)).
2. A modification using an amino reduction in place of ascorbic acid (ASTM D515-72B) allows for a fourfold increase in color intensity.
3. Silica, arsenic and ferric ions cause interference.
4. Alternatively the reduction may be accomplished using amino-naphthol-sulfuric acid (Anal. Chem. 32 824 (1960)).

Edition: 7/78

C-147
5. Arsenic must be reduced first to avoid significant interference.
Phosphate

**Analysis:**
Modified Molybdophosphoric Acid Spectrophotometric Method

**No.** 144-A

**Method:**
Orthophosphate and molybdate react in acidic solution to give a yellow color of molybdophosphoric acid. The molybdophosphoric acid is extracted with 20% by volume of 1-butanol in chloroform and the resultant extract measured at a wave length of 310 nm.

**Sample Handling:**
Use filtered unacidified brine.

**Range:** 2.5-25 ppm

**Precision:** ±30%

**Accuracy:** ±30%

**Cross Reference:**
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 142-A, 143-A

**Reagents:**
Potassium dihydrogen phosphate reagent grade KH$_2$PO$_4$
Sodium molybdate reagent grade Na$_2$MoO$_4$·2H$_2$O
1-Butanol - reagent grade
Chloroform reagent grade

**Remarks:**
The selective extraction of molybdophosphoric acid eliminates interference due to silicate, arsenate, and germanate.

**Equipment:**
Spectrophotometer for use at 310 nm
Absorption cells 1 cm light path

**Literature Reference:**
Phosphate

Analysis: **X-Ray Fluorescence**

Method: Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

Sample Handling: Use filtered acidified, raw unacidified or filtered unacidified brine.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 18-S, 29-S

Reagents:
Potassium dihydrogen phosphate or other phosphate standard

Equipment:
X-ray fluorescence spectrophotometer

Remarks: 1. Analysis gives result as phosphorus concentration. To obtain the phosphate concentration multiply by the gravimetric factor PO₄⁻³ (i.e., \([\text{PO}_4^{3-}] = [\text{P}] \times 3.07\)).

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C-149
Phosphate

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 213.62 nm.

Sample Handling: Use filtered acidified or raw acidified brine.

3-5 orders of magnitude from Range: a single spectral line. Precision: ± 1-10% Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Potassium dihydrogen phosphate or other phosphate standard

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks:
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.
3. Background correction and standard additions method recommended.

Edition: 7/78
4. Analysis gives result as phosphorous concentration. To obtain the phosphate concentration multiply by the gravimetric factor \( \frac{P_{04}}{P} \) (i.e., \([P_{04}^{-3}] = [P] \times 3.07\)).
**Analysis:** Spark Source Mass Spectrometry  
**No.:** 147-A

**Method:** Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Phosphorous is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

**Sample Handling:** Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate brine samples and analyze residue.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision: ±25%</th>
<th>Accuracy: ±25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-1000 mg/l</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
- Potassium dihydrogen phosphate or other phosphate standard

**Equipment:**
- Spark source mass spectrometer

**Remarks:** 1. Analysis gives result as phosphorous concentration. To obtain the phosphate concentration multiply by the gravimetric factor $P_4^3$ (i.e., $[P_4^3] = [P] \times 3.07$).

**Edition:** 7/78
## Analysis:

**Specific Ion Electrode**

**Method:**
A potassium specific electrode is used to measure potassium ion activity in a solution of pH 1-12.

## Sample Handling:
Use raw unacidified, filtered unacidified, raw acidified or filtered acidified brine.

## Range:

<table>
<thead>
<tr>
<th>Accuracy</th>
<th>Precision</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&gt;0.04 mg/l</td>
</tr>
</tbody>
</table>

## Cross Reference:

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Sampling Methods</th>
<th>Analysis Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>11-S, 29-S</td>
<td>182-A</td>
</tr>
</tbody>
</table>

## Reagents:

- Potassium standard solutions or potassium chloride
- Sodium chloride

## Equipment:

- Potassium specific ion electrode
- Specific ion meter
- Magnetic stirrer
- Reference electrode compatible with potassium electrode.

## Remarks:
1. Easily adapted for field measurement.

**Edition:**
7/78
## Potassium Analysis: Atomic Absorption

### Method:
Potassium is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the potassium absorbance at 766.5 nm is measured and is proportional to the potassium concentration.

### Sample Handling:
Use filtered acidified or raw acidified brine.

### Range:
(linear) 0.05-2 mg/l

### Precision:
±5%

### Accuracy:
±10%

### Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 150-A

### Literature Reference:
- Instrument Manufacturer's Std. Methods Manual
- EPA 00937 (1976)
- ASTM D3561-77 (1977)

### Reagents:
- Potassium atomic absorption standard solution or potassium chloride
- Sodium chloride
- Cesium chloride or cesium nitrate

### Equipment:
- Atomic absorption spectrophotometer

### Remarks:
1. Ionization in air-acetylene flame can be suppressed by the addition of cesium nitrate or cesium chloride to give 1000 ppm Cs in all solutions.
2. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).
3. On some AA spectrophotometers a red filter is used to reduce background radiation.

### Edition:
7/78 (Cont. on back)
4. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.

5. 1% strontium wt/vol is also effective in suppressing ionization.

6. Use of standard additions recommended.
Appendix 2

Sampling Methods: 11-S, 29-S
Analysis Methods: 149-A

Reagents:
Potassium atomic absorption standard solution or potassium chloride
Sodium chloride
Cesium chloride or cesium nitrate

Analysis: Flame Emission

Method: Potassium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 766.5 nm from potassium is measured by a spectrophotometer. Alternatively, the intensity at 404.4 nm may be measured.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HNO₃ per liter of sample.

Range: >0.05 mg/l
Precision: <0.5 mg/l ±25%
>0.5 mg/l ±5%
Accuracy: <0.5 mg/l ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 149-A

Reagents:
Potassium atomic absorption standard solution or potassium chloride
Sodium chloride
Cesium chloride or cesium nitrate

Equipment:
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.

Remarks:
1. Ionization of potassium in an air-acetylene flame is suppressed by the addition of 1000 ppm cesium.
2. Careful matrix matching between sample and standards is necessary (especially sodium chloride).
3. On some AA spectrophotometers a red filter is used to reduce background radiation.
4. 1% strontium wt/vol is also effective in suppressing ionization.
5. Use of standard additions recommended.

Edition: 7/78

Potassium

K

Potassium atomic absorption standard solution or potassium chloride
Sodium chloride
Cesium chloride or cesium nitrate


Ionization of potassium in an air-acetylene flame is suppressed by the addition of 1000 ppm cesium.

On some AA spectrophotometers a red filter is used to reduce background radiation.

1% strontium wt/vol is also effective in suppressing ionization.

Use of standard additions recommended.

C-154
Potassium

Analysis: X-Ray Fluorescence

Method: Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

Sample Handling: Use filtered acidified, raw unacidified, or filtered unacidified brine.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2 Nuc. Inst. and Methods, Vol. 106, pp. 525-538

Reagents: Equipment:
Potassium chloride or other X-ray fluorescence spectrophotometer potassium standard

Remarks:

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C-155
**Potassium**

**Analysis:** Inductively Coupled Plasma-Atomic Emission Spectroscopy

**Method:** Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards.

**Sample Handling:** Use filtered acidified or raw acidified brine.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cross Reference:</strong></td>
<td><strong>Literature Reference:</strong></td>
<td><strong>Equipment:</strong></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reagents:**
- Potassium chloride or other potassium standard

**Remarks:**
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.
3. Background correction and standard additions method recommended.

**Edition:** 7/78
Analysis: Ion Exchange Chromatography

Method: Ion components are separated on sulfonated polymer based columns. A solution of nitric acid is used to elute potassium from the column. The separation column is followed by a suppressor column which removes high background conductivity due to the solvent. Ions are detected with a conductivity detector.

Sample Handling: Use raw unacidified, filtered unacidified, or filtered acidified brine.

Range: Precision: ±1.24% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Potassium chloride or other potassium standard
Nitric acid

Remarks: 1. High rubidium concentrations cause interference because rubidium elutes at the same time as potassium.

Literature Reference:
Dionex Corp., Sunnyvale, CA, Literature

Equipment:
Ion exchange chromatograph

Edition: 7/78
Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Potassium is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l

Precision: ±5% (isotope dil.)

Accuracy: ±5% (isotope dil.)

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Potassium chloride or other potassium standard.

**Potential Analysis:** Neutron Activation

**Method:** Sample is exposed to neutron source (reactor) and radioactive potassium isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of potassium present is proportional to the measured activity.

**Sample Handling:** Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td></td>
<td>Literature Reference:</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reagents:</td>
<td>Equipment:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reactor (neutron source)</td>
<td>Multichannel analyzer</td>
</tr>
<tr>
<td>Remarks:</td>
<td></td>
<td>Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.</td>
</tr>
</tbody>
</table>

Edition: 7/78
Potassium

Analysis: Emission Spectrometry

Method: The sample containing potassium in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Dilute to Range: \( \leq 1.0 \text{ mg/l} \)

Precision: Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Potassium chloride or other potassium standard

Equipment:
Emission spectrometer

Remarks:
1. Some flames (e.g. \( \text{O}_2-\text{H}_2-\text{N}_2 \)) may not be hot enough to vaporize completely the aerosols from solutions with high solids contents.
2. Reference standards should contain as high a salt content as unknowns.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Analysis: Gamma Spectrometry

Method: Raw unacidified brine is put in a Merinelli flask which is placed on a gamma detector. Peak energies and areas are analyzed by a computer program and compared with values obtained with radioactive standards.

Sample Handling: Use raw unacidified brine.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Procedures Manual
Health and Safety Lab, ERDA-NY HASL-300

Reagents: Equipment:
Nuclear reference solutions
Gamma detector system [Ge(Li)-semiconductor]

Remarks: Precipitates are analyzed by filtering the samples and analyzing the residue on planchets.
Radioactive Isotopes

Analysis: Lead-210

Method: Bi-210 daughter is chemically separated from the Pb-210 parent and other contaminants and is measured by beta counting on a low-background beta counter.

Sample Handling: Use raw unacidified brine. Solutions are made acid to a pH of 1 with HNO₃ and allowed to equilibrate with stable carriers.

Range: >0.1 pCi/ml
Precision: ±10%
Accuracy: ±20%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Standardized Bi carrier
Pb carrier (10 mg/ml)
Thioacetamide
Normal acids and bases of varying molarities

Literature Reference:

Equipment:
Normal glassware
Hot water bath
Centrifuge
Filtering apparatus
Low-background beta proportional counter

Remarks:

Edition:
7/78
Analysis: Ra-226 (Radon Emanation Method)

Method: Radium is concentrated and separated by coprecipitation with barium sulfate. Precipitate is treated to remove silicates, to decompose insoluble radium compounds, and treated to remove SO₃. Precipitate is dissolved in HCl and placed in a bubbler to allow for radon growth. Rn-222 is removed from the solution by aeration, transferred to a scintillation cell and counted with an alpha scintillation counter. The amount of Rn-222 counted is proportional to the original amount of Ra-226.

Sample Handling: Use filtered acidified, raw acidified, or raw unacidified brine.

Range: >0.1 pCi/l  Precision: ±5%  Accuracy: ±8%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 17-S, 29-S
Analysis Methods: 160-A

Reagents:
Barium chloride
Hydrochloric acid
Stock Ra-226 sol'n.
Sulfuric acid
Hydrofluoric acid
Ammonium sulfate
Phosphoric acid
Ascarite
Magnesium perchlorate
EDTA-sodium salt

Potassium carbonate
Sodium carbonate
Sodium tetraborate
Hydrogen peroxide
Silicone grease
Sealing wax
Helium, nitrogen or air

Equipment:
Scintillation counter
Scintillation cells
Radon bubblers
Manometer
Gas purification tube
Sample bottles
Membrane filters
Platinum crucibles or dishes

Remarks:
1. Barium chloride should be checked for Ra-226 content (requires blank correction).
2. Alpha-emitting radionuclides Rn-219 and Rn-220 interfere.
3. An equilibration time of 4 hours must be allowed after Rn-222 transfer to the scintillation cell before the sample is counted.

Edition: 7/78
RADIOACTIVE ISOTOPES

Analysis: Ra-226

Method: Radium is carried on Pb and Ba carriers as the nitrates and sulfates; the Ba and Ra are selectively precipitated as the sulfate from EDTA solution; finally the Ba-Ra sulfate is dried on stainless steel and counted for alpha activity using disposable Zn-S phosphors and a photo-multiplier counting system. Ba-133 is used for yield correction and decay counting is used for purity checks.

Sample Handling: Use raw unacidified brine. Solutions are made acid to pH 1 using HNO₃ and allowed to equilibrate with carriers and tracer.

| Range: | >1 x 10⁻³ pCi/ml | Precision: | ±10% | Accuracy: | ±20% |

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 159-A

Reagents:
Ba-133 tracer
Ba carrier, 10 mg/ml
Pb carrier, 10 mg/ml
0.25 EDTA solution
98% HNO₃
Normal acids

Literature Reference:
(See remarks)

Equipment:
Hot water bath
Centrifuge
15 ml centrifuge cones
Gamma detection system (spectrometer or other)
Disposable Zn-S phosphors
Ludlum-type alpha counter

Remarks: References
3. Harley, J. R., Editor, "HASL Procedures Manual", Health and Safety Laboratory, HASL-78/78

(cont. on back) C-164
5. Large precipitates may form upon H₂SO₄ addition and may not completely dissolve in EDTA. This material should be analyzed separately for activity.
Analysis: Thorium Isotopes

Method: Thorium-234 tracer is equilibrated with thorium isotopes in the sample. All the thorium isotopes are carried on Pr as a fluoride and hydroxide and finally extracted into thienyltrifluoro-acetone-xylene. The organic complex is dried on stainless steel plate and the thorium evaluated by absolute alpha measurement using solid-state, surface barrier detectors and alpha spectroscopy.

Sample Handling: Use raw unacidified brine. Solutions are made acid to a pH of 1 using HNO₃ and allowed to equilibrate with carriers and tracers.

Range: \( >1 \times 10^{-3} \text{pCi/ml} \) (liter sample)  
Precision: \( \pm 10\% \)  
Accuracy: \( \pm 20\% \)

Cross Reference:
Appendix 2  
Sampling Methods: 11-S, 29-S

Reagents:
Thorium-234 tracer  
Praseodymium, 5 mg/ml  
0.5 M thienyltrifluoroacetone in xylene  
0.4 M K₂Cr₂O₇  
2 M Al(NO₃)₃  
Normal acids and bases

Equipment:
Vortex mixer  
40 ml screw-cap  
50 ml plastic centrifuge tubes  
Centrifuge  
Stainless steel plates  
Surface barrier detectors and alpha spectrometer

Literature Reference:

Remarks:

Edition:
7/78  
C-165
### Analysis: Uranium Isotopes

**Method:** Uranium-332 tracer is equilibrated with the isotopes of uranium in the sample. All of the uranium isotopes are chemically purified by anion exchange and extraction into hexone (methyl isobutyl ketone) which is dried on stainless steel. The uranium isotopes are measured by alpha spectroscopy using surface barrier detectors, and the sample activities evaluated by ratio to the tracer activity.

### Sample Handling:
Use raw unacidified brine. Solutions are made acid to a pH of 1 using HNO₃ and allowed to equilibrate with the tracer.

<table>
<thead>
<tr>
<th>Range:</th>
<th>&gt;1 x 10⁻³ pCi/ml (liter sample)</th>
<th>Precision:</th>
<th>±10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy:</td>
<td>±20%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S

### Reagents:
- Standardized U-232 tracer
- Dowex 1-x4 (50-100 mesh) anion resin
- 2.8 M Al(NO₃)₃
- Normal acids

### Equipment:
- Resin column
- Vortex mixer
- Centrifuge
- Normal glass ware
- 40 ml screw-cap vials

### Remarks:

**Literature Reference:**
Rubidium

Analysis: Atomic Absorption

Method: Rubidium is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the rubidium absorbance at 780 nm is measured and is proportional to the rubidium concentration.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: (linear) 0.07-2 mg/l  Precision: ±5%  Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 164-A

Reagents:
- Rubidium atomic absorption standard solution or rubidium chloride
- Sodium chloride
- Potassium chloride or potassium nitrate
- Ammonium oxalate (option)
- Ammonium hydroxide (option)

Remarks:
1. Ionization in an air-acetylene flame can be suppressed by the addition of potassium chloride or potassium nitrate to give 2000 ppm K in all solutions.
2. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl other alkali metal and alkaline earth metal ions).
3. An electrodeless discharge lamp will allow for better sensitivity.
4. On same AA spectrophotometers a red filter is used to reduce background radiation.

Edition: 7/78

Literature Reference:
Instrument Manufacturer's Std. Methods Manual

Equipment:
Atomic absorption spectrophotometer
5. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.
6. Use of a graphite furnace will increase sensitivity.
7. Use of standard additions recommended.
8. Potassium and calcium can interfere and give slightly higher results if background correction at 779.0 nm is not used. Calcium may be removed as an oxalate with ammonium oxalate and ammonium hydroxide.
Rubidium

<table>
<thead>
<tr>
<th>Analysis:</th>
<th>Flame Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>Rubidium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 780 nm from rubidium is measured by a spectrophotometer.</td>
</tr>
</tbody>
</table>

**Sample Handling:** Use filtered acidified or raw acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HNO₃ per liter of sample.

<table>
<thead>
<tr>
<th>Range:</th>
<th>&gt;0.05 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precision:</td>
<td>&lt;0.5 mg/l ±25%</td>
</tr>
<tr>
<td>Accuracy:</td>
<td>&gt;0.5 mg/l ±5%</td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 163-A

**Literature Reference:**

**Reagents:**
- Rubidium atomic absorption standard solution or rubidium chloride
- Sodium chloride
- Potassium chloride or potassium nitrate

**Equipment:**
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.

**Remarks:**
1. Ionization of rubidium in an air-acetylene flame is suppressed by the addition of 2000 ppm potassium.
2. Careful matrix matching between sample and standards is necessary (especially sodium chloride).
3. On some AA spectrophotometers a red filter is used to reduce background radiation.
4. Use of standard additions recommended.

**Edition:** 7/78
Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Rubidium is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l
Precision: ±25%
Accuracy: ±25%

Literature Reference:


Edition: 7/78
Rubidium

**Analysis:** Neutron Activation

**Method:** Sample is exposed to neutron source (reactor) and radioactive rubidium isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of rubidium present is proportional to the measured activity.

**Sample Handling:** Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td></td>
<td>Literature Reference:</td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reagents:**

**Equipment:**

- Reactor (neutron source)
- Multichannel Analyzer

**Remarks:** Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

**Edition:** 7/78
Analysis: Emission Spectrometry

Method: The sample containing rubidium in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: | Precision: | Accuracy:
---|---|---
Cross Reference: | Literature Reference: | Instrument Manufacturer's Literature
Appendix 2 | | |
Sampling Methods: 11-S, 29-S | | |
Reagents: | Equipment: | |
Rubidium chloride or other rubidium standard | Emission spectrometer | |
Remarks: 1. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Analysis: Gravimetric

Method: Silica in water is concentrated and precipitated as partially dehydrated silica by evaporation with HCl. The residue is ignited at 1000-1200°C and weighed; subsequently the silica present is converted to volatile silicon tetrafluoride by addition of HF. The silicon tetrafluoride is driven off by a second ignition and the difference between the weights of the remaining residue and the residue before HF treatment is considered to be the silica content.

Sample Handling: Use raw unacidified or filtered unacidified brine.

Range: Precision: Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
ASTM D859-68A (1977)
APHA 426A (1975)

Reagents:
Hydrochloric acid
Sulfuric acid
Hydrofluoric acid
Perchloric acid

Equipment:
Platinum crucibles with covers
Platinum evaporating dishes
Muffle furnace
Drying oven
Analytical balance

Remarks: 1. Avoid use of glassware as much as possible to avoid introducing SiO₂.
**SiO₂**

**Silica**

**Analysis:** Colorimetric (Heteropoly Blue)

**Method:** Soluble silica reacts with molybdate ion to produce a greenish-yellow complex which is then reduced by 1-amino-2-naphthol-4-sulfonic acid to produce a blue complex which is measured at (preferably) 815 nm or, with reduced sensitivity, at 640-700 nm.

**Sample Handling:** Use raw uncaidified brine, dilute on site if SiO₂ > 100 ppm.

**Range:** >1 mg/l  
**Precision:** ±15%  
**Accuracy:** ±15%

**Cross Reference:**
- Appendix 2  
- Sampling Methods: 11-S, 29-S  
- Analysis Methods: 170-A

**Literature Reference:**
- APHA 426 C (1975)  
- ASTM D859-68 B, C (1977)  
- EPA 00955 (1976)

**Reagents:**
- 1-amino-2-naphthol-4-sulfonic acid  
- Sodium sulfite  
- Sodium bisulfite  
- Sodium bicarbonate  
- Sulfuric acid  
- Hydrochloric acid  
- Sodium or ammonium hydroxide  
- Ammonium molybdate  
- Oxalic acid  
- Sodium meta silicate

**Equipment:**
- Spectrophotometer to measure at 815 nm or 640-700 nm.

**Remarks:**
1. If SiO₂ > 100 ppm dilute 1/10 with distilled water.  
2. Avoid use of glassware or reagents which may contain silica.  
3. Turbidity, iron, sulfide, color interfere; phosphate removed by oxalic acid.

**Edition:**
7/78  
C-173
**SiO₂**

**Silica**

**Analysis:** Colorimetric (Molybdosilicate)  
**Method:** Soluble silica reacts with molybdate ion to produce a greenish-yellow complex. The yellow silica-molybdate complex is measured directly at 410 nm with a spectrophotometer.

**Sample Handling:** Use raw unacidified brine, dilute on site if SiO₂ > 100 ppm.

**Range:** 10-100 mg/l  
**Precision:** ±14%  
**Accuracy:** ±20%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 169-A

**Literature Reference:**  
APHA 426 B (1975)  
EPA 00955 (1976)  
ASTM D859-68 B, C (1977)

**Reagents:**  
Sodium bicarbonate  
Sulfuric acid  
Hydrochloric acid  
Sodium or ammonium hydroxide  
Ammonium molybdate  
Oxalic acid  
Sodium metasilicate  
Sodium bicarbonate

**Equipment:**  
Spectrophotometer to measure at 410 nm.

**Remarks:**  
1. If SiO₂ > 100 dilute 1/10 with distilled water.  
2. Avoid use of glassware or reagents which may contain silica.  
4. Any silica present as "molybdate-unreactive" silica must be pretreated by digesting with NaHCO₃ on a steam bath for one hour.

**Edition:** 7/78
Analysis: Atomic Absorption

Method: Silicon (Si) is determined by aspirating the sample into a nitrous oxide-acetylene flame of an atomic absorption spectrophotometer. The intensity of the silicon absorbance at 251.6 nm is measured and is proportional to the silicon concentration. Silica concentration is calculated by multiplying the silicon value by the gravimetric factor - SiO₂/Si = 2.14.

Sample Handling: Use filtered acidified or raw acidified brine. Sample should be diluted in field if SiO₂ > 250 mg/l, otherwise precipitation may occur before analysis (10:1 dilution suggested).

Range: (linear) 3-150 mg/l  Precision: ±5-25%  Accuracy: ±5-25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 172-A

Reagents:
Silicon atomic absorption standard solution or sodium metasilicate
Nitrous oxide gas cylinder

Remarks: 1. HF, boric acid and potassium at a level of 1% or greater cause severe depression in silicon absorbance. Use of a slightly reducing flame with red feather height of 5mm minimizes this effect.
2. Burner height position is very important since there is a narrow region of nitrous oxide-acetylene flame where Si absorbs. Burner height of 7mm is recommended.
3. Low-acetylene tank pressure can cause acetone to be aspirated (with commercial grade acetylene). This will result in complete lack of sensitivity being observed on absorbance.

Equipment:
Atomic absorption spectrophotometer
Nitrous oxide burner head

Edition: 7/78

Revision: C-175
4. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).

5. Use of standard additions recommended.

6. If samples show Tyndall effect filter through 0.45 μ membrane filter.
**Silica**

**Analysis:** Flame Emission

**Method:** Silicon is determined by aspirating the sample into a nitrous oxide-acetylene flame and the emission intensity at 251.6 nm from silicon is measured by a spectrophotometer. Silica concentration is calculated by multiplying the silicon value by the gravimetric factor $\frac{SiO_2}{Si} = 2.14$.

**Sample Handling:** Use filtered acidified or raw acidified brine. Sample should be diluted in field if $SiO_2 > 100$ mg/l (10:1 dilution suggested).

<table>
<thead>
<tr>
<th>Cross Reference</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis Methods: 171-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon atomic absorption standard solution or sodium metasilicate</td>
<td>Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.</td>
</tr>
<tr>
<td>Nitrous oxide cylinder</td>
<td>Nitrous oxide burner head</td>
</tr>
</tbody>
</table>

**Remarks:**
1. HF, boric acid and potassium at a level of 1% or greater cause severe depression in silicon absorbance. Use of a slightly reducing flame with red feather height of 5mm minimizes this effect.
2. Burner height position is very important since there is a narrow region of nitrous oxide-acetylene flame where Si absorbs. Burner height of 7mm is recommended.
3. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions.

**Edition:** 7/78

C-176
**SiO₂**

**Silica**

<table>
<thead>
<tr>
<th>Analysis:</th>
<th>Inductively Coupled Plasma-Atomic Emission Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 288.16 nm or alternate wavelength.</td>
</tr>
</tbody>
</table>

| Sample Handling:  | Use filtered acidified or raw acidified brine. Sample should be diluted in field if SiO₂ > 100 mg/l (10:1 dilution suggested). |

| Range:            | 3-5 orders of magnitude from a single spectral line |
| Precision:        | ± 1-10% |
| Accuracy:         | |

| Sample Handling:  | |
| Equipment:        | Inductively coupled plasma-atomic emission spectrometer |

**Reagents:**
- Sodium metasilicate or other silica standard

**Remarks:**
- 1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.

**Edition:** 7/78 (cont. on back)
3. Background correction and standard additions method recommended.

4. Upper limit of concentration range may be extended by using alternate spectral lines.

5. To convert from silicon to silica concentration multiply by the gravimetric factor \( \frac{\text{SiO}_2}{\text{Si}} \) (i.e., \([\text{SiO}_2] = [\text{Si}] \times 2.14\)).
### Analysis: Spark Source Mass Spectrometry

**Method:** Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Silicon is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

### Sample Handling:
Use filtered acidified, raw acidified, filtered unacidified or raw unacidified brine. Evaporate samples and analyze residue.

### Range: 0.1-1000 mg/l
### Precision: ±25%
### Accuracy: ±25%

### Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S

### Literature Reference:

### Reagents:
- Sodium metasilicate or other silica standard

### Equipment:
- Spark source mass spectrometer

### Remarks:
1. If SiO$_2$ > 100 mg/l field dilution is recommended. (10:1 dilution suggested.)
2. To convert from silicon to silica concentration multiply by the gravimetric factor $\frac{SiO_2}{Si} = [Si] \times 2.14$. 

**Edition:**
7/78

C-178
Analysis: Emission Spectrometry

Method: The sample containing silica in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine. Sample should be diluted in field if SiO₂ > 100 mg/l (10:1 dilution suggested).

Range: 0.2-2 mg/l (as Si)  Precision: ±10%  Accuracy:  

Cross Reference:  
Appendix 2  
Sampling Methods: 11-S, 29-S

Reagents:  
Sodium metasilicate or other silica standard  
Vanadium internal standard

Remarks: 1. Matrix matching (use of equivalent amounts of alkali and alkaline earth metals) in standards important.  
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78  
C-179
Analysis: Atomic Absorption

Method: Silver is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the silver absorbance at 328.1 nm is measured and is proportional to the silver concentration.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter.

Range: (linear) 0.01-4 mg/l

Precision: <3 mg/l ±25%  >3 mg/l ±5%

Accuracy: <3 mg/l ±25%  >3 mg/l ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 177-A

Reagents:
Silver Atomic Absorption standard solution or silver nitrate
Sodium chloride

Equipment:
Atomic absorption spectrophotometer

Remarks:
1. No known interferences with AA method.
2. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).
3. Graphite furnace atomization may be used to detect low concentrations.
4. Some matrix interferences can be eliminated by using a deuterium arc background correction system.

Edition: 7/78

(Cont. on back)
5. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.

6. Recovery of precipitated silver can affect accuracy. Precipitated silver is determined by filtration of sample through a 0.45 μ filter, ashing filter paper followed by dissolution with ammonia and measurement via AA.

7. Use of standard additions recommended.
Ag

Silver

Analysis: MIBK Extraction

Method: Silver is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is then aspirated directly into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the silver absorbance at 328.1 nm is measured and is proportional to the silver concentration.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: Precision: Accuracy: ±15%

Cross Reference: Appendix 2
Sampling Methods: 11-2, 29-S
Analysis Methods: 176-A

Reagents:
Silver atomic absorption standard solution or silver nitrate
Methyl isobutyl ketone
Ammonium pyrrolidine dithiocarbamate

Literature Reference:
APHA 301 A (1975)

Equipment:
Atomic absorption spectrophotometer
Separatory funnels

Remarks:
1. No known interferences with AA method.
2. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).
3. Some matrix interferences can be eliminated by using a deuterium arc background correction system.
4. Use of standard additions recommended.

Edition: 7/78

C-181
**Silver**

<table>
<thead>
<tr>
<th>Analysis:</th>
<th>Inductively Coupled Plasma-Atomic Emission Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method:</td>
<td>Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 328.07 nm or at alternate spectral line.</td>
</tr>
</tbody>
</table>

**Sample Handling:** Use filtered acidified or raw acidified brine.

- **3-5 orders of magnitude from**
- **Range:** a single spectral line
- **Precision:** ± 1-10%
- **Accuracy:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver nitrate or other silver standard</td>
<td>Inductively coupled plasma-atomic emission spectrometer.</td>
</tr>
</tbody>
</table>

**Remarks:**
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.
3. Probable spectral interference from iron at silver 328.07 nm line when analyzing concentrated brines.

4. Use of standard additions and background correction recommended.

5. Upper limit of concentration range may be extended by using alternate spectral lines.
<table>
<thead>
<tr>
<th>Analysis: Spark Source Mass Spectrometry</th>
<th>No. 179-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Silver is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.</td>
<td></td>
</tr>
</tbody>
</table>

**Sample Handling:**
Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate brine samples and analyze residue.

<table>
<thead>
<tr>
<th>Range: 0.1-1000 mg/l</th>
<th>Precision: ±25%</th>
<th>Accuracy: ±25%</th>
</tr>
</thead>
</table>

**Cross Reference:**
Appendix 2
Sampling Methods: 11-S, 29-S

**Literature Reference:**

**Reagents:**
Silver nitrate or other silver standard

**Equipment:**
Spark source mass spectrometer

**Remarks:**
Analysis: Neutron Activation

Method: Sample is exposed to neutron source (reactor) and radioactive silver isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of silver present is proportional to the measured activity.

Sample Handling: Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Sampling Methods: 11-S, 29-S

Reagents: Equipment:

Remarks: Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

Edition: 7/78
Ag

Silver

Analysis: Emission Spectrometry

Method: The sample containing silver in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: 0.04-0.2 mg/l

Precision: ±10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Instrument Manufacturer's Literature

Reagents:
Silver nitrate or other silver standard
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Use of matrix matching (equivalent amounts of alkali and alkaline earth metals) in standards important.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
**Na**

**Sodium**

**Analysis:** Specific Ion Electrode

**Method:** A sodium specific electrode is used to measure sodium ion activity in a solution with the pH buffered at 11.0.

**Sample Handling:** Use raw unacidified or filtered unacidified brine.

**Range:** >0.02 mg/l  
**Precision:** ±5%  
**Accuracy:**

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 148-A

**Literature Reference:**  
ASTM D2791-77A (1977)  
Orion Research Inc., Literature

**Reagents:**  
- Sodium standard solutions or sodium chloride  
- Ammonium chloride  
- Ammonium hydroxide

**Equipment:**  
- Sodium specific ion electrode  
- Specific ion meter  
- Magnetic stirrer

**Remarks:**  
1. Interferences are from Ag⁺, Li⁺, H⁺, K⁺, NH₄⁺. Elevation of pH so that H⁺ concentration is 3-4 orders of magnitude lower than that for sodium makes electrode response independent of H⁺ concentration.  
2. Easily adapted for field measurement.

**Edition:**  
7/78  
C-186
### Analysis:
Atomic Absorption

### No.
183-A

### Method:
Sodium is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the sodium absorbance at 589 nm is measured and is proportional to the sodium concentration.

### Sample Handling:
Use filtered acidified or raw acidified brine.

<table>
<thead>
<tr>
<th>Range: (linear) 0.02-1 mg/l</th>
<th>Precision: ±5%</th>
<th>Accuracy: ±10%</th>
</tr>
</thead>
</table>

### Cross Reference:
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 184-A

### Literature Reference:
- EPA 00929 (1976)

### Reagents:
- Sodium atomic absorption standard solution or sodium chloride
- Potassium chloride or potassium nitrate

### Equipment:
- Atomic absorption spectrophotometer

### Remarks:
1. Sodium is partially ionized in an air-acetylene flame. This ionization may be suppressed by adding either potassium nitrate or potassium chloride to give a potassium concentration of 2000 ppm potassium.
2. Careful matrix matching between sample and standards must be made (i.e. use same amounts of alkali metal and alkaline earth metal ions).
3. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.

**Edition:** 7/78
4. Use of standard additions recommended.

5. All glass and plasticware should be acid washed and thoroughly rinsed to prevent sodium contamination.
**Sodium Analysis:** Flame Emission

**Method:** Sodium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 589 nm from sodium is measured by a spectrophotometer. Alternatively the emission at 330.3 nm may be measured.

**Sample Handling:** Use filtered acidified or raw acidified brine. Sample may be stabilized by dilution with 9 parts distilled water and adding 5 ml HNO₃ per liter.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0.05 mg/l</td>
<td>&lt;0.5 mg/l ±25%</td>
<td>&lt;0.5 mg/l ±25%</td>
</tr>
</tbody>
</table>

**Cross Reference:**
- Appendix 2
- Sampling Methods: 11-S, 29-S
- Analysis Methods: 183-A

**Reagents:**
- Sodium atomic absorption standard solution or sodium chloride
- Potassium chloride or potassium nitrate

**Literature Reference:**

**Equipment:**
- Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer

**Remarks:**
1. Sodium is partially ionized in an air-acetylene flame. This ionization may be suppressed by adding either potassium nitrate or potassium chloride to give a potassium concentration of 2000 ppm potassium.
2. Careful matrix matching between sample and standards must be made (i.e. use same amounts of alkali metal and alkaline earth metal ions).

**Edition:**
7/78
Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: 

Precision:

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Sodium chloride or other sodium standard

Equipment:
Inductively coupled plasma-atomic emission spectrometer


2. Background correction and standard additions method recommended.

Edition: 7/78
Analysis: Ion Exchange Chromatography

Method: Ion components are separated on sulfonated polymer based columns. A solution of nitric acid is used to elute sodium from the column. The separation column is followed by a suppressor column which removes high background conductivity due to the solvent. Ions are detected with a conductivity detector.

Sample Handling: Use raw or filtered unacidified brine or filtered acidified brine.

Range: Precision: ±0.40% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Sodium chloride or other sodium standard
Nitric acid

Literature Reference:

Equipment:
Ion exchange chromatograph

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Sodium is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l  Precision: ±25%  Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Sodium chloride or other sodium standard

Remarks:

Edition: 7/78
**Na**

**Sodium**

**Analysis:** Neutron Activation

**No.** 188-A

**Method:** Sample is exposed to neutron source (reactor) and radioactive sodium isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of sodium present is proportional to the measured activity.

**Sample Handling:** Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

**Range:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature Reference:</td>
<td>Equipment:</td>
<td></td>
</tr>
</tbody>
</table>

**Remarks:**

**Edition:** 7/78 C-192
### Analysis: Emission Spectrometry

**Method:** The sample containing sodium in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

### Sample Handling: Use filtered acidified or raw acidified brine.

### Range:  ≤ 1.0 mg/l

### Precision:  

### Accuracy:  

### Cross Reference:  
  - Appendix 2
  - Sampling Methods: 11-S, 29-S

### Literature Reference:  
  - Instrument Manufacturer's Literature

### Equipment:  
  - Emission spectrometer

### Reagents:  
  - Sodium chloride or other sodium standard

### Remarks:  
1. Some flames (e.g. O₂-H₂-N₂) may not be hot enough to vaporize completely the aerosol from solutions with high solids contents.
2. Reference standards should contain as high a salt content as unknowns.
3. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

**Edition:** 7/78

**C-193**
Sr

Strontium

Analysis: Atomic Absorption

Method: Strontium is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the strontium absorbance at 460.7 nm is measured and is proportional to the strontium concentration.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: (linear) 0.02-5 mg/l  Precision: ±5%  Accuracy: ±10%

Cross Reference: Appendix 2  Sampling Methods: 11-S, 29-S  Analysis Methods: 191-A

Reagents:
- Strontium atomic absorption standard solution or strontium nitrate
- Potassium chloride or potassium nitrate
- Nitrous oxide gas cylinder (option)
- Lanthanum chloride

Remarks:
1. Strontium is partially ionized in an air-acetylene flame. Ionization is suppressed by adding 2000 ppm potassium to the standards and samples.
2. Silica, aluminum, titanium, zirconium, phosphate and sulfate depress Sr absorbance in an air-acetylene flame. These effects can be eliminated by adding 1% (w/v) lanthanum or 0.01 M EDTA with 2000 ppm lanthanum also being present. These effects can also be removed by using a nitrous oxide-acetylene flame and adding 2000 ppm K.
3. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).

Equipment:
- Atomic absorption spectrophotometer
- Nitrous oxide burner head (option)

Literature Reference:
- Instrument Manufacturer's Std. Methods Manual
- ASTM D3352-74 (1977)

Reagents:
- Strontium atomic absorption standard solution or strontium nitrate
- Potassium chloride or potassium nitrate
- Nitrous oxide gas cylinder (option)
- Lanthanum chloride

Remarks:
1. Strontium is partially ionized in an air-acetylene flame. Ionization is suppressed by adding 2000 ppm potassium to the standards and samples.
2. Silica, aluminum, titanium, zirconium, phosphate and sulfate depress Sr absorbance in an air-acetylene flame. These effects can be eliminated by adding 1% (w/v) lanthanum or 0.01 M EDTA with 2000 ppm lanthanum also being present. These effects can also be removed by using a nitrous oxide-acetylene flame and adding 2000 ppm K.
3. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).

Edition: 7/78
4. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.
5. Use of a graphite furnace will increase sensitivity.
6. Use of standard additions recommended.
Sr

Strontium

Analysis: Flame Emission

Method: Strontium is determined by aspirating the sample into an air-acetylene flame and the emission intensity at 460.7 nm from strontium is measured by a spectrophotometer.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by dilution with 9 parts distilled water and adding 5 ml HNO₃ per liter.

<table>
<thead>
<tr>
<th>Range:</th>
<th>&gt;0.05 mg/l</th>
<th>Precision:</th>
<th>&lt;0.5 mg/l ±25%</th>
<th>&gt;0.5 mg/l ±5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy:</td>
<td>&lt;0.5 mg/l ±25%</td>
<td>&gt;0.5 mg/l ±5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 190-A

Reagents:
Strontium atomic absorption standard solution or strontium nitrate
Potassium chloride or potassium nitrate
Nitrous oxide gas cylinder (option)

Literature Reference:

Equiiment:
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer
Nitrous oxide burner head (option)

Remarks:
1. Strontium is partially ionized in an air-acetylene flame. Ionization is suppressed by adding 2000 ppm potassium to the standards and samples.
2. Silica, aluminum, titanium, zirconium, phosphate and sulfate depress Sr absorbance in an air-acetylene flame. These effects can be eliminated by adding 1% (w/v) lanthanum or 0.01 M EDTA with 2000 ppm lanthanum also being present. These effects can also be removed by using a nitrous oxide-acetylene flame and adding 2000 ppm K.
3. Careful matrix matching between sample and standards must be made (i.e. using same amounts of NaCl, other alkali metal and alkaline earth metal ions).

Edition: 7/78
4. Use of standard additions recommended.

5. Background determined by reading donor solution blank at 460.7 nm instead of at 454.0 nm as specified on same instruments.
Analysis: X-Ray Fluorescence

Method: Liquid samples are made to fluoresce by X-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

Sample Handling: Use filtered acidified, raw unacidified or filtered unacidified brine.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2 Nuc. Inst. and Methods, Vol. 106, pp. 525-538

Reagents: Equipment:
Strontium nitrate or other strontium X-ray fluorescence spectrophotometer standard

Remarks:

Edition: 7/78
Strontium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

Method: Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 338.07 nm or alternate wavelength.

Sample Handling: Use filtered acidified or raw acidified brine.

3-5 orders of magnitude from a single spectral line

Range: Precision: ± 1-10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Strontium nitrate or other strontium standard

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks:
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.

Edition: 7/78 (cont. on back)
3. Background correction and standard additions method recommended.

4. Upper limit of concentration range may be extended by using alternate spectral lines.
Sr

Strontium

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Strontium is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l

Precision: ±5% (isotope dil)

Accuracy: ±5% (isotope dil.)

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Strontium nitrate or other strontium standard

Equipment:
Spark source mass spectrometer


Edition: 7/78 C-198
**Sr**

**Strontium**

**Analysis:** Neutron Activation

**Method:** Sample is exposed to neutron source (reactor) and radioactive strontium isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of strontium is proportional to the measured activity.

**Sample Handling:** Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

<table>
<thead>
<tr>
<th>Range:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Reference:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appendix 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Literature Reference:</th>
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<table>
<thead>
<tr>
<th>Reagents:</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Equipment:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor (neutron source)</td>
<td>Multichannel analyzer</td>
</tr>
</tbody>
</table>

**Remarks:** Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

**Edition:** 7/78
Sr

Strontium

Analysis: Emission Spectrometry

Method: The sample containing strontium in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: 10-100 mg/l
Precision: ±10%
Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Strontium nitrate or other strontium standard
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks: 1. Matrix matching (using equivalent amounts of alkali and alkaline earth metals) in standards important.
2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

Edition: 7/78

C-200
Sulfate

Analysis: Gravimetric

Method: Sulfate is precipitated as barium sulfate in a hydrochloric acid medium by the addition of barium chloride. After a period of digestion, the precipitate is filtered, washed with hot water until free of chloride, ignited, and weighed as BaSO₄.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range: >10 mg/l
Precision: ±2%
Accuracy: ±2%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 31-A, 198-A

Literature Reference:
APHA 427 A, B (1975)
ASTM D516-68A (1977)
API 2.71 (1968)

Reagents:
Methyl red indicator
Hydrochloric acid
Barium chloride
Silver nitrate
Nitric acid
Silicone fluid
Anticreep fluid

Equipment:
Steam bath
Drying oven
Muffle furnace
Dessicator
Analytical balance
Porous bottom silica or porcelain crucible
Fritted glass filter or membrane filter
Filtering apparatus appropriate to filter selected

Remarks:
1. Interferences leading to high results are suspended matter, silica, barium chloride precipitant, nitrate, sulfite and water.
2. Interferences leading to low results are alkali metal sulfates, hydrogen sulfates of alkali metals, chromium and iron.

Edition: (cont. on back)
7/78
C-201
3. A modification to this procedure for high SiO₂ brines involves addition of BaCl₂ to a hot HCl acidified (pH adjusted to 1-2) sample. After this the solution is allowed to boil and the solid produced allowed to floculate and settle. The precipitate is filtered and ashed. The material is then fused with Na₂CO₃ and Na₂O₂. The melt is then leached with water, cooled and filtered. Filtrate is acidified slowly with HCl. Filtrate is evaporated and residue baked until dry. Residue is re-dissolved with water and filtered. Filtrate is acidified with HCl and boiled followed by treatment with BaCl₂. Precipitate is filtered and ashed at 800°C and resulting solid weighed as BaSO₄. (John Bricarelo, Westec Services, Inc., Calipatria, CA).

4. Samples containing suspended or insoluble material must be filtered before analyses.

5. A cleanup procedure when large amounts of calcium are present is presented below: Sulfate analysis by BaCl₂ - thorin titration can be done after running sample through cation exchange resin mainly to remove calcium. An alternative cleanup technique would be to run sample through an ammonium exchanger on an aluminum support.
Analysis: Turbidimetric

Method: Sulfate is converted to a barium sulfate colloidal suspension under controlled conditions. The concentration of the sulfate is then determined turbidimetrically.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range: 500-1500 mg/l

Precision: ±9%

Accuracy: ±20%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 31-A, 197-A

Reagents:
Glycerol
Hydrochloric acid
Ethyl alcohol (95%) or isopropyl alcohol
Sodium chloride
Barium chloride
Sulfuric acid
Sodium sulfate
Glycerol (option)

Literature Reference:
APHA 427-C (1975)
ASTM D516-68 B (1977)
API 2.72 (1968)
EPA 00945 (1976)

Equipment:
Magnetic stirrer
Nephelometer or spectrophotometer to measure at 420 nm or filter photometer with violet filter having maximum transmittance at 420 nm.
Stopwatch
Measuring spoon 0.2-0.3 ml. capacity

Remarks:
1. Color or suspended matter in large amounts interferes. Suspended matter may be removed by filtration.
2. Silica in excess of 500 mg/l interferes.
3. Precision and accuracy may be influence by the ionic strength of some brines.

Edition: 7/78

(cont. on back)
4. A conditioning reagent of glycerol-sodium chloride solution can be added to stabilize the suspension and minimize interferences.

5. All parameters of the method must be closely controlled in order to obtain reproducible results, i.e. acid concentration, crystal size of BaCl₂, stirring time, and loose time between adding BaCl₂ crystals and spectrophotometric reading.
Analysis: Atomic Absorption

Method: The sample containing sulfate is treated with a quantitative excess of barium chloride. The amount of barium remaining in solution following precipitation of barium sulfate is determined by atomic absorption, using a nitrous oxide-acetylene flame and measuring the absorbance at 553.6 nm.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range:  

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Precision:</th>
<th>Accuracy:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling Methods: 11-S, 29-S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis Methods: 32-A, 200-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagents:</th>
<th>Equipment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium chloride</td>
<td>Atomic absorption spectrophotometer</td>
</tr>
<tr>
<td>Barium atomic absorption standard solution</td>
<td>Filtration apparatus</td>
</tr>
<tr>
<td>Nitrous oxide gas cylinder</td>
<td>Nitrous oxide burner head</td>
</tr>
<tr>
<td>Potassium chloride or potassium nitrate</td>
<td></td>
</tr>
</tbody>
</table>

Remarks: 1. Barium is partially ionized in the nitrous oxide-acetylene flame. This ionization can be suppressed by adding 2000 ppm K.
2. Careful matrix matching between sample and standards must be made (i.e. use same amounts of NaCl, alkali metal and alkaline earth metal ions).
3. Graphite furnace atomization may be used for barium instead of the nitrous oxide-acetylene flame.

Edition: 7/78
Sulfate

**Analysis:** Flame Emission - Indirect

**Method:** Sulfate is determined by precipitation of the sulfate in acid solution with barium chloride. The barium sulfate is removed by centrifugation, washed with acetone and water and dissolved in warm EDTA at pH of 10.5. The solution is aspirated into a nitrous oxide-acetylene flame and the emission intensity at 553.5 nm is measured using a spectrophotometer.

**Sample Handling:** Use filtered unacidified or raw unacidified brine.

**Range:** 40-1000 mg/l  
**Precision:** ±2%  
**Accuracy:** ±2%

**Cross Reference:**  
Appendix 2  
Sampling Methods: 11-S, 29-S  
Analysis Methods: 33-A, 199-A

**Reagents:**  
Barium chloride  
Barium atomic absorption standard solution  
Nitrous oxide gas cylinder  
Potassium chloride or potassium nitrate  
Acetone  
EDTA  
Thymol blue indicator  
Leconal wetting agent

**Literature Reference:**  

**Equipment:**  
Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer  
Nitrous oxide burner head  
Centrifuge

**Remarks:**  
1. Barium is partially ionized in the nitrous oxide-acetylene flame. This ionization can be suppressed by adding 2000 ppm K.  
2. Careful matrix matching between sample and standards must be made (i.e. use same amounts of NaCl, alkali metal and alkaline earth metal ions).

**Edition:** 7/78  
C-204
Analysis: Ion Exchange Chromatography

Method: Anion components are separated on sulfonated cation exchange columns coated with finely ground anion resin. A solution of sodium bicarbonate-sodium carbonate is used to elute sulfate from the column. The separation column is followed by a suppressor column which removes high background conductivity due to the solvent. Ions are detected with a conductivity detector.

Sample Handling: Use raw or filtered unacidified brine or filtered acidified brine.

Range: Precision: ±0.06% Accuracy: ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Sulfuric acid, sodium sulfate, or other sulfate standard
NaHCO₃
Na₂CO₃

Remarks:

Equipment:
Ion exchange chromatograph

Edition:
7/78
Sulfide Analysis: Titrimetric (Iodine)  

Method: Sulfide is indirectly determined by stripping hydrogen sulfide from an acidified sample with an inert gas. Hydrogen sulfide is collected in zinc acetate solution to which excess iodine in water is added to oxidize sulfide to elemental sulfur. Excess iodine is titrated with thiosulfate.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range: 0.5-10 mg/l  
Precision: ±5% on S\(^-\) >10 mg/l  
Accuracy: ±5% on S\(^-\) >10 mg/l

Cross Reference: Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S  
Analysis Methods: 94-A

Reagents:  
Zinc acetate  
Inert gas (N\(_2\) or CO\(_2\))  
Potassium iodide  
Hydrochloric acid  
Sodium thiosulfate  
Starch  
Sodium hydroxide  
Iodine

Remarks:  
1. Reducing substances such as heavy metal ions, sulfite, thiosulfate and hydrosulfite will use up iodine and contribute positive errors.  
2. Oxygen and other oxidants react with hydriodic acid and contribute negative errors.  
3. Field analysis for sulfide is advised.  
4. Alternatively ZnS is decanted, distilled water washed and returned the contents acidified to the original container. Iodine standard solution is added with hydrochloric acid and the test proceeds as before [APHA 428D (1975)].

Edition: 7/78
Analysis: Antimony Test (Qualitative)

Method: The sample is treated with potassium antimony tartrate in the presence of hydrochloric acid. Yellow antimony sulfide, \( \text{Sb}_2\text{S}_3 \), is discernible at sulfide concentrations greater than 0.5 mg/l.

Sample Handling: Use raw unacidified or filtered unacidified brine.

Range: >0.5 mg/l

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td>APHA 428 (1975)</td>
</tr>
<tr>
<td>Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S</td>
<td></td>
</tr>
</tbody>
</table>

Reagents: Potassium antimony tartrate
Hydrochloric acid

Equipment:

Remarks: 1. Metallic ions such as lead interfere because the sulfide is held so firmly that it does not produce antimony sulfide.

2. Dithonite, which decomposes in acid solution to produce sulfide, interferes.

Edition: 7/78
**Sulfide**

**Analysis:** Colorimetric (Methylene Blue)  
**Method:** Methylene blue is formed when sulfide is reacted with 4-amino-N,N-dimethylaniline in the presence of ferric chloride. Ammonium phosphate is then added to destroy excess Fe(III). The color is measured at 600 nm.

**Sample Handling:** Use filtered unacidified or raw unacidified brine.

<table>
<thead>
<tr>
<th>Range: 0.01-1.0 mg/l</th>
<th>Precision: 0.2-400 µg/l (Lauth's Violet)</th>
<th>Accuracy:</th>
</tr>
</thead>
</table>

**Cross Reference:**  
Sampling Methods: 4-A, 11-S, 12-A, 29-S, 34-S  
Analysis Methods: 95-A

**Reagents:**  
- Potassium Iodide  
- Zinc acetate  
- Sodium Thiosulfate  
- Sodium carbonate  
- Hydrochloric acid  
- N,N-dimethyl-phenylene-diamine oxalate (also called p-amino-dimethylarniline oxalate)  
- Sulfuric acid  
- Ferric chloride  
- Diammonium hydrogen phosphate  
- Sodium sulfide  
- Sodium Hydroxide  
- Iodine  
- Starch

**Remarks:**  
1. Reducing substances such as heavy metal ions, sulfite, thiosulfate and hydrosulfite inhibit color formation.  
2. Field analysis for sulfide is advised.  
3. A modification of this method using Lauth's violet dye instead of methylene blue gives more consistent color development with brine samples.

**Literature Reference:**  
- APHA 428 C (1975)  
- API 3.10.2 (1968)

**Equipment:**  
- Spectrophotometer to measure at 600 nm  
- Burets

**Edition:**  
7/78

C-208
Sulfide

**Analysis:** Specific Ion Electrode

**Method:** The potential of a silver sulfide-silver electrode relative to a reference electrode is measured in the sample. A series of sulfide standards is used to determine the potential-concentration relationship.

**Sample Handling:** Use filtered unacidified or raw unacidified brine.

**Range:**

<table>
<thead>
<tr>
<th>Cross Reference:</th>
<th>Literature Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 2</td>
<td>Analytical Letters, 1 (13), 825 (1968).</td>
</tr>
<tr>
<td>Reagents: Sodium sulfide or other sulfide standard</td>
<td>Orion Res. Inc., Cambridge, MA Literature</td>
</tr>
<tr>
<td>EDTA</td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td></td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td></td>
</tr>
</tbody>
</table>

**Precision:**

**Accuracy:**

**Remarks:**

1. Antioxidant buffer should be added in the field to avoid negative errors from oxidation.
2. Field analysis for sulfide is advised.
3. Standard additions should be made to verify results.

**Edition:** 7/78
**Sulfide**

**Analysis:** X-Ray Fluorescence

**Method:** Liquid samples are made to fluoresce by x-ray bombardment. Secondary fluorescence is separated into wavelengths by a crystal and the radiation is detected by a scintillation counter or a flow proportional counter. A vacuum is required for the lighter elements. Standardization of instrument required.

**Sample Handling:** Use filtered unacidified or raw unacidified brine.

<table>
<thead>
<tr>
<th>Range</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cross Reference:</strong></td>
<td><strong>Reagents:</strong></td>
<td><strong>Equipment:</strong></td>
</tr>
<tr>
<td>Appendix 2 Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S</td>
<td>Sodium sulfide or other sulfide standard</td>
<td>X-ray fluorescence spectrophotometer</td>
</tr>
</tbody>
</table>

**Literature Reference:**

**Remarks:**

**Edition:** 7/78

C-210
Sulfide Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Sulfur is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered unacidified or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l

Precision: ±25%

Accuracy: ±25%

Cross Reference: Appendix 2
Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S

Reagents:
Sodium sulfide or other sulfide standard

Equipment:
Spark source mass spectrometer

Remarks:

Edition: 7/78
Sulfide Analysis: Neutron Activation

Method: Sample is exposed to neutron source (reactor) and radioactive sulfur isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of sulfide present is proportional to the measured activity.

Sample Handling: Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S

Literature Reference:

Reagents:

Equipment:
Reactor (neutron source)
Multichannel analyzer

Remarks: Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

Edition: 7/78

C-212
SUSPENDED SOLIDS

Suspended Solids

Analysis: Gravimetric

Method: Suspended solids (nonfiltrable residue) are usually determined in conjunction with filtrable solids and total solids content. Suspended solids are determined directly by filtering sample through a tared filter, drying at 103-105°C and weighing.

Sample Handling: Use raw unacidified brine. Analyze as soon as possible.

Range: 5-10,000 mg/l

Precision: ±25%

Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 210-A, 211-A, 212-A, 213-A

Literature Reference:
APHA 208 D(1975)
EPA 00530 1976
ASTM D1888-67A (1977)

Reagents:
None

Equipment:
Gooch crucible or membrane filter apparatus
Suction flash and appropriate crucible holder
Glass fiber filter mats or membrane filters
Drying oven
Desiccator
Analytical balance

Remarks:
1. Accuracy cannot be obtained since the true concentration of suspended matter is unknown.
2. Too much residue on filter will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
3. Filtration into pre-weighed crucibles on-site would be a preferred method.

Edition: 7/78

(cont. on back) C-213
4. Precipitation of iron, manganese, and silica in highly concentrated brines causes higher results than would be obtained on site.
TOTAL DISSOLVED SOLIDS (TDS)

Analysis: Gravimetric

Method: A sample is filtered through a membrane filter, evaporated in a tared drying dish, oven dried and weighed for nonfilterable residue.

Sample Handling: Use filtered unacidified brine.

Range: >2 mg/l
Precision: ±10% Below 25 mg/l ±5% Higher
Accuracy: ±10% Below 25 mg/l ±5% Higher

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 209-A

Reagents:
Drierite® or silica gel

Equipment:
Evaporating dishes
Drying oven
Desiccator
Analytical balance

Remarks:
1. Highly mineralized waters with considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing.
2. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate.
3. Too much residue in evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

Edition: 7/78

(cont, on back) C-214
4. Under certain conditions SiO₂ will settle out of brine solution upon standing. Better results should be obtainable using the suspended solids filtrate (filtered on site) and then include any further precipitation with TDS.
TURBIDITY

Analysis: Absorptometric

Method: Sample is inserted into a spectrophotometer and the amount of light not attenuated by the sample is detected. Results are determined in formazin turbidity units (= Jackson candle units).

Sample Handling: Use RU brine, determine as quickly after collection as possible.

Range: 0.1-1000 FTU

Precision: ±1%

Accuracy: ±1%

Cross Reference: Appendix 2

Sampling Methods: 11-S, 29-S

Analysis Methods: 209-A, 212-A, 213-A

Literature Reference:

Hach manual

Reagents:

Standard formazin solutions

Equipment:

Spectrophotometer or filter photometer

Remarks:

1-Interferences: true color, air bubbles, settleable matter, dirty glassware.

2-Unstable brines will yield changes in turbidity with time; field analysis of turbidity recommended.

Edition: 7/78

C-215
TURBIDITY

Analysis: Visual Matching

Method: Turbidity of sample is visually measured against turbidity standards made of Kaolin, formazin, or similar material.

Sample Handling: Use KU brine; determine as quickly after collection as possible.

Range: Precision: Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 209-A, 211-A, 213-A

Literature Reference:
APHA 214 B
"Eco Lab" Literature

Reagents: Equipment:
Kaolin bottles or test tubes or commercial material

Remarks: 1. Interferences: rapidly settleable matter, color, air bubbles.
2. Unstable brines will yield changes in turbidity with time; field analysis of turbidity recommended. Commercial kits available.
3. Precipitation of iron, manganese and silica in highly concentrated brines can cause color which contributes to error.

Edition: 7/78
TURBIDITY

Turbidity

Analysis: Nephelometric (Turbidimetric)

Method: Scattered light from a turbidity sample is measured at right angles to the incident light in a nephelometer and compared with standard formazin turbidity solutions.

Sample Handling: Use RU brine; determine as quickly after collection as possible.

Range: 0.01-100 NTU

Precision: ±1%

Accuracy: ±1%

Cross Reference: Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 209-A, 211-A, 212-A

Reagents:
Standard formazin turbidity solutions

Equipment:
Nephelometer (Turbidimeter)

Remarks:
1. Interferences: true color, air bubbles, quickly settleable matter, dirty glassware.
2. Results reported in nephelometric turbidity units.
3. Unstable brines will yield changes in turbidity with time; field analysis of turbidity recommended.

Edition: 7/78
Zn

Analysis: Atomic Absorption

Method: Zinc is determined by aspirating the sample into an air-acetylene flame of an atomic absorption spectrophotometer. The intensity of the zinc absorbance at 213.9 nm is measured and is proportional to the zinc concentration.

Sample Handling: Use raw acidified or filtered acidified brine. Sample may be stabilized by adding 5 ml HNO₃ per liter.

Range: (linear) 0.05-1 mg/l Precision: ±5% Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 71-S, 29-S
Analysis Methods: 215-A

Literature Reference:
EPA 01092 (1976) ASTM D2576-79
APHA 301 A (1975) D1691-77C (1977)
Instrument Manufacturer's Std. Methods Manual

Reagents:
Zinc atomic absorption standard solution or zinc metal
Hydrochloric acid if zinc metal is used

Equipment:
Atomic absorption spectrophotometer

Remarks:
1. No chemical interferences in an air-acetylene flame.
2. Non atomic species absorb strongly in an air acetylene flame. Use of a deuterium background correction system is recommended.
3. Careful matrix matching between sample and standards must be made (i.e. use same amounts of NaCl, other alkali metal and alkaline earth metal ions).
4. Use of a graphite furnace will increase sensitivity.

Edition: 7/78

(Cont. on back) C-218
5. If sample shows Tyndall effect, filter through 0.45 μm membrane filter.

6. Sodium and calcium cause spectral interferences which must be corrected. Sodium interferences cannot be corrected by using D₂ background compensation.

7. Use of standard additions recommended.
Zn

Analysis: Atomic Absorption Using APDC and MIBK Extraction

Method: Zinc is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is then aspirated directly into an air acetylene flame of an atomic absorption spectrophotometer. The intensity of the silver absorbance at 213.9 nm is measured and is proportional to the zinc concentration.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: <0.2 mg/l
Precision: ±10%
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 214-A

Reagents:
Zinc atomic absorption standard solution or zinc metal
Hydrochloric acid if zinc metal is used
Methyl isobutyl ketone
Ammonium pyrrolidine dithiocarbamate

Remarks:
1. No chemical interferences in an air-acetylene flame.
2. Non atomic species absorb strongly in an air-acetylene flame. Use of a deuterium background correction system is recommended.
3. Careful matrix matching between sample and standards must be made (i.e. use same amounts of NaCl, other alkali metal and alkaline earth metal ions).
4. Use of a graphite furnace will increase sensitivity.

Edition: 7/78
5. Alternatively, chloroform may be used as the extraction solvent (ASTM D1691-77D (1977)).
Zn

Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 216-A

Sample is aspirated into the argon plasma and the intensity of the emission spectrum is analyzed and compared with standards. Intensity is measured at 213.86 nm or alternate wavelength.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: a single spectral line

Precision: ± 1-10%

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:

Reagents:
Zinc metal or other zinc standard
Hydrochloric acid (to dissolve zinc)

Equipment:
Inductively coupled plasma-atomic emission spectrometer

Remarks:
1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.


Edition: 7/78 (cont. on back)
3. Background correction and standard additions method recommended.

4. Upper limit of concentration range may be extended by using alternate spectral lines.
Zn

Analysis: Spark Source Mass Spectrometry

Method: Dehydrated sample is vaporized and ionized by an arc source and enters an evacuated chamber. Zinc is separated and detected by its mass/charge ratio, and determined quantitatively by comparison with standards.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate samples and analyze residue.

Range: 0.1-1000 mg/l

Precision: ±5% (isotope dil.)

Accuracy: ±25%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Zinc metal or other zinc standard
Hydrochloric acid (to dissolve zinc)

Literature Reference:

Equipment:
Spark source mass spectrometer

Remarks:

Edition:
7/78
Zinc Analysis: Neutron Activation

Method: Sample is exposed to neutron source (reactor) and radioactive zinc isotopes are formed. The isotopes and their associated beta and gamma spectra are identified by multichannel analyzers. The amount of zinc present is proportional to the measured activity.

Sample Handling: Use raw acidified or filtered acidified brine. Evaporate samples and irradiate residue with neutron source.

Range: Precision: Accuracy:

Cross Reference: Literature Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents: Equipment:

Remarks: Sufficient time must be allowed for sodium decay if the sodium spectrum masks the element of interest.

Edition: 7/78
Analysis: Emission Spectrometry

Method: The sample containing zinc in either solid or liquid state is vaporized by a flame, d-c arc, or a-c spark and the intensity of the selected emission line is measured against standards.

Sample Handling: Use filtered acidified or raw acidified brine.

Range: 10-100 mg/l
Precision: ±10%
Accuracy: ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S

Reagents:
Zinc metal or other zinc standard
Hydrochloric acid (to dissolve zinc)
Vanadium internal standard

Equipment:
Emission spectrometer
Photo processor
Microphotometer

Remarks:
1. Matrix matching (using equivalent amounts of alkali and alkaline earth metals) in standards important.

2. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).
Analytical Methods

References

A. Standard and Recommended Methods Publications and Handbooks:


2. API Recommended Practice for Analysis of Oil-Field Waters, American Petroleum Institute, Dallas, TX, 1968.


B. Atomic Absorption and Flame Emission Spectroscopy:


C. Inductively Coupled Plasma-Atomic Emission Spectroscopy:


D. Ion Exchange Chromatography:


E. X-Ray Fluorescence:

F. Neutron Activation:

G. Ion Selective Electrodes:


H. Miscellaneous References:


I. Radioactive Counting:

J. Colorimetric Techniques:

K Spark Source Mass Spectrometry:

Correction of Brine Component Concentrations for
Steam Loss During Flashing

It may be necessary to correct the concentration of a dissolved brine component for steam loss. This can be estimated for a single stage flash if the concentration of that component after the flash is known along with the temperatures of the brine before and after flashing, the heat capacity and the heat of vaporization of the liquid at the flash temperature. The concentration of the component before flashing is calculated using the equation:

\[ A = B \left( 1 - \frac{C_p \Delta T}{\Delta H} \right) \]

where \( A \) is the concentration before flashing, \( B \) is the concentration after flashing and steam loss, \( \Delta T \) is the temperature change during the flash in degrees centigrade, \( C_p \) is the heat capacity of the liquid, and \( \Delta H \) is the heat of vaporization at the temperature of the flashed brine. \( \Delta H \) and \( C_p \) are dependent on the weight percent NaCl and the values used in the equation should be those values corresponding to the weight percent NaCl in the flashed sample. \( C_p \) and \( \Delta H \) values at various weight percentages of NaCl are given in Tables 1 and 2 respectively.

Examples of this type of calculation are given below:


From Table 2-1 of this report, the conditions of the GLEF using Woolsey #1 well are:

<table>
<thead>
<tr>
<th>Unit</th>
<th>Temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>399.6</td>
</tr>
<tr>
<td>1st Stage flash unit</td>
<td>322</td>
</tr>
<tr>
<td>2nd Stage flash unit</td>
<td>305.4</td>
</tr>
<tr>
<td>3rd Stage flash unit</td>
<td>284.4</td>
</tr>
<tr>
<td>4th Stage flash unit</td>
<td>194.5</td>
</tr>
</tbody>
</table>
TABLE 1

Heat Capacities (cal deg⁻¹ g⁻¹) for solutions containing various weight percentages of NaCl

<table>
<thead>
<tr>
<th>% NaCl</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.996</td>
<td>0.936</td>
<td>0.874</td>
<td>0.809</td>
<td>0.740</td>
<td>0.664</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>0.997</td>
<td>0.937</td>
<td>0.876</td>
<td>0.812</td>
<td>0.745</td>
<td>0.671</td>
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<tr>
<td>10</td>
<td>0.997</td>
<td>0.938</td>
<td>0.878</td>
<td>0.815</td>
<td>0.749</td>
<td>0.678</td>
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<tr>
<td>15</td>
<td>0.998</td>
<td>0.939</td>
<td>0.880</td>
<td>0.818</td>
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<td>0.684</td>
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<tr>
<td>20</td>
<td>0.998</td>
<td>0.940</td>
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<td>0.758</td>
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<td>0.883</td>
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<td>35</td>
<td>1.000</td>
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<td>0.892</td>
<td>0.839</td>
<td>0.786</td>
<td>0.729</td>
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<td>0.892</td>
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<td>0.786</td>
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<tr>
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<td>1.001</td>
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<td>0.892</td>
<td>0.840</td>
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<td>0.730</td>
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<tr>
<td>50</td>
<td>1.001</td>
<td>0.946</td>
<td>0.893</td>
<td>0.840</td>
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<td>0.731</td>
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<tr>
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<td>0.893</td>
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<td>0.730</td>
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<td>0.948</td>
<td>0.893</td>
<td>0.839</td>
<td>0.785</td>
<td>0.730</td>
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<tr>
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<td>0.949</td>
<td>0.893</td>
<td>0.839</td>
<td>0.785</td>
<td>0.729</td>
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<tr>
<td>Temp. (°C)</td>
<td>% NaCl</td>
<td>Cp</td>
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<tr>
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<td>5</td>
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<td>25</td>
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<td>0.783</td>
<td>0.726</td>
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<td>0.782</td>
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<td>205</td>
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Reference
Document No. USGS-OFR-75-675. Values in Table above were calculated from USGS values.
From Table 3-3 of the same report:

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<tr>
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<th>mg/l Potassium</th>
<th>Weight % NaCl</th>
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<td>Wellhead</td>
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<td>10,500</td>
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<tr>
<td>3rd Brine</td>
<td>11,200</td>
<td>18</td>
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<tr>
<td>4th Brine</td>
<td>12,000</td>
<td>19</td>
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The potassium concentration in the third stage brine can be calculated from the potassium concentration in the fourth stage:

\[ A = 12,000 \text{ mg/l} \left( 1 - \frac{C_p \Delta T}{\Delta H} \right) \]

From Table 1 the temperatures in degrees centigrade most closely corresponding to 284.4°F and 194.5°F are 140°C and 90°C respectively. 
Cp and \( \Delta H \) at 90°C for 19% NaCl (using the closest values for Cp and \( \Delta H \) at 20% NaCl) are 0.749 cal deg\(^{-1}\)g\(^{-1}\) and 567.8 cal g\(^{-1}\):

\[ A = 12,000 \text{ mg/l} \left( 1 - \frac{0.749 \text{ cal deg}\,^{-1}\text{g}\,^{-1}}{567.8 \text{ cal g}\,^{-1}} (140 - 90) \text{ deg} \right) \]

\[ = 11,209 \text{ mg/l} \]

This compares favorably with the experimentally determined value of 11,200 mg/l potassium in the third stage flash unit.

Example 2: The potassium concentration of the Woolsey #1 wellhead brine can be calculated from the potassium concentration of the first stage flashed brine. From Table 1 the temperatures of the wellhead and first stage flashed brine (in °C) which most closely correspond to those reported are 205°C for the wellhead brine and 160°C for the flashed brine.

From Tables 1 and 2 the Cp and \( \Delta H \) values at 16% NaCl (using the closest values at 15% NaCl and 160°C) are 0.839 cal deg\(^{-1}\)g\(^{-1}\) and 525.2 cal g\(^{-1}\), respectively:
\[ A = 10,500 \text{ mg/l} \left( 1 - 0.839 \text{ cal deg}^{-1} \text{ g}^{-1} \frac{(205 - 160) \text{ deg}}{525.2 \text{ cal g}^{-1}} \right) \]

\[ = 9745 \text{ mg/l} \]

This compares favorably with the experimentally determined potassium wellhead concentration of 9800 mg/l.
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