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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

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(a) J. G. Douglas et al., Geothermal Water and Gas -- Collected Methods for Sampling and Analysis - Comment Issue, BNWL-2094, Battelle-Northwest, Richland, WA, August 1976.

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

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(b) D. W. Shannon et al., Sampling and Analysis Methods for Geothermal Fluids and Gases, January 1978, Preliminary Edition, PNL-2750, Battelle Pacific Northwest Laboratories, Richland, WA.

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 interrelationships 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.

MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES

TASK OR OBJECTIVE	SAMPLE FORM - 1	SAMPLING PROCEDURE - 2	PROPERTY OF INTEREST - 3	pH	REDOX POTENTIAL	CONDUCTIVITY	ALKALINITY	HARDNESS	SUSPENDED SOLIDS	TURBIDITY
EXPLORATION										
LOCATE POTENTIAL RESERVOIR	SLG	D		FL						
TRACE PARENT AQUIFER	LG	D								
EVALUATE GEOTHERMAL FIELD POTENTIAL										
ESTIMATE RESERVOIR TEMPERATURE	LG	D								
CHARACTERIZE TEST WELL FLUID	L	D		FL		FL	FL	L	FL	L
DETERMINE GAS CONTENT	G	D								
DETERMINE POTENTIAL FOR MINERAL RECOVERY	L	D		FL						
DETERMINE POTENTIAL ENVIRONMENTAL IMPACTS	LG	D		FL						
ESTABLISH DESIGN CRITERIA FOR ENERGY RECOVERY SYSTEM										
DETERMINE CORROSION POTENTIAL	LG	D		FL	FL	FL	FL			
DETERMINE SCALING POTENTIAL	LG	D		FL					L	
DETERMINE REINJECTION FOULING POTENTIAL	L	D		FL					L	
SUPPORT OPERATING ENERGY RECOVERY SYSTEM										
MONITOR PRODUCED FLUID CHARACTERISTICS	L	D		FL						
MONITOR PRODUCED GAS CONTENT	G	D								
MONITOR CONDENSATE	L	D								
CHARACTERIZE SCALE	S	U	PETROGRAPHY, X-RAY DIFFRACTION, MICROPROBE AND SCANNING ELECTRON MICROSCOPY							
CHARACTERIZE ENTRAINED PARTICULATES	S	N	SCANNING ELECTRON MICROSCOPY							
MONITOR GAS RELEASED TO ATMOSPHERE	G	D								
MONITOR LIQUID WASTE - SURFACE RUN-OFF	L	D	VARIES WITH LOCATION. USE ENVIRONMENTAL IMPACT EVALUATION ABOVE AS A GUIDE							
GROUND WATER	L	D								
MONITOR DEEP RE-INJECTION FLUID	L	D		FL					L	
MONITOR DESALINATION PRODUCT - LIQUID	L	D	DETERMINED BY NATURE OF SOURCE, END USE, AND VALUE							
MINERAL	S	N								

TASK OR OBJECTIVE	DISSOLVED SOLIDS - 4	ALUMINUM	AMMONIA	ANTIMONY	ARSENIC	BICARBONATE, CARBONATE	BARIUM	BERYLLIUM	BORON	BROMIDE	CADMIUM	CALCIUM	CESIUM	CHLORIDE	CHROMIUM	COPPER	FLUORIDE	GOLD	IODIDE	IRON	LEAD
EXPLORATION																					
LOCATE POTENTIAL RESERVOIR						FL R			LR			LR		LR			LR				
TRACE PARENT AQUIFER					LR				LR	LR		LR	LR	LR			LR				
EVALUATE GEOTHERMAL FIELD POTENTIAL																					
ESTIMATE RESERVOIR TEMPERATURE									L			LR M					L				
CHARACTERIZE TEST WELL FLUID		L	FL		L	FL R			LR	L		LR	L	LR			LR		L	L	
DETERMINE GAS CONTENT																					
DETERMINE POTENTIAL FOR MINERAL RECOVERY			FL	L	L			L	L	L		L	L	L		L		L	L	L	L
DETERMINE POTENTIAL ENVIRONMENTAL IMPACTS			FL	L	L				L		L				L	L					L
ESTABLISH DESIGN CRITERIA FOR ENERGY RECOVERY SYSTEM																					
DETERMINE CORROSION POTENTIAL			FL	L	L	FL						L		L		L					
DETERMINE SCALING POTENTIAL		L	FL			FL	L					L		L						L	
DETERMINE REINJECTION FOULING POTENTIAL						FL						L					L			L	
SUPPORT OPERATING ENERGY RECOVERY SYSTEM																					
MONITOR PRODUCED FLUID CHARACTERISTICS						FL						LR	L	L							
MONITOR PRODUCED GAS CONTENT																					
MONITOR CONDENSATE																					
CHARACTERIZE SCALE																					
CHARACTERIZE ENTRAINED PARTICULATES																					
MONITOR GAS RELEASED TO ATMOSPHERE																					
MONITOR LIQUID WASTE - SURFACE RUN-OFF																					
GROUND WATER																					
MONITOR DEEP RE-INJECTION FLUID						FL								L						L	
MONITOR DESALINATION PRODUCT - LIQUID																					
MINERAL																					

TASK OR OBJECTIVE	LITHIUM	MAGNESIUM	MANGANESE	MERCURY	NICKEL	NITRATE	NITRITE	PHOSPHATE	POTASSIUM	RADIUM	RUBIDIUM	SILICA (SiO2)	SILVER	SODIUM	STRONTIUM	SULFATE	SULFIDE	TELLURIUM	THALLIUM	TIN	TITANIUM	ZINC	TOTAL DISSOLVED SOLIDS
EXPLORATION																							
LOCATE POTENTIAL RESERVOIR	LR	LR		L					LR			FL		LR		L							
TRACE PARENT AQUIFER	L		L						LR			L		LR		L							
EVALUATE GEOTHERMAL FIELD POTENTIAL																							
ESTIMATE RESERVOIR TEMPERATURE									LR			L		LR		L							
CHARACTERIZE TEST WELL FLUID	L	LR							LR		L	FL		LR		L	FL						L
DETERMINE GAS CONTENT																							
DETERMINE POTENTIAL FOR MINERAL RECOVERY	L	L		L				L	L		L		L	L	L		FL		L	L	L	L	
DETERMINE POTENTIAL ENVIRONMENTAL IMPACTS				L	L					L		L					FL	L					
ESTABLISH DESIGN CRITERIA FOR ENERGY RECOVERY SYSTEM																							
DETERMINE CORROSION POTENTIAL				L					L				L	L		L							
DETERMINE SCALING POTENTIAL		L										FL		L		L							L
DETERMINE REINJECTION FOULING POTENTIAL	L	L							L			FL			L	L							L
SUPPORT OPERATING ENERGY RECOVERY SYSTEM																							
MONITOR PRODUCED FLUID CHARACTERISTICS									LR			FL		LR									
MONITOR PRODUCED GAS CONTENT																							
MONITOR CONDENSATE																							
CHARACTERIZE SCALE																							
CHARACTERIZE ENTRAINED PARTICULATES																							
MONITOR GAS RELEASED TO ATMOSPHERE																							
MONITOR LIQUID WASTE - SURFACE RUN-OFF																							
GROUND WATER																							
MONITOR DEEP RE-INJECTION FLUID		L										FL				L							L
MONITOR DESALINATION PRODUCT - LIQUID																							
MINERAL																							

TASK OR OBJECTIVE	GASES - 5	AMMONIA	ARGON	CARBON DIOXIDE	CARBON MONOXIDE	HELIUM	HYDROCARBONS	HYDROGEN	HYDROGEN SULFIDE	KRYPTON	MERCURY	METHANE	NEON	NITROGEN	NITROUS OXIDES	OXYGEN	OXIDES OF SULFUR	RADON	XENON	
EXPLORATION																				
LOCATE POTENTIAL RESERVOIR		L		FL		FL		Lδ	FL			L				Lδ	FL			1,2,3,4,5,6,7,8,9,10
TRACE PARENT AQUIFER			L δR			FL δR		Lδ		L δR			LR						LR	5,11,12
EVALUATE GEOTHERMAL FIELD POTENTIAL																				
ESTIMATE RESERVOIR TEMPERATURE				L				L				L								2,4,5,13,14,15,16,17,18,19
CHARACTERIZE TEST WELL FLUID		L		L			L	LR	FL			L		L		FL				2,20,21,22,23
DETERMINE GAS CONTENT		L	L	L			L	L	L		L	L		L		L				23,24,25,26,27,28
DETERMINE POTENTIAL FOR MINERAL RECOVERY																				2,5,11,29,30,31,32
DETERMINE POTENTIAL ENVIRONMENTAL IMPACTS		L		FL					FL		L							L		33,34,35
ESTABLISH DESIGN CRITERIA FOR ENERGY RECOVERY SYSTEM																				
DETERMINE CORROSION POTENTIAL		L		FL				L	FL		L						FL			36
DETERMINE SCALING POTENTIAL		L		FL																36,37
DETERMINE REINJECTION FOULING POTENTIAL				FL													FL			36
SUPPORT OPERATING ENERGY RECOVERY SYSTEM																				
MONITOR PRODUCED FLUID CHARACTERISTICS																				11,38,39
MONITOR PRODUCED GAS CONTENT		LR		LR					LR											11,38,39
MONITOR CONDENSATE				LR					LR											38,39
CHARACTERIZE SCALE																				40
CHARACTERIZE ENTRAINED PARTICULATES																				
MONITOR GAS RELEASED TO ATMOSPHERE		L		L					L		L									34,35
MONITOR LIQUID WASTE - SURFACE RUN-OFF																				
GROUND WATER																				
MONITOR DEEP RE-INJECTION FLUID				FL												FL				35
MONITOR DESALINATION PRODUCT - LIQUID																				
MINERAL																				

LEGEND

1 SAMPLE FORM

S - SOLID
L - LIQUID
G - GAS

2 SAMPLING PROCEDURE (S)

E - ESTABLISHED
D - DEVELOPED BUT NOT UNIVERSALY APPLIED
U - UNDER DEVELOPMENT
N - NONE DISCOVERED BY AUTHORS. GEOPHYSICAL OR OTHER ANALYTIC METHODS MAY SATISFY REQUIREMENTS

3 PROPERTY OF INTEREST

F - FIELD ANALYSIS
L - LABORATORY ANALYSIS

4 DISSOLVED SOLIDS, 5 GASES

F - FIELD ANALYSIS
L - LAB ANALYSIS
R - RATIO WITH OTHER CONSTITUENT
M - CONSTITUENT MODIFIES INTERPRETATION OF OTHER RESULTS
δ - ISOTOPIC COMPOSITION

REFERENCES FOR MATRIX OF GEOTHERMAL TASKS AND RELATED CHEMICAL ANALYSES

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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

NO. Sampling Reference Number

SAMPLE TYPE:

Gas or liquids

SAMPLE POINT:
Pipeline, wellbore,
fumarole, etc.

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.

EDITION:
Month and
year of
current page

PAGE:

METHOD TITLE:

Immersible bottle method for collecting air-free water.

NO. 1-S

SAMPLE TYPE:

Liquid

SAMPLE POINT:

Hot springs or weir box

APPLICATION:

Sampling hot springs or weir boxes (from silencers).

REFERENCES:

Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977. (See note V on page B-1)

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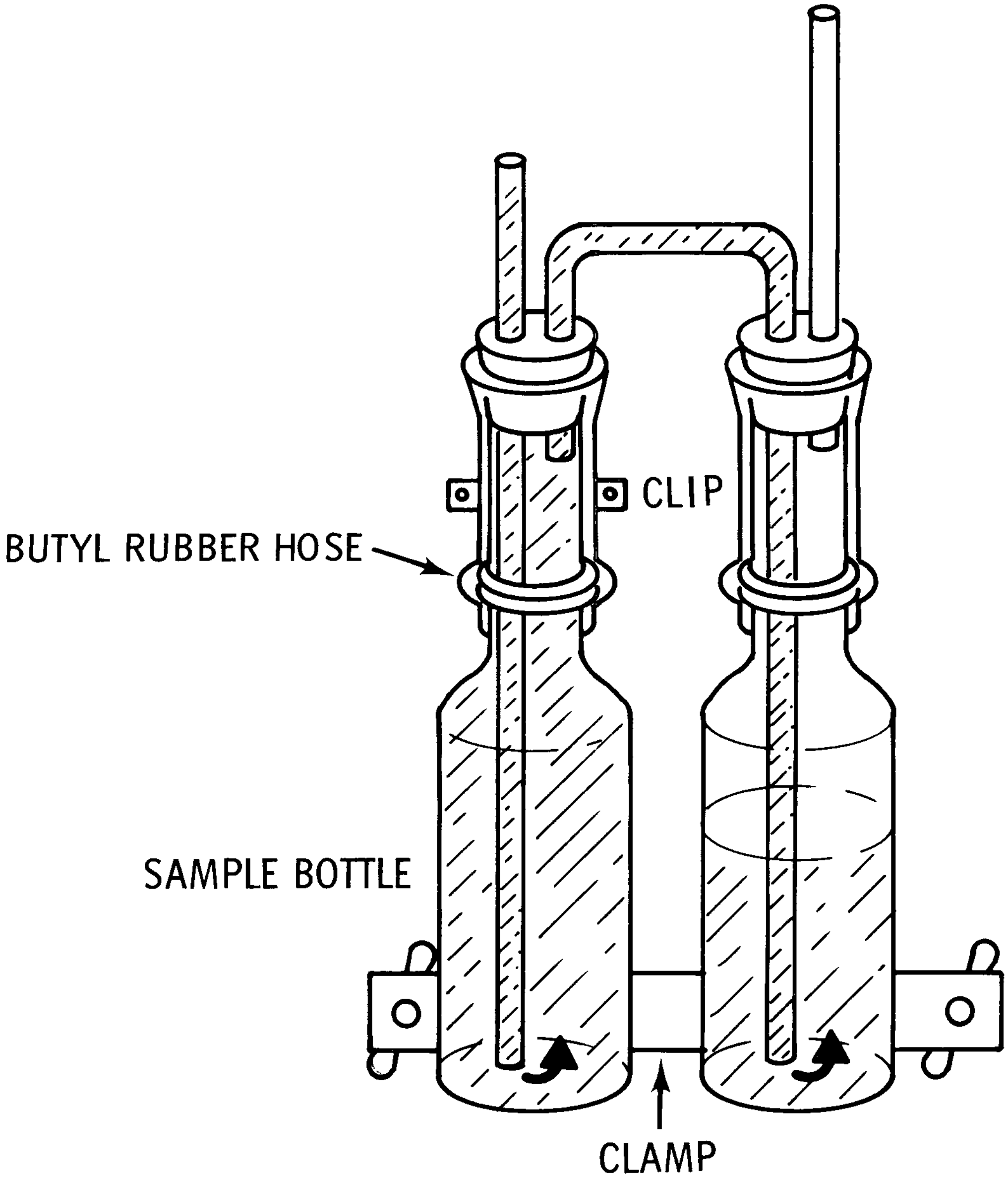
DESCRIPTION

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.	**NO.** 2-S	
	SAMPLE TYPE: Gas	**SAMPLE POINT:** Hot springs
APPLICATION: Sampling gases from hot springs.	**REFERENCES:** Finlayson, J.B. "The Collection and Analysis of Volcanic and Hydrothermal Gases," Geothermics Special Issue 2, Vol. 2, p. 1344-1354, 1970. Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977. (See note V on page B-1)	

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:

EDITION: 7/78

ILLUSTRATION:

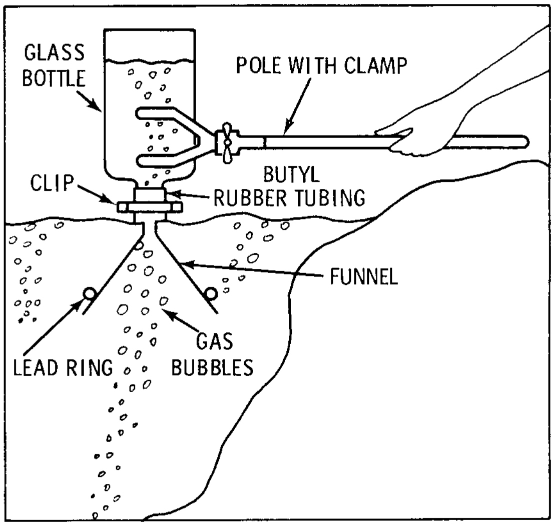


FIG 1. GAS COLLECTION FROM A BUBBLING SPRING BY WATER DISPLACEMENT

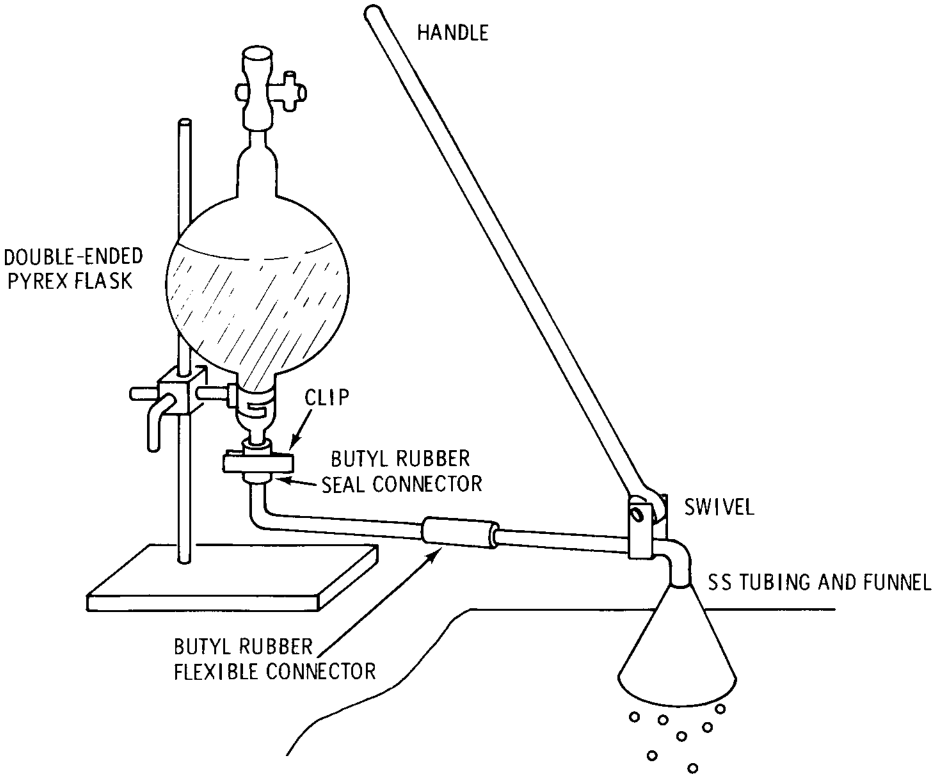


FIG 2. APPARATUS FOR COLLECTING GAS SAMPLES FROM SPRINGS

METHOD TITLE:

Seep (from hot springs) sampling method.

NO. 3-S

SAMPLE TYPE: Liquid

SAMPLE POINT: Hot springs seep

APPLICATION:

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

REFERENCES:

Wollenberg, H.A. "Sampling Hot Springs for Radioactive and Trace Elements," Lawrence Berkeley Laboratory Report LBL-4422, October 1975.

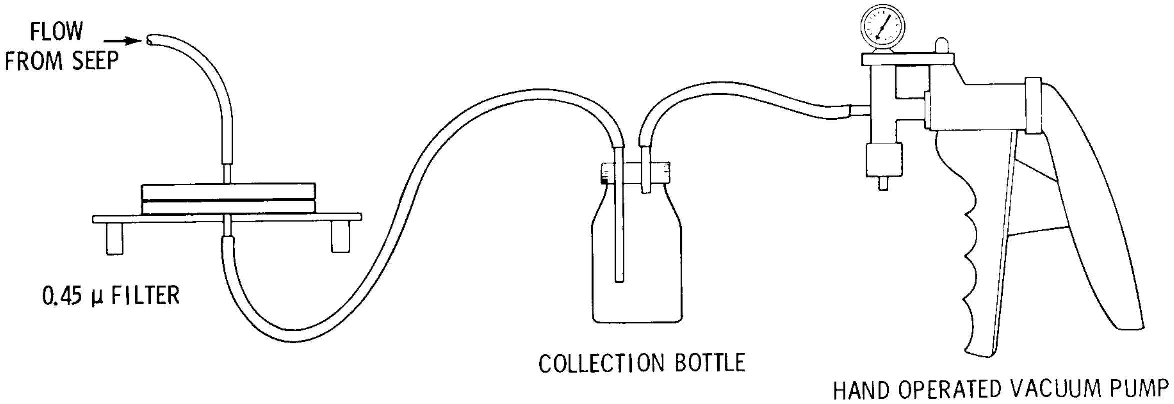
DESCRIPTION

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

COMMENTS:

EDITION: 7/78

ILLUSTRATION:



Portable filtering apparatus with hand-operated vacuum pump.

METHOD TITLE:

Round bottom flask method for collecting volcanic gases.

NO. 4-S

SAMPLE TYPE:

Gas

SAMPLE POINT:

Fumarole

APPLICATION:

Sampling volcanic gases.

REFERENCES:

Giggenbach, W. F., "A Simple Method for Collection and Analysis of Volcanic Gas Samples," in press Bul. Volc.

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_2O_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.

EDITION: 7/78

ILLUSTRATION:

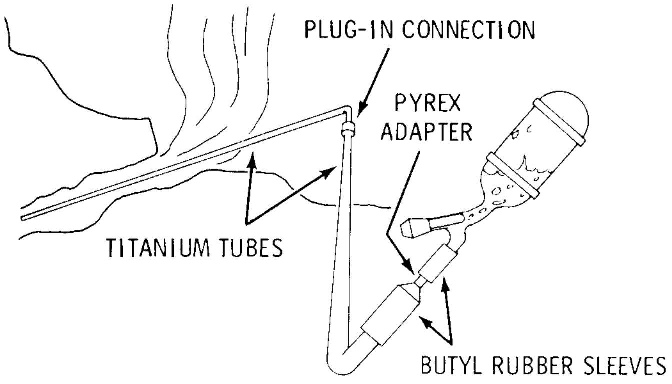


Figure 1. Apparatus for collection of volcanic gas samples.

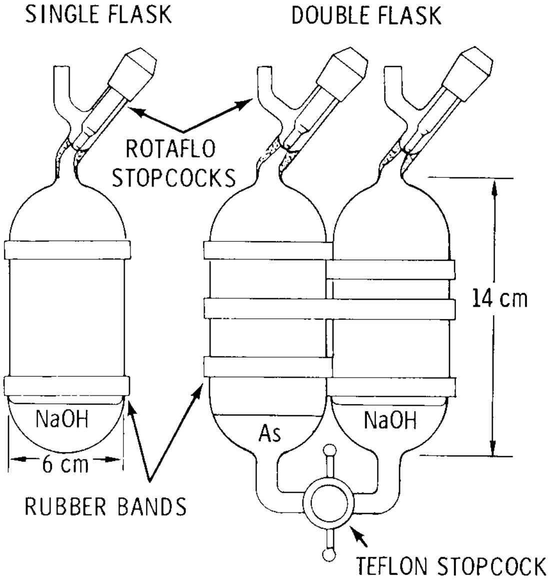


Figure 2. Collection bottles for volcanic gas samples.

METHOD TITLE:

Evacuated flask method for fumarole sampling.

NO. 5-S

SAMPLE TYPE: Gas

SAMPLE POINT: Fumarole

APPLICATION:

Sampling steam and gas from volcanic fumaroles.

REFERENCES:

Ellis, A.J. et al., "Methods of Collection and Analysis of Geothermal Fluids," Report No. C.D. 2103 New Zealand Dept. of Sci. and Ind. Res., New Zealand, July 1968.

Finlayson, J.B. "The Collection and Analysis of Volcanic and Hydrothermal Gases," Geothermics Special Issue 2, Vol. 2, p. 1344-1354, 1970.

Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977. (See note V on page B-1)

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 CO_2 and H_2S. Separate collections for NH_3, F, B, and SiO_2 are made in evacuated flasks containing no alkali.
4. The residual gases N_2, CH_4, H_2, 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 H_2S and CO_2 can be achieved by attaching a vacuum pump to the flask outlet and removing the residual gases.

EDITION: 7/78

ILLUSTRATION:

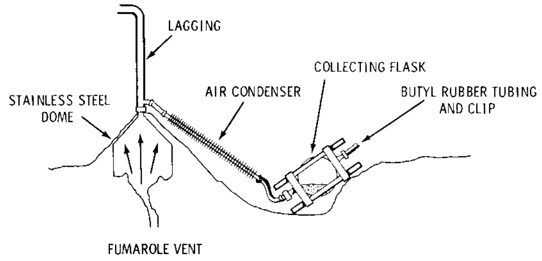


FIG 1. METHOD OF SAMPLING FUMAROLIC GAS & STEAM BY CONDENSATION IN EVACUATED FLASKS

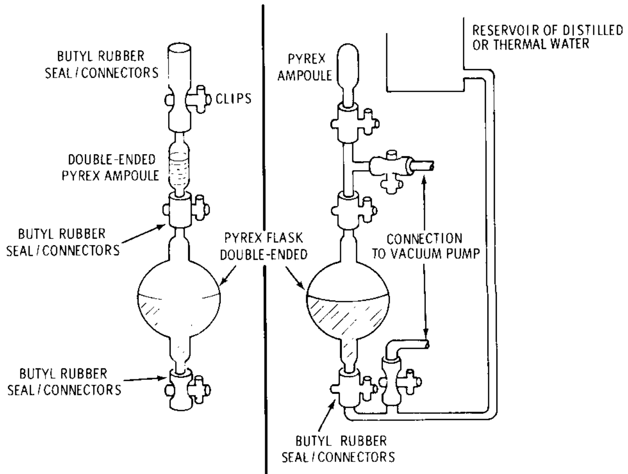


FIG 2.

FIG 3.

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

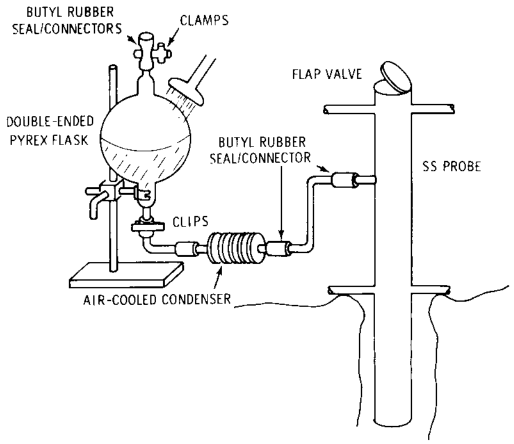


FIG 4. APPARATUS FOR SAMPLING LARGE FUMAROLES

METHOD TITLE:

Naughton tube method for sampling volcanic fumaroles.

NO. 6-S

SAMPLE TYPE:

Gas

SAMPLE POINT:

Fumarole

APPLICATION:

Sampling of gases from fumaroles.

REFERENCES:

Finlayson, J.B. "The Collection and Analysis of Volcanic and Hydrothermal Gases," Geothermics Special Issue 2, Vol. 2, p. 1344-1354, 1970.

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.

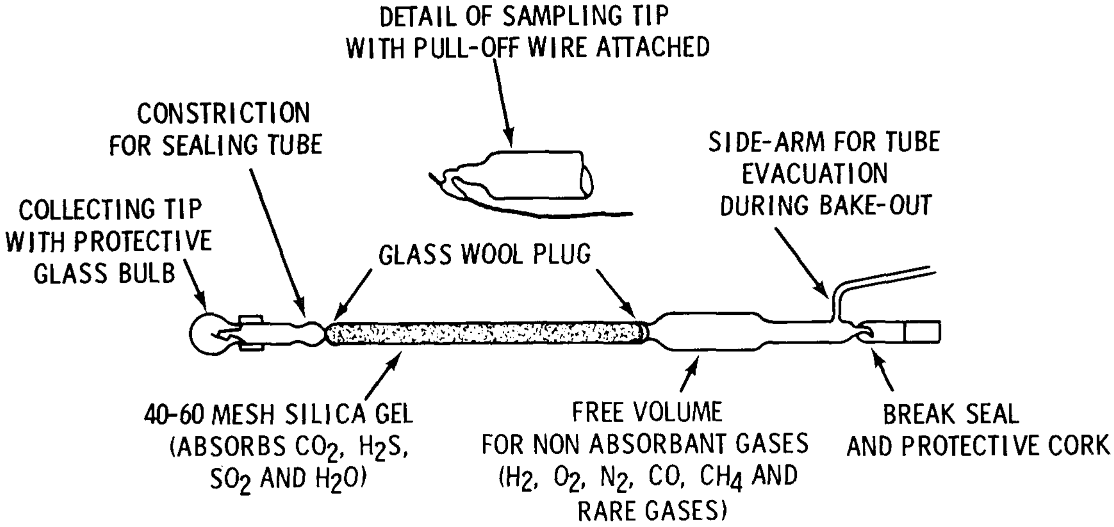
COMMENTS:

Reactions between collected gases (especially H_2S and SO_2) 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.

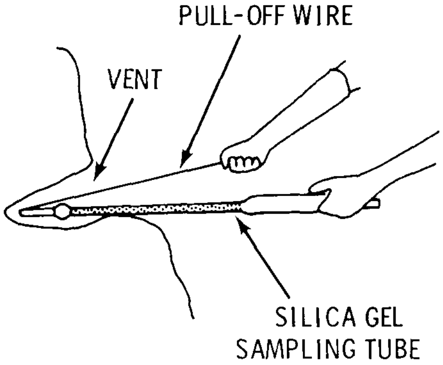
EDITION:

7/78

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.	**NO.** 7-S	
	SAMPLE TYPE: Gas	**SAMPLE POINT:** Fumarole
APPLICATION: Sample fumarole gases	**REFERENCES:** Finlayson, J.B. "The Collection and Analysis of Volcanic and Hydrothermal Gases," <u>Geothermics Special Issue 2</u>, Vol. 2, p. 1344-1354, 1970.	

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.

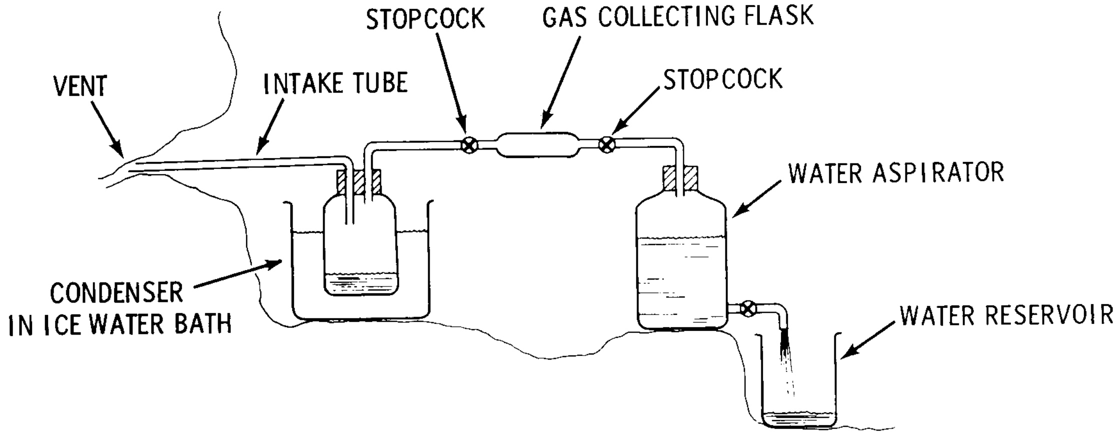
A water aspirator or pump is often used to pull the sample through the collecting train if insufficient pressure is present.

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.

EDITION:
7/78

ILLUSTRATION:



Gas collection from a fumarole by air displacement.

METHOD TITLE:

Syringe method for sampling entrained gases.

NO. 8-S

SAMPLE TYPE:

Gas

SAMPLE POINT:

Fumarole, hot spring or steam well.

APPLICATION:

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

REFERENCES:

Truesdell, A. H. and K. L. Pering, "Geothermal Gas Sampling Methods," U.S.G.S. Openfile Report 74-361, Menlo Park, CA, 1974.

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 CO_2 and H_2S 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 glass sample bottle is then opened by unscrewing its threaded bushing slightly

(over)

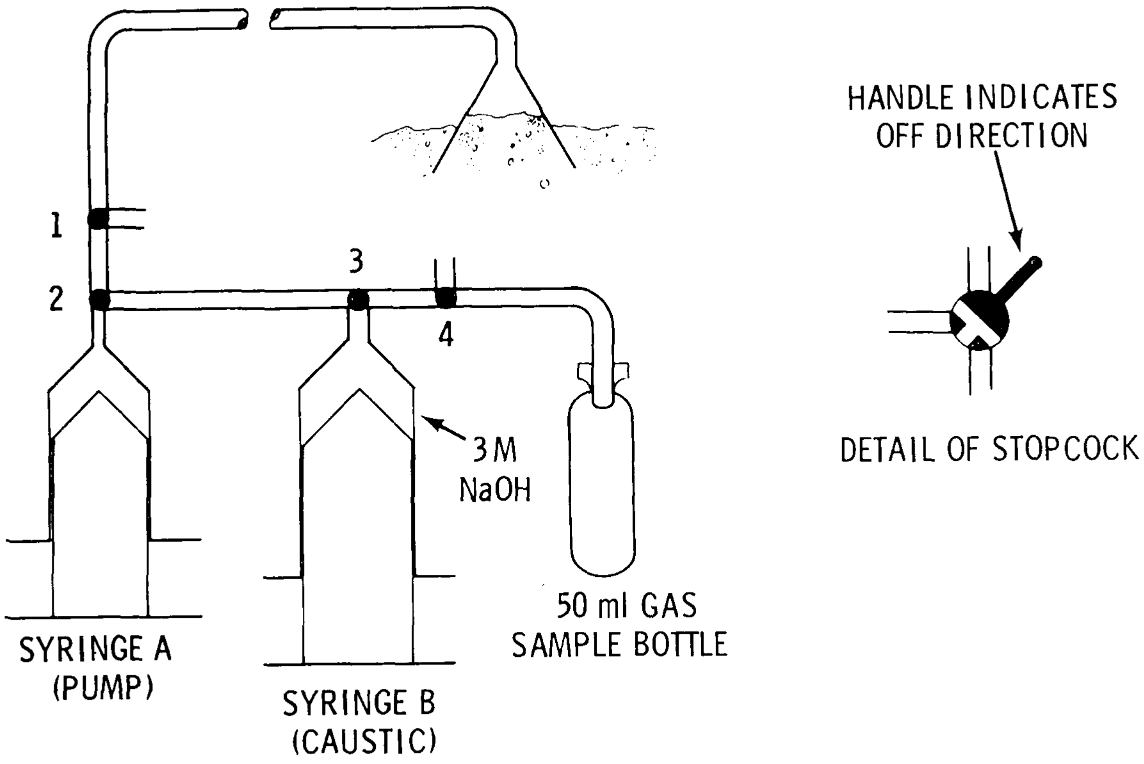
COMMENTS:

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.

EDITION: 7/78

PAGE: B-10

ILLUSTRATION:



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.	NO. 9-S
	SAMPLE TYPE: Liquid SAMPLE POINT: Weir box
APPLICATION: Sampling silencer weir boxes for liquid.	REFERENCES: Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977.

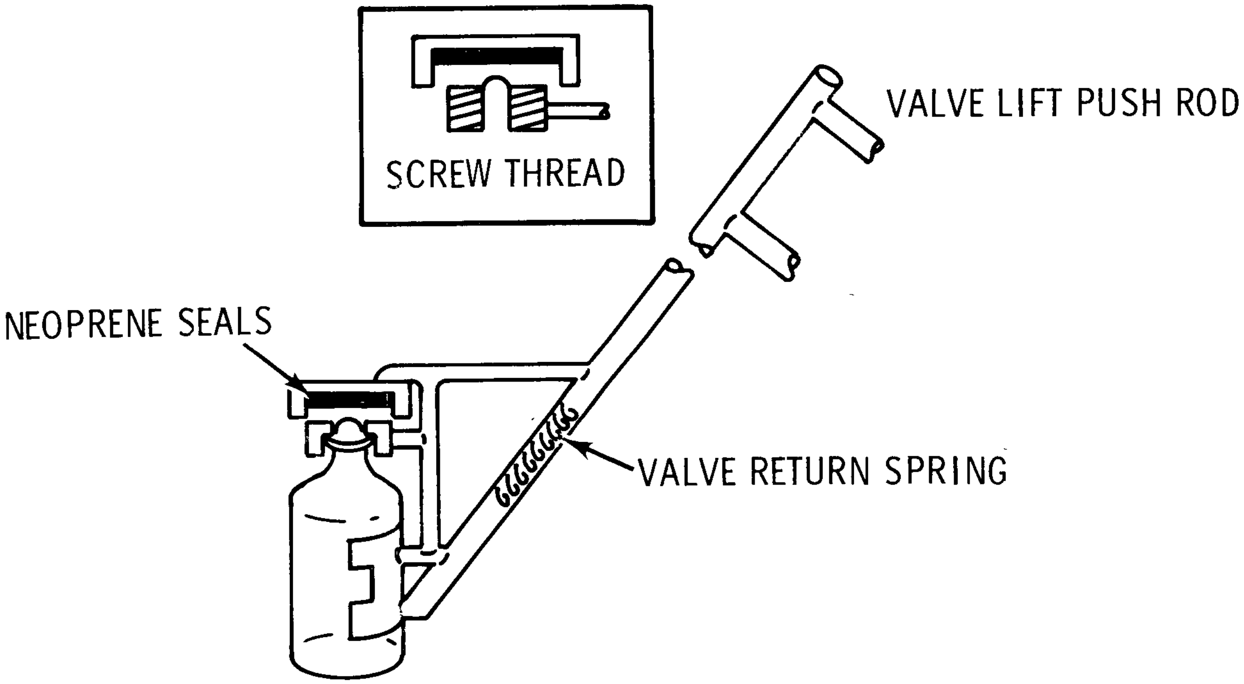
DESCRIPTION

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.

COMMENTS:

EDITION:
7/78

ILLUSTRATION:



SAMPLER FOR COLLECTING WATER SAMPLES FROM THE WEIR BOX OF A GEOTHERMAL WELL

METHOD TITLE:

Naughton tube method for sampling volcanic gases.

NO. 10-S

SAMPLE TYPE:	SAMPLE POINT:
Gas	Drill hole

APPLICATION:

Sampling volcanic gases.

REFERENCES:

Finlayson, J. B. "The Collection and Analyses of Volcanic and Hydrothermal Gases," Geothermics Special Issue 2, Vol. 2, p. 1344-1354, 1970.

DESCRIPTION

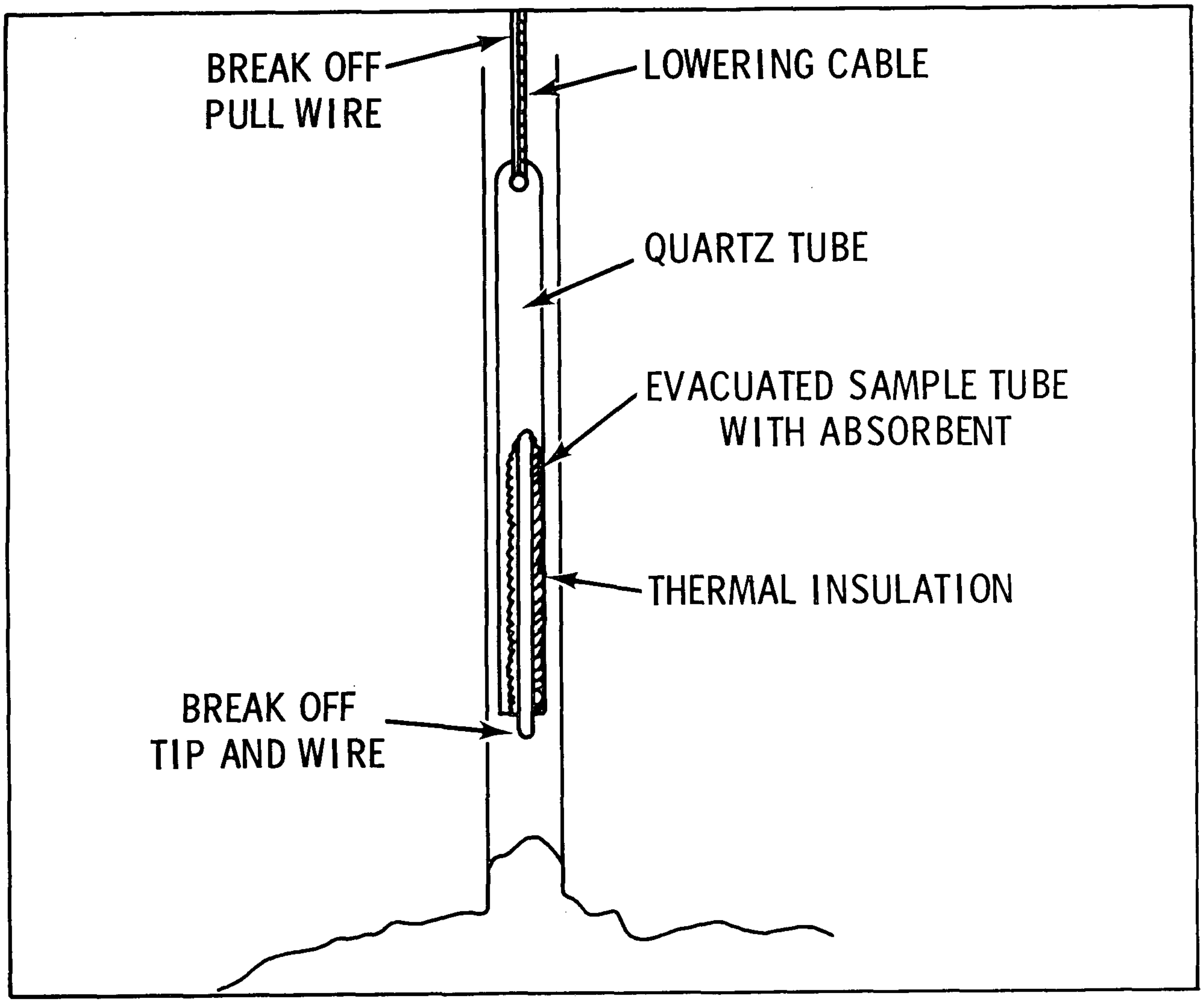
1. Naughton tubes containing a silica gel absorbent are thermally insulated by placing them in a silica jacket with the annular space filled with crushed fire brick.
2. Stainless steel wire cable is used to lower the tubes into the drill holes and a wire pull-off is used to open the tip at the desired 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.

EDITION:
7/78

ILLUSTRATION:



Method of sampling gases in holes drilled through the crust of a lava lake.

METHOD TITLE:

Cooling coils

NO. 11-S

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:

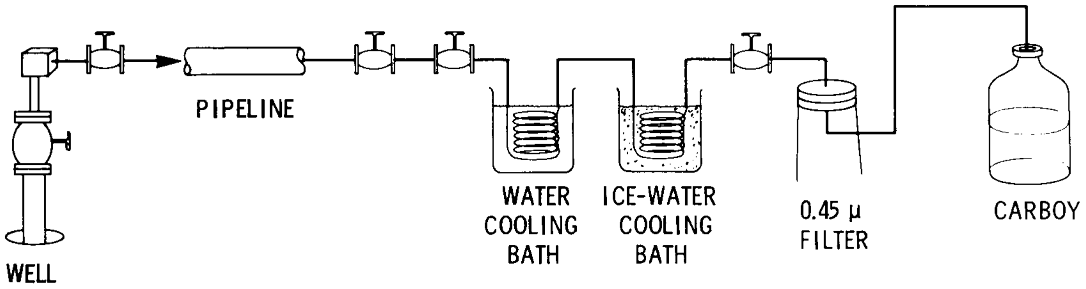
1. During field test Whitey or equivalent shutoff or regulating needle valves were used for maintaining proper flow rates through the coils. Gate or ball valves are not suitable for regulating flow,
2. Flexible armored lines equipped with quick disconnect fittings were used upstream of coils to connect 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

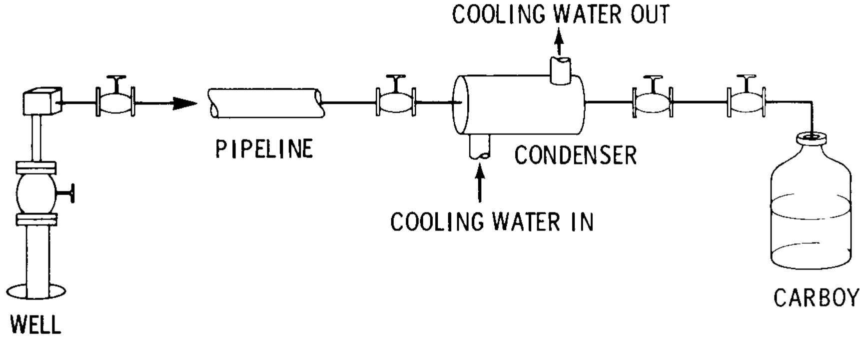
EDITION:

7/78

ILLUSTRATION:

SAMPLING CONDENSED BRINE USING COOLING COILS





SAMPLING CONDENSED BRINE USING JACKETED CONDENSER

high velocity through the coils resulting in a potentially dangerous burn situation for the operator.

METHOD TITLE:	NO. 12-S	
Sparging method for trapping gases.	SAMPLE TYPE: Gas	SAMPLE POINT: Pipeline

APPLICATION:	REFERENCES:
Sampling of dissolved and entrained gases in brine.	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.

EDITION:
7/78

ILLUSTRATION:

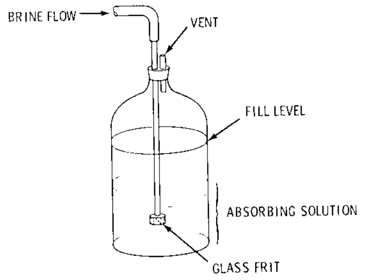


FIG 1. CARBOY CONTAINING ABSORBING SOLUTION TO TRAP ENTRAINED GAS

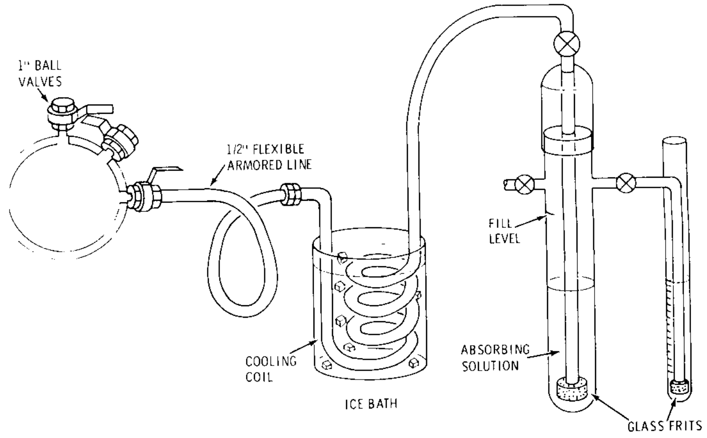


FIG 2. SPARGER ARRANGEMENT USED IN FIELD TEST FOR TRAPPING ENTRAINED GASES

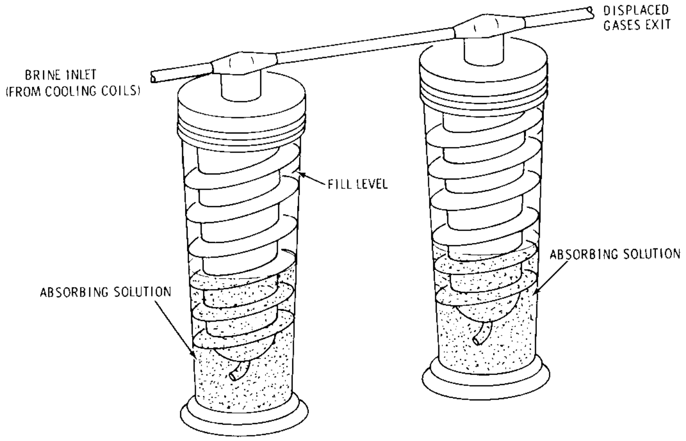


FIG 3. FISHER-MILLIGAN BOTTLE SYSTEM USED IN FIELD TEST FOR TRAPPING NONCONDENSABLE GASES

METHOD TITLE:

Cerro Prieto method for sampling noncondensables and CO_2.

NO. 13-S

SAMPLE TYPE: Gas and Liquid

SAMPLE POINT: Pipeline from separator

APPLICATION:

Sampling noncondensable gases and CO_2.

REFERENCES:

1. Mercado, Sergio, "Preliminary Geothermochemical Exploration of La Primavera, Jalisco," Fifth Mexican Chemistry Congress, Merida, Yucatan, April 1970.
2. Mercado, Sergio, "Hydrothermal Fluid Sampling for Isotopic C-13 and C-14: Geothermic Zone of La Primavera, Jalisco and Surroundin reas," Federal Electricity Commission, Electr city Industry Research Institute, April 1971.
3. Appendix 1: Field Test 1978.

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 CO_2 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 CO_2 while the gas phase is analyzed for residual gases (CH_4, N_2, H_2, etc.)
2. During a field test of this method (Figure 2) the 5-liter flask was initially fille 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 t fill the flask until the flask pressure had equilibrated with the steam line pressur 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 CO_2.
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.

EDITION: 7/78

ILLUSTRATION:

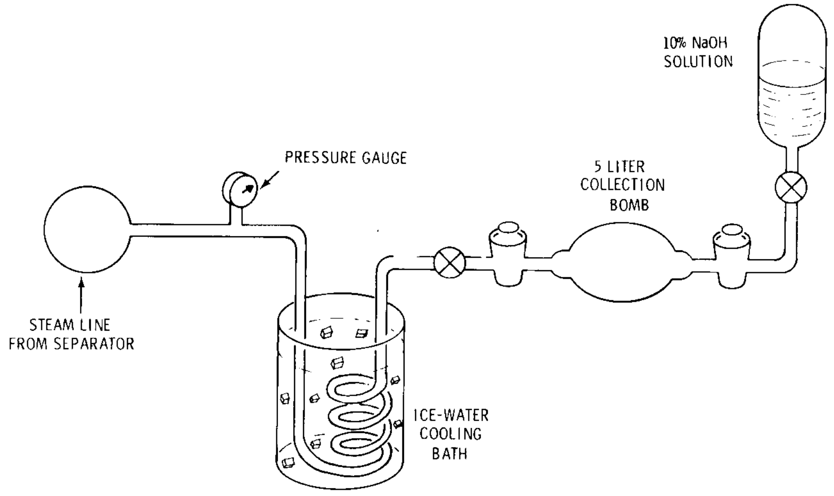


FIG 1. CERRO PRIETO METHOD FOR COLLECTING NON-CONDENSABLES & CO_2

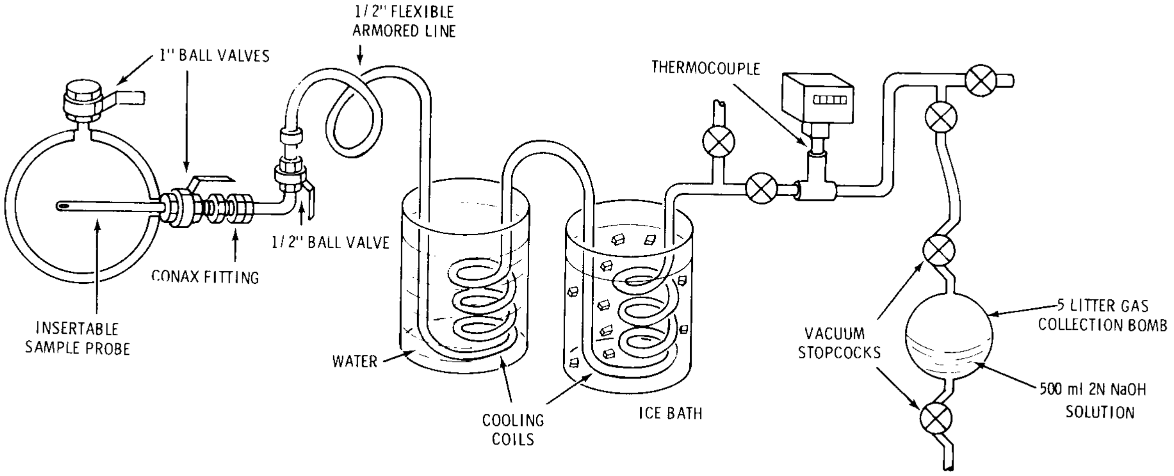


FIG 2. CERRO PRIETO METHOD USED IN FIELD TEST

METHOD TITLE:

Hypodermic syringe method for sampling noncondensables.

NO. 14-S

SAMPLE TYPE:

Liquid and gas

SAMPLE POINT:

Steam line from separator

APPLICATION:

Sampling noncondensable gases in steam line.

REFERENCES:

Michels, D.E. "CO_2 in Geothermal Steam. A Rapid, Precise, and Accurate Field Assay Technique," presented at Geothermal Resources Council Meeting, Hilo, Hawaii, July 1978.

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 % CO_2:

$$\%CO_2 = KP_{T_1}\left(\frac{V_{G1}}{V_{L1}}\right)\underbrace{\left(1+\frac{M_cV_{L1}}{V_{G1}}\right)\left[1-\underbrace{\left(\frac{V_{G2}}{V_{G1}}\right)\left(\frac{V_{L1}}{V_{L2}-V_{NaOH}}\right)\left(1+\frac{M_nV_{L2}}{V_{G2}}\right)}_{F_1}\right]}_{F_2}$$

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_{T_1}, due to non-CO_2 gases.

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

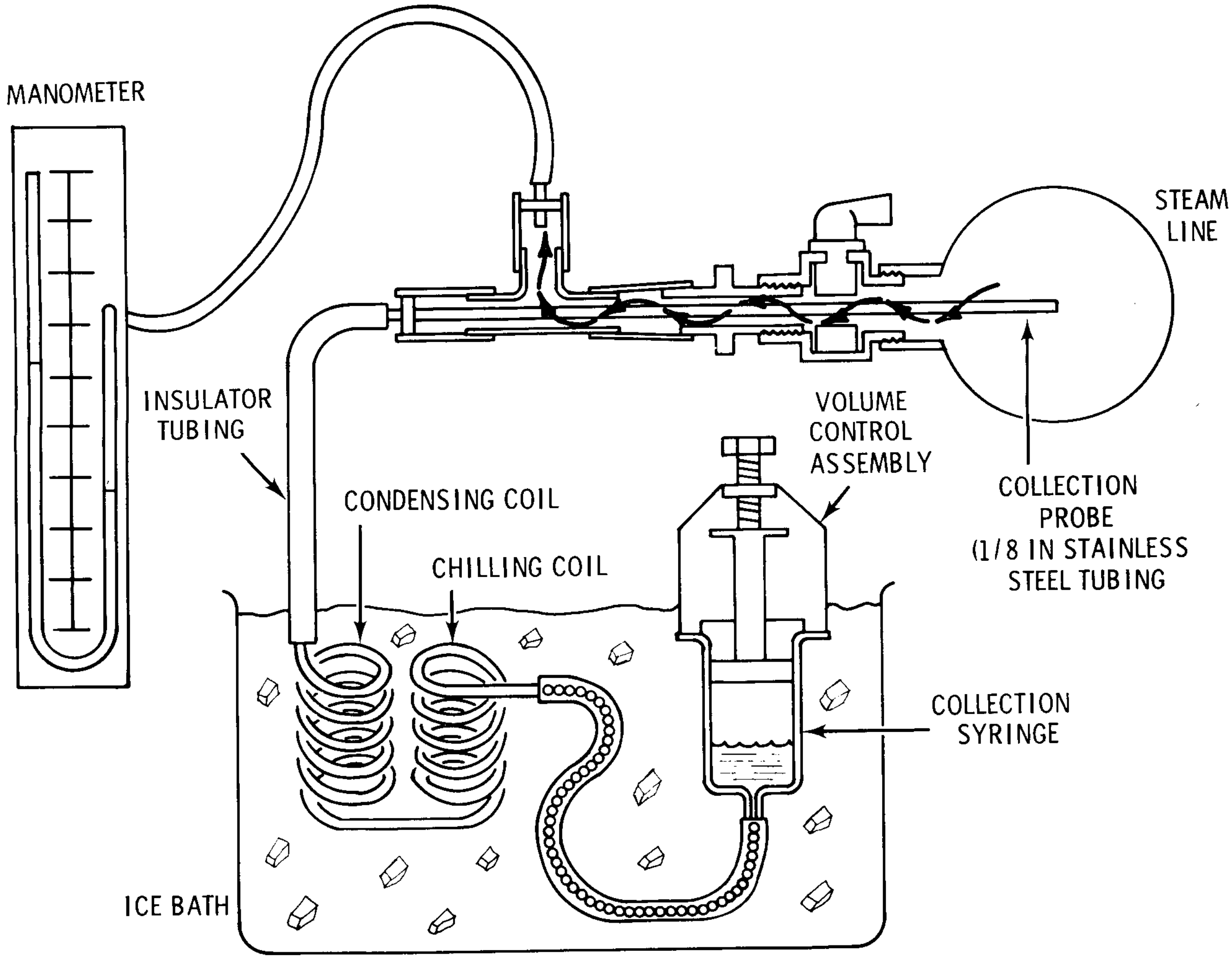
COMMENTS:

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.

EDITION:

7/78

ILLUSTRATION:



SYSTEM FOR SAMPLING & MEASURING NON-CONDENSABLE GAS IN STEAM

dominates the non-CO_2 fraction.

f) F_2 represents virtual pressure fraction for CO_2.

The non-CO_2 fraction is given by: non-CO_2 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.

METHOD TITLE:
Tedlar bag method for sampling steam condensate and noncondensable gases

NO. 15-S

SAMPLE TYPE:
Gas and condensate

SAMPLE POINT:
Particle separators, condensate traps, cooling towers, off gas ejectors.

APPLICATION:
Sampling of steam condensate and noncondensable gases.

REFERENCES: Soinski, A.J., D.E. Claridge, and Rodney Melgard, "Field Sampling of Radioactive Geothermal Effluents," Proceedings of the 1st Workshop on Sampling Geothermal Effluents, Las Vegas, NV, Oct. 1975, p. 126-142.

Soinski, A.J., "The Use of Gas Sampling Bags for the Collection and Storage of Hydrothermal Gases," Proceedings, 2nd Workshop on Sampling and Analysis of Geothermal Effluents, Las Vegas, NV, February 1977.

Personal Communication, Letter of March 30, 1978.

DESCRIPTION

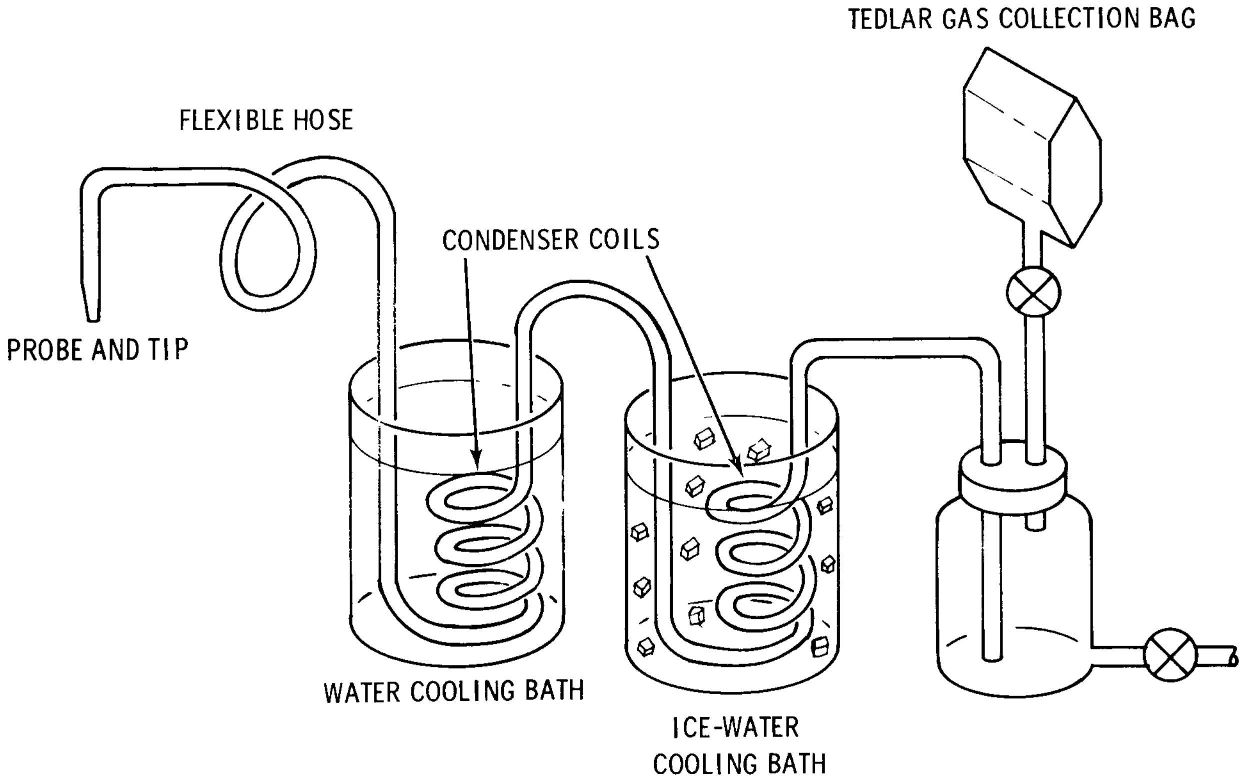
The arrangement of the sampling apparatus is shown in the illustration. The total volume of the tubing is approximately 1 liter. The stainless steel probe is inserted into the flow stream in such a way that only steam passes through the collection train; the high steam flow rates make this simple to 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.

EDITION:
7/78

ILLUSTRATION:



STEAM SAMPLING SYSTEM USING TEDLAR BAG

METHOD TITLE:

Wet test meter method.

NO.

16-S

SAMPLE TYPE:

Gas

SAMPLE POINT:

Steam line from separator.

APPLICATION:

Sampling steam for noncondensable gases.

REFERENCES:

1. Christofferson, D.J., R.N. Wheatley, and J.A. Baur, "Union Oil Co. of California's Geothermal Sampling Techniques," Proceedings of the 1st Workshop on Sampling Geothermal Effluents, Las Vegas, NV, Oct. 1975, pp. 165-173
2. Appendix 1: Field Test 1978.

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 noncondensible 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 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.

EDITION:

7/78

PAGE:

ILLUSTRATION:

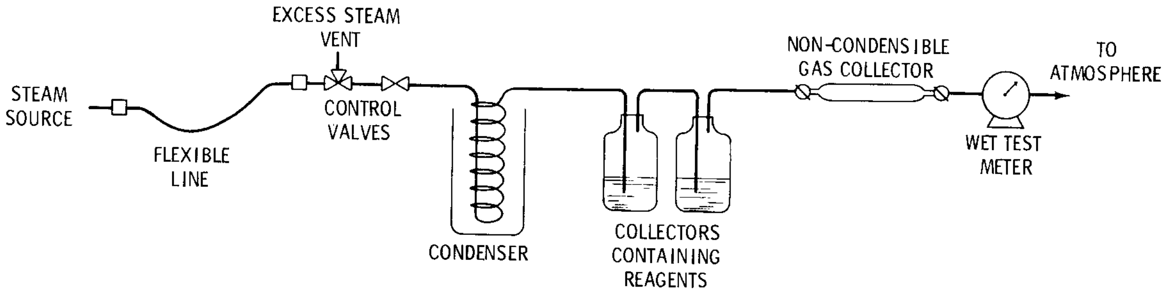


FIG 1. STEAM SAMPLING APPARATUS

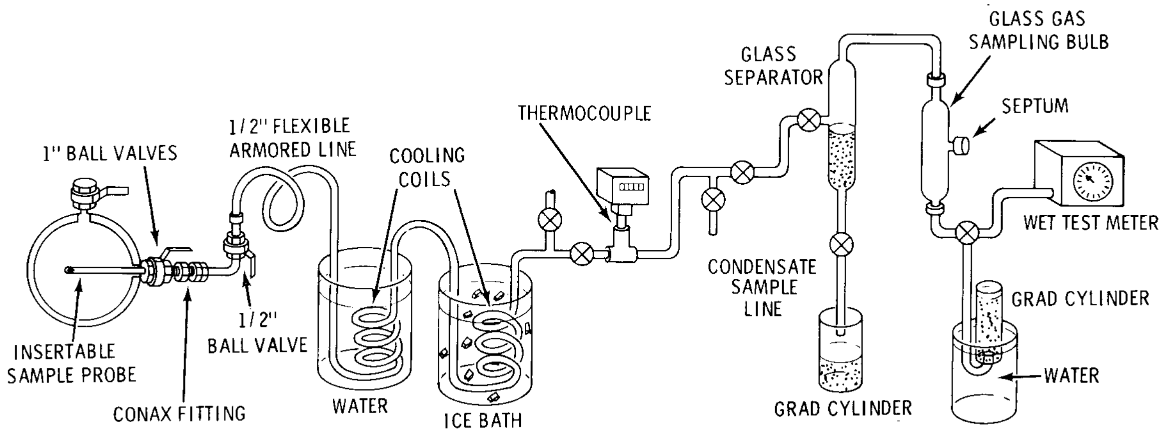


FIG 2. WET TEST METER METHOD USED IN FIELD TEST TO SAMPLE NONCONDENSABLES IN STEAM LINE

collected in gas sampling bulbs. The noncondensable gas flow rate can be checked using the graduated cylinder water displacement method.

METHOD TITLE:

Radon Gas Collection and Measurement

NO. 17-S

SAMPLE TYPE:

Noncondensable gas

SAMPLE POINT:

Noncondensable gas line

APPLICATION:

Measurement of radon gas concentrations in geothermal gases.

REFERENCES:

J. D. Ludwick, Battelle, Pacific Northwest Laboratories, Richland, WA 99352.
H. F. Lucas, Rev. Sci. Inst., 28, 680 (1957).

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 2μ 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.

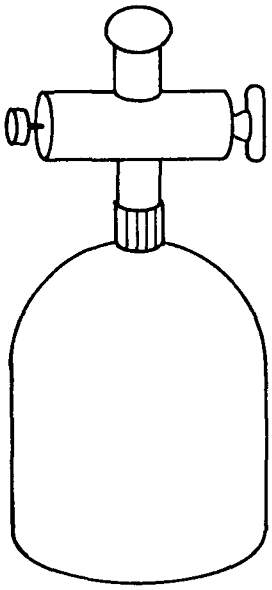
COMMENTS:

EDITION:

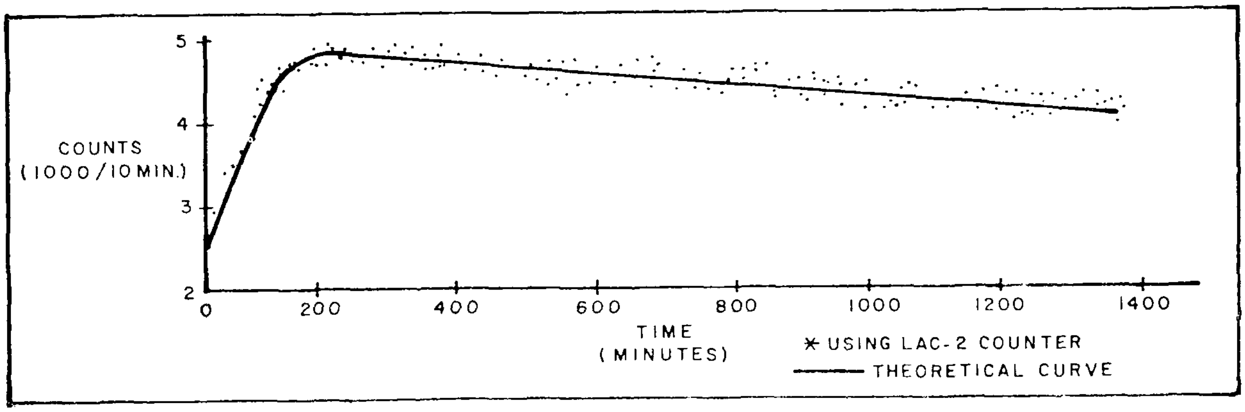
7/78

ILLUSTRATION:

LUCAS TUBE RADON COUNTER



GROWTH AND DECAY OF RADON DAUGHTERS



METHOD TITLE:

Determination of the Chemical Forms of Gaseous Mercury.

NO. 18-S

SAMPLE TYPE:

Gaseous Mercury

SAMPLE POINT:

Noncondensable gas line

APPLICATION:

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

REFERENCES:

D. E. Robertson, E. A. Crecelius, J. S. Fruchter and J. D. Ludwick, "Mercury Emissions from Geothermal Power Plants," Science 196, 1094-1097 (1977).

R. W. Braman and D. L. Johnson, "Selective Adsorption Tubes & Emissions Techniques for Determination of Ambient Forms of Mercury in Air." Env. Sci. Tech. 12, 996-1003 (1974).

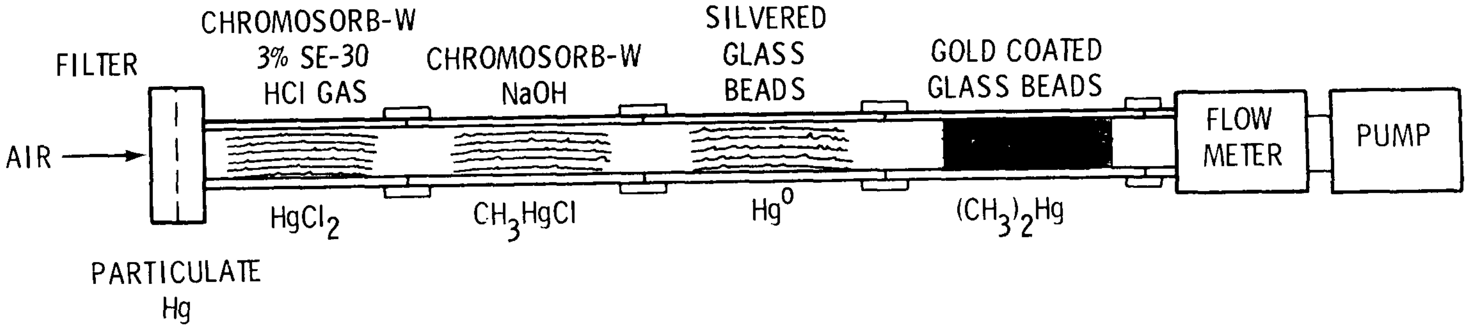
DESCRIPTION

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^{++} 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° 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:

EDITION: 7/78

ILLUSTRATION:



SELECTIVE ABSORPTION TUBES FOR MERCURY FORMS IN GASES

METHOD TITLE: Evacuated bottle method for collecting residual, dissolved and entrained gases.	NO. 19-S
	SAMPLE TYPE: Gas
	SAMPLE POINT: Steam and gas from steam condensate, condensed brine
APPLICATION: Sampling dissolved gases in equilibrium with water.	REFERENCES: Nehring, Nancy, and Alfred H. Truesdell, "Collection of Chemical, Isotope and Gas Samples from Geothermal Wells," Proceedings, 2nd Workshop on Sampling and Analysis of Geothermal Effluents, Las Vegas, February, 1977.

DESCRIPTION

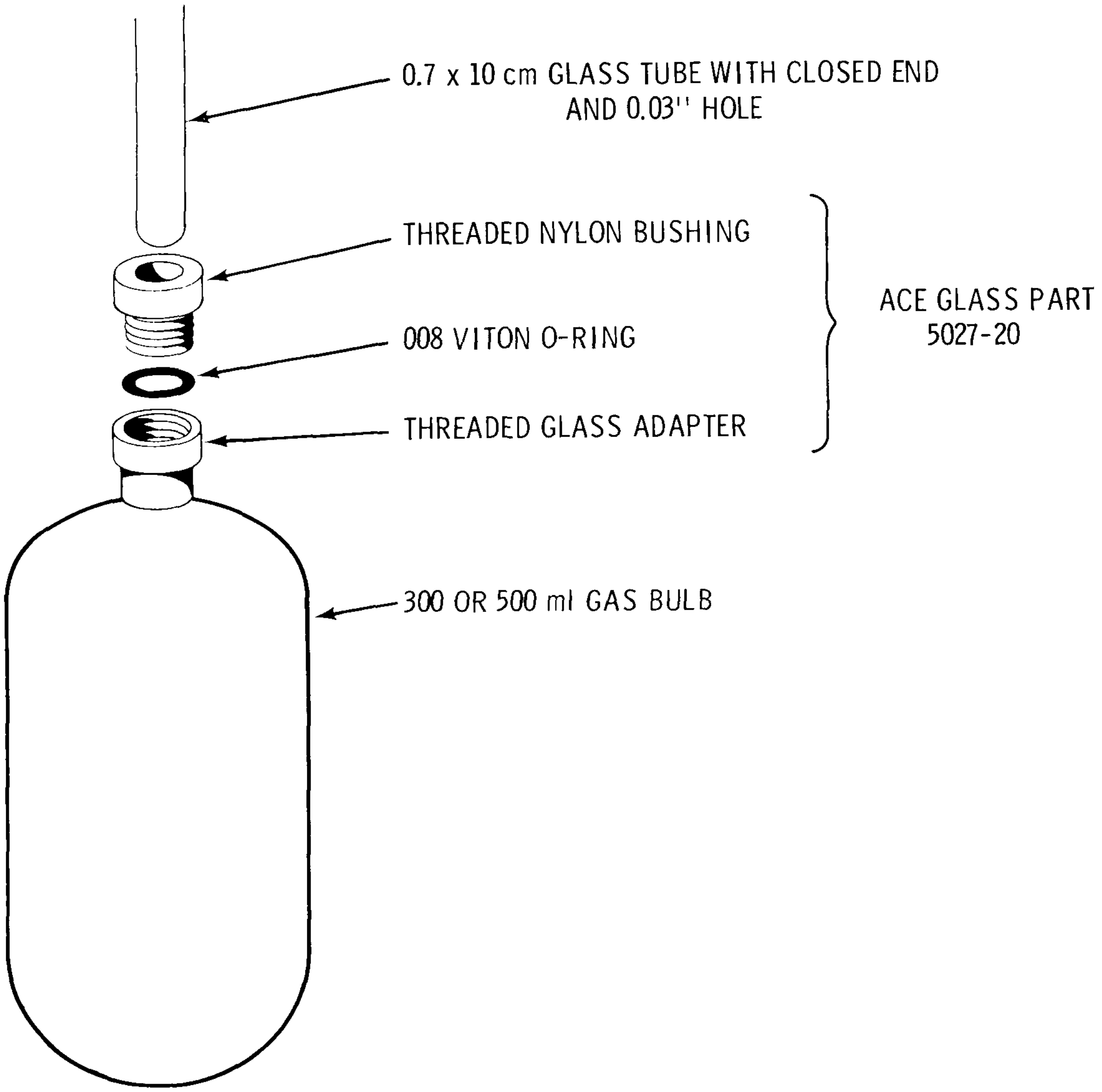
1. Brine is collected in an evacuated pre-weighed 300 - 500 ml bottle by attaching vinyl tubing from the condenser to the bottle.
2. Gases in equilibrium with the water (in head space) are analyzed by gas chromatography or other means.
3. Dissolved gases such as CO_2 are determined in the liquid phase. For steam condensate and gas samples, the bottle is filled with 50 - 100 ml 4N NaOH (as carbonate free as possible). This traps both CO_2 and H_2S. 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.

EDITION:
7/78

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.

NO. 20-S

SAMPLE TYPE:

Liquid and gas

SAMPLE POINT:

Pipeline

APPLICATION:

Separating two phase flow from low pressure source.

REFERENCES:

Appendix 1: Field Test 1978.

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 CO_2 and H_2S prior to collecting the residual gases (CH_4, H_2, N_2, 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 2N NaOH was used in the sparger (back pressure was created). Reduction to 750 cc NaOH sol'n in the sparger remedied this problem.
3. 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).
4. This system should be used for low pressure sources only.

(cont. on back)

EDITION:

7/78

ILLUSTRATION:

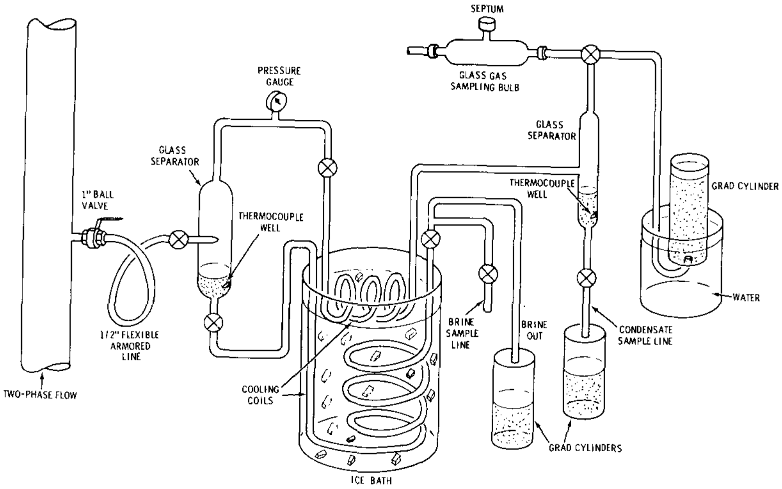


FIG 1. GLASS SEPARATOR SYSTEM FOR SAMPLING TWO-PHASE FLOW (USED IN FIELD TEST)

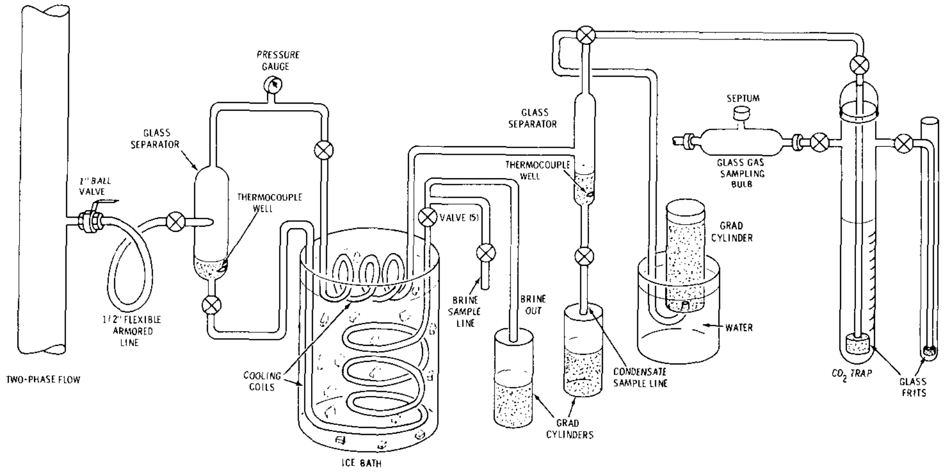


FIG 2. GLASS SEPARATOR SYSTEM USED IN FIELD TEST FOR SAMPLING TWO-PHASE FLOW (WITH CO_2 TRAP ATTACHED)

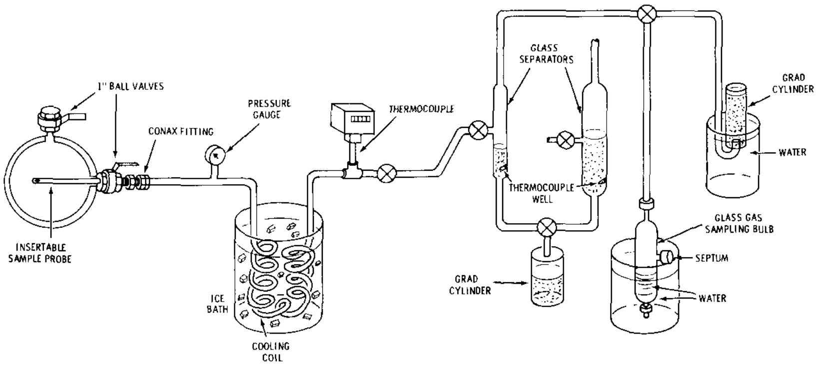


FIG 3. GLASS SEPARATOR - INSERTABLE PROBE ARRANGEMENT FOR SAMPLING NON-CONDENSABLES ON STEAM LINE (USED IN FIELD TEST)

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 allowi[illegible] the gas to displace the water proved to be a useful way to determine if air wa[illegible] excluded, (Figure 3). Collection is continued for 3-4 volume displacements.

METHOD TITLE:

Non-metallic Steam Condenser

NO. 21-S

SAMPLE TYPE:
Steam & Gas

SAMPLE POINT:
Pipeline after steam separator

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

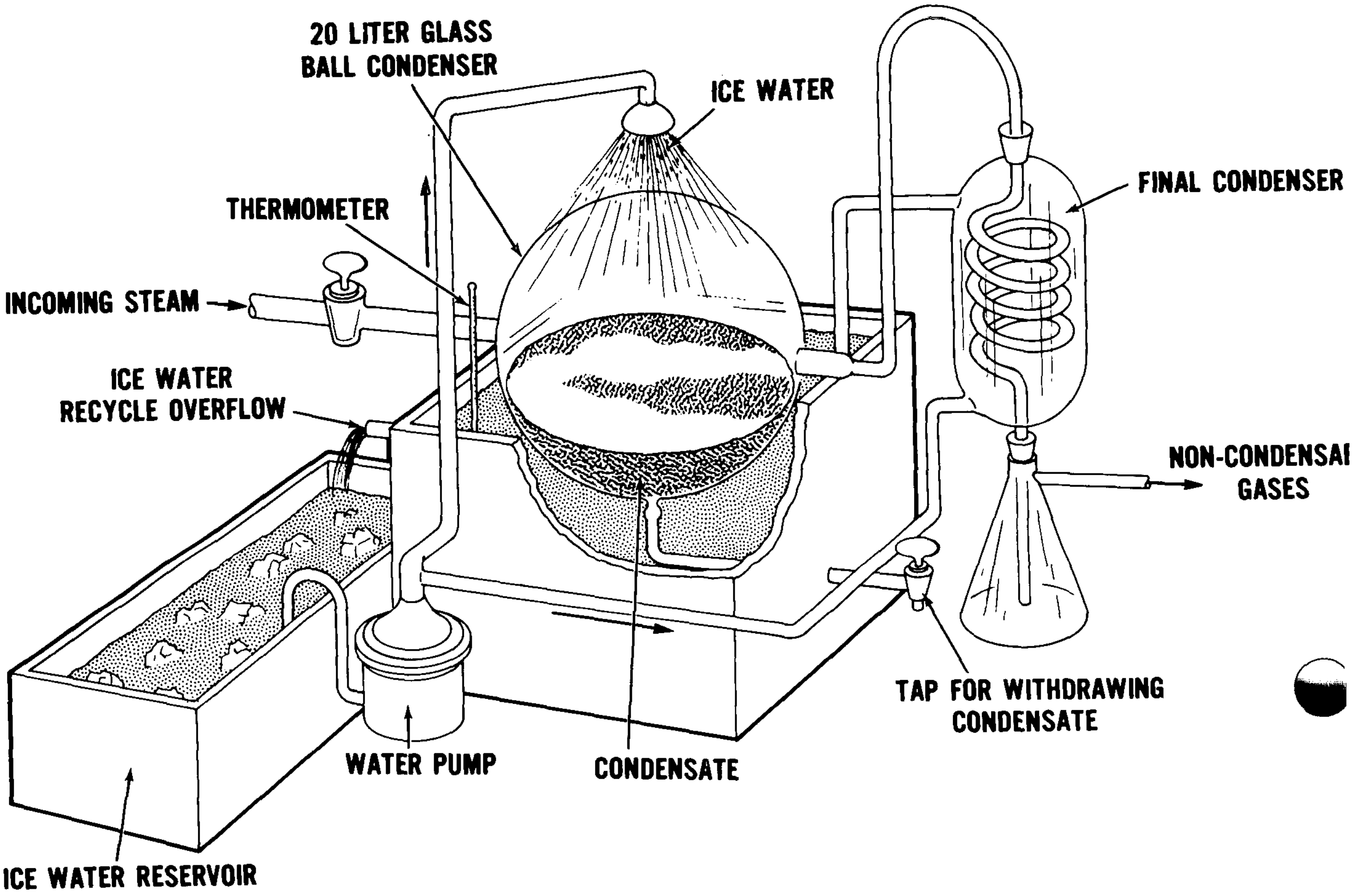
Incoming steam from a steam-brine separator or from a dry steam well-head enters the 20-liter Pyrex glass sphere which is cooled by a spray of circulating cold water. The steam swirls around in the sphere and condenses on the walls. A final Pyrex glass condenser coil assures complete steam condensation, 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.

EDITION:
7/78

ILLUSTRATION:



NON-METALLIC STEAM CONDENSER

METHOD TITLE:

Low pressure separator method.

NO. 22-S

SAMPLE TYPE:

Gas and Liquid

SAMPLE POINT:

Two-phase flow source

APPLICATION:

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

REFERENCES:

Ellis, A.J. et al., "Methods of Collection and Analysis of Geothermal Fluids," Report No. C.D. 2103, New Zealand Dept. of Sci. and Ind. Res., New Zealand, July 1968.

P.B. Needham, Jr., and W.D. Riley, "Chemical Analyses for the Brines of Four Imperial Valley Geothermal Wells," College Park Metallurgy Research Center, Bureau of Mines, U.S. Department of the Interior, College Park, MD 20740.

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 CO_2 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:

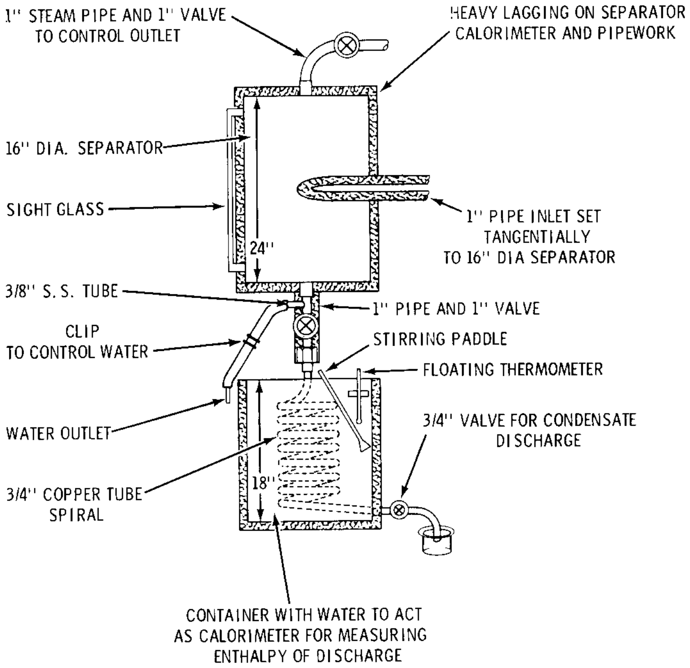


FIG 1. LOW PRESSURE SEPARATOR SAMPLING APPARATUS

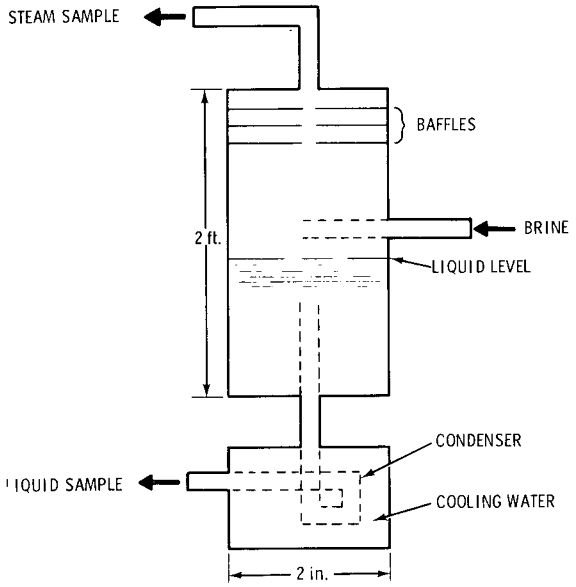


FIG 2. BRINE SAMPLING SYSTEM USED TO MINIMIZE READSORPTION OF NONCONDENSABLE GASES IN FLUID SAMPLES

METHOD TITLE: Steam-gas separator using modified graduated cylinder.	**NO.** 23-S	
	SAMPLE TYPE: Condensate and Gas	**SAMPLE POINT:** Condenser or separator

APPLICATION:

Separation of steam condensate from gas.

REFERENCES:

Nehring, Nancy and Alfred H. Truesdell, "Collection of Chemical, Isotope and Gas Samples from Geothermal Wells," Proceedings, 2nd Workshop on Sampling and Analyses of Geothermal Effluents, Las Vegas, February, 1977.

DESCRIPTION

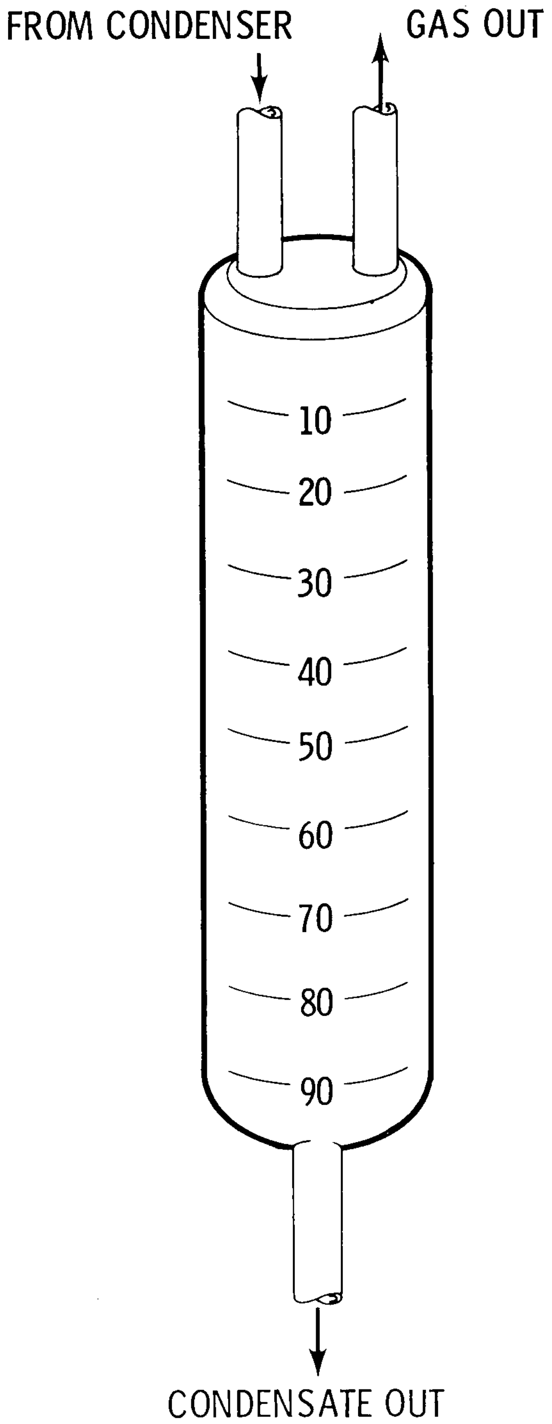
This steam condensate-gas separator is constructed from a graduated cylinder by attaching two tubulations at the top and one at the bottom. Flow from the condenser enters at the top (vinyl tubing is used for all connections) and the flow of condensate from the bottom is restricted with a clamp so that 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.

EDITION:
7/78

ILLUSTRATION:



- Steam-gas separator modified from a 100 ml graduated cylinder.

METHOD TITLE:

Portable gas-liquid separator.

NO. 24-S

SAMPLE TYPE:

Liquid and gas

SAMPLE POINT:

Pipeline

APPLICATION:

Separating two-phase flow into liquid and gas.

REFERENCES:

Christoffersen, D.J., R.N. Wheatley and J.A. Baur, "Union Oil Company of California's Geothermal Sampling Techniques," Proceedings, First Workshop on Sampling Geothermal Effluents," Las Vegas, NV, October 1975.

DESCRIPTION

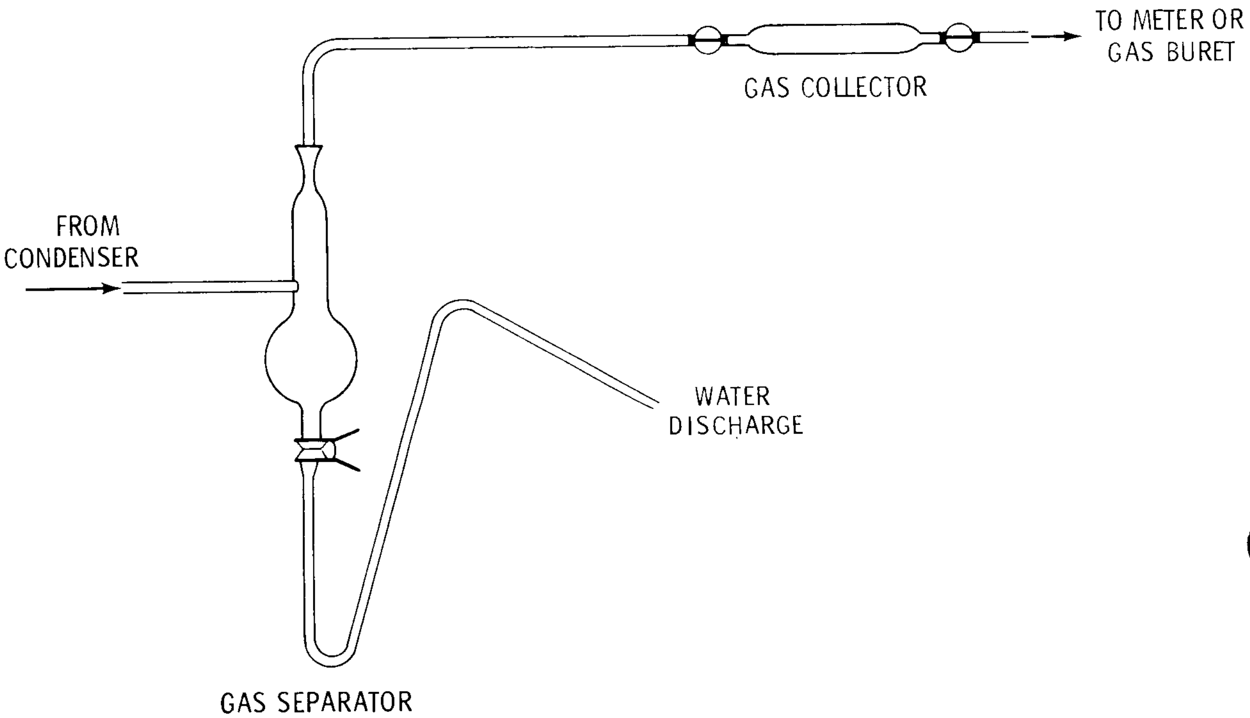
A simple gas-liquid separator which can be used in situations where a larger separator is not available is shown in the illustration. The volume of noncondensable gases is measured by water displacement in a graduated cylinder. Noncondensable gases are trapped in gas collectors for later laboratory analysis.

COMMENTS:

EDITION:

7/78

ILLUSTRATION:



Collection of air free gas sample.

METHOD TITLE:

Webre separator method

NO. 25-S

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: 1. Pollak, A., and L.E. Work Amer. Soc. Mech. Eng., 64 (1942), 31. 2. A.J. Ellis et al, "Methods of Collection an Analysis of Geothermal Fluids" Report No. C.D. 2103, New Zealand Dept. of Sci. & Rad. Re New Zealand, 1968. 3. Nehring, Nancy L. and Alfred H. Truesdell, "Collection of Chemical, Isotope and Gas Samples from Geothermal Wells,' Proceedings, 2nd Workshop on Sampling and Analyses of Geothermal Efflunets, Las Vegas, February 1977.
4. Appendix 1: Field Test 1978.

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 CO_2 and H_2S 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 CO_2 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.

EDITION:

7/78

(over)

ILLUSTRATION:

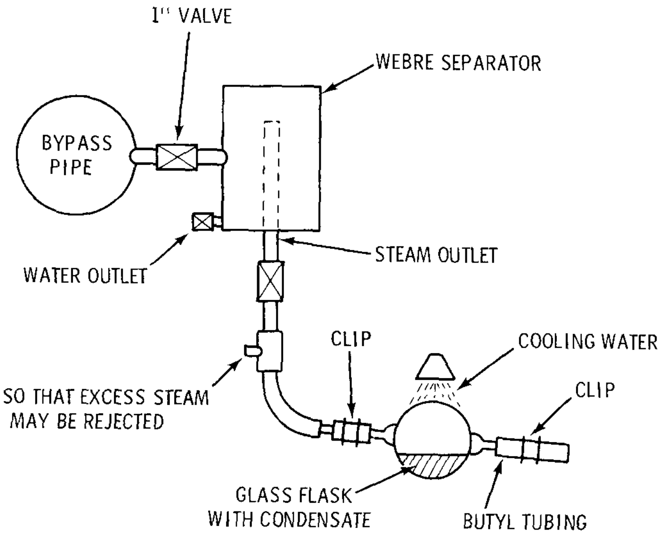


FIG 1. HIGH PRESSURE SEPARATOR SAMPLING APPARATUS

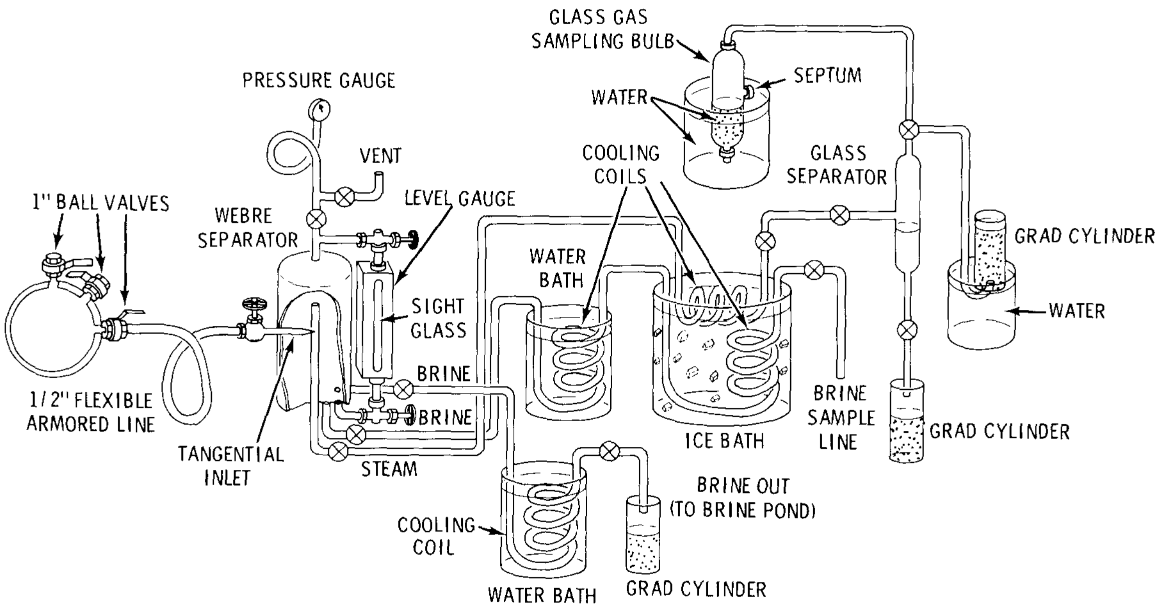


FIG 2. WEBRE SEPARATOR SAMPLING SYSTEM USED IN FIELD TEST

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.

NO. 26-S

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:
1. Ellis, A. J. and W. A. J. Mahon, "Chemistr and Geothermal Systems,"Academic Press, New York, 1977. (See note V on page B-1)
2. Nehring, Nancy and Alfred H. Truesdell, "Collection of Chemical, Isotope and Gas Samples from Geothermal Wells," Proceedings, 2nd Workshop on Sampling and Analyses of Geothermal Effluents, Las Vegas, February, 1977.

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.

ILLUSTRATION:

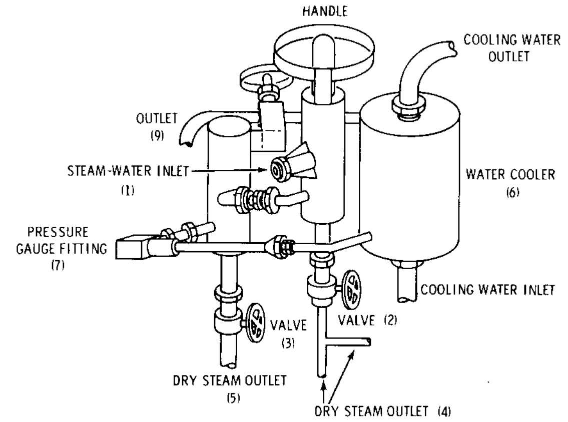


FIG 1. WEBRE CYCLONE SEPARATOR FOR COLLECTING STEAM & WATER SAMPLES UNDER PRESSURE FROM A DISCHARGING GEOTHERMAL WELL

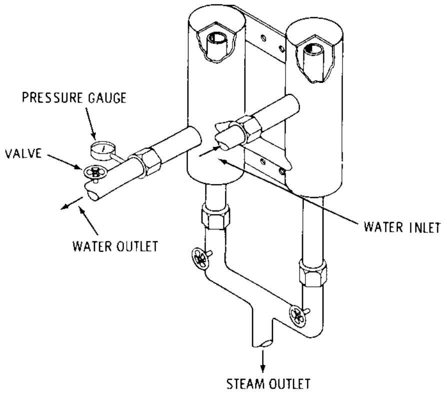


FIG 2. MINI CYCLONE SEPARATOR OF NEW ZEALAND DESIGN

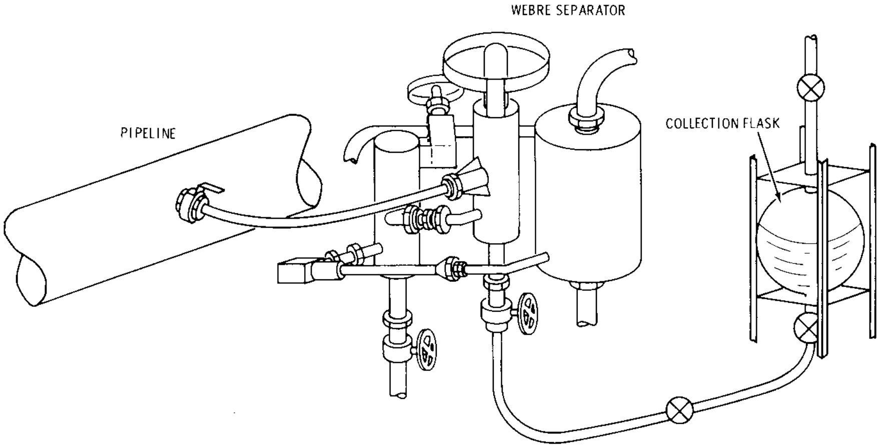


FIG 3. FIELD ARRANGEMENT FOR DUAL WEBRE SEPARATOR SYSTEM

METHOD TITLE:

Steam-Water Separator

NO. 27-S

SAMPLE TYPE:

Steam and liquid

SAMPLE POINT:

Pipeline

APPLICATION:

Separation of Flashed 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

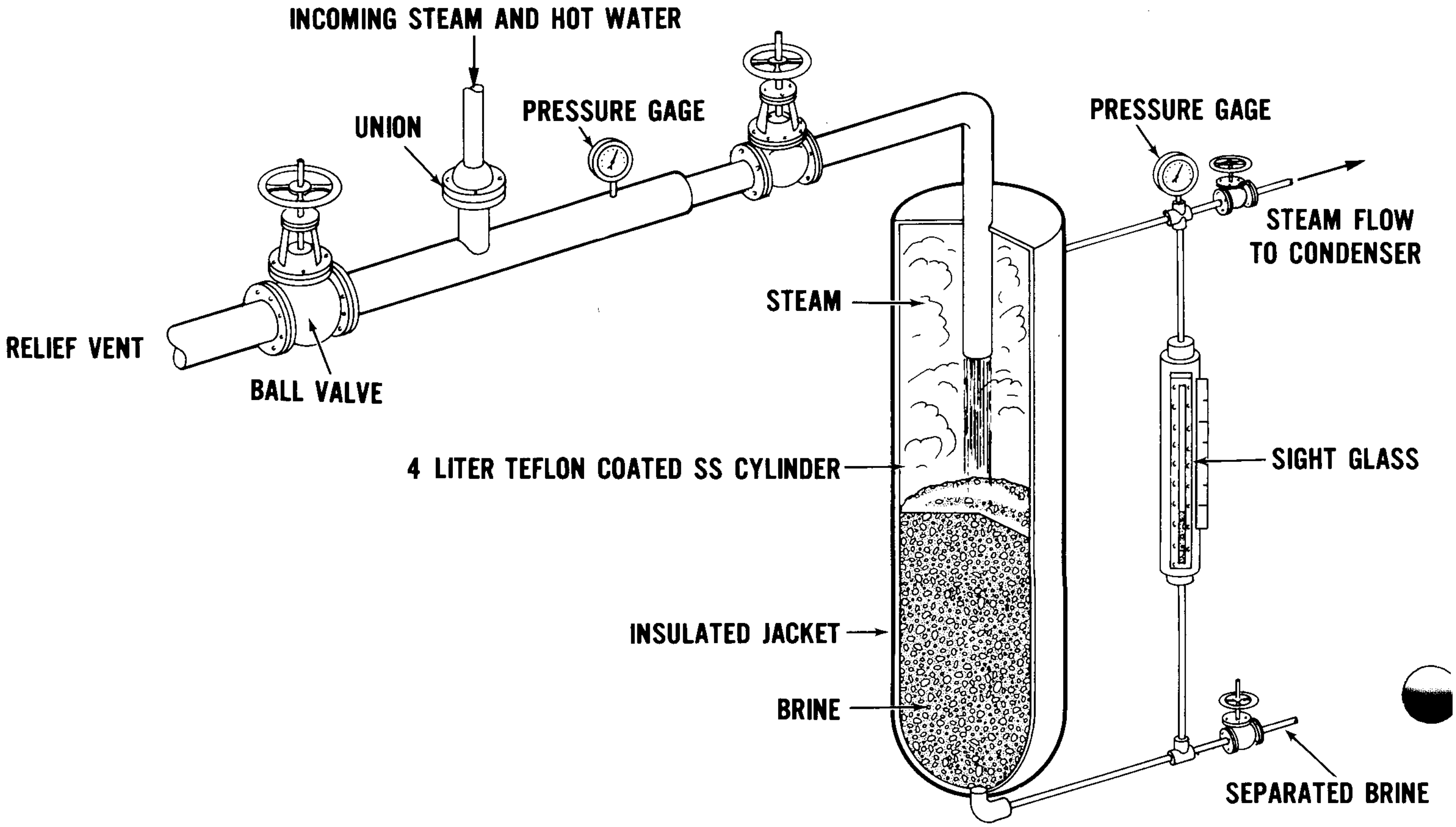
Incoming steam and hot water (or unflashed brine) enter through the top of a 4-liter teflon-coated stainless steel cylinder from a pipe extending about one-third of the way into the cylinder. Flashed steam is removed from a sidearm at the top of the cylinder and the brine is withdrawn through a tap at 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 isoenthalphic 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.

EDITION: 7/78

ILLUSTRATION:



HIGH PRESSURE STEAM-WATER SEPARATOR

METHOD TITLE:

Insertable sample probe method.

NO. 28-S

SAMPLE TYPE: Liquid and gas

SAMPLE POINT: Pipeline

APPLICATION:

Sampling two phase systems for liquid and gas.

REFERENCES:

1. Hill, J.H. and C.J. Morris, "Sampling a Two-Phase Geothermal Brine Flow for Chemical Analysis," Lawrence Livermore Laboratory Repor UCRL-77544, December 1975.
2. Appendix 1: Field Test 1978.

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.

EDITION: 7/78

ILLUSTRATION:

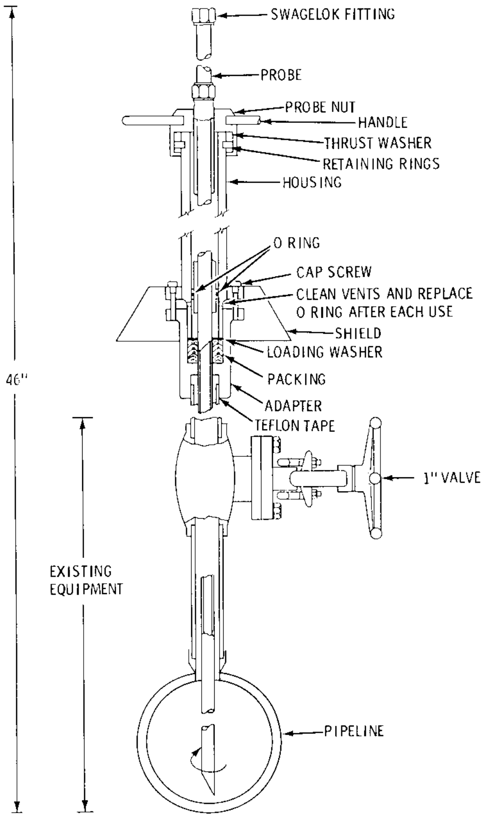


FIG 1. INSERTABLE SAMPLING PROBE (LLL DESIGN)

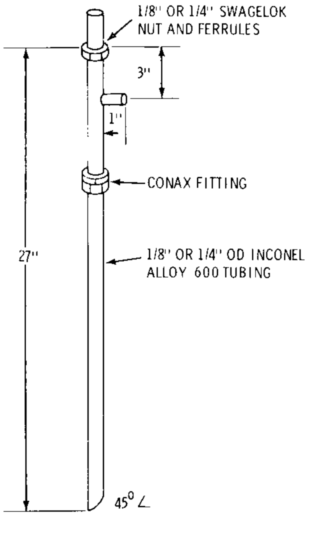


FIG 2. INSERTABLE SAMPLING PROBE USED IN FIELD TEST

METHOD TITLE:

"Porcupine" arrangement.

NO. 29-S

SAMPLE TYPE: Liquid and gas

SAMPLE POINT: Pipeline

APPLICATION:

Sampling multiphase systems.

REFERENCES:

Appendix 1: Field Test 1978.

DESCRIPTION

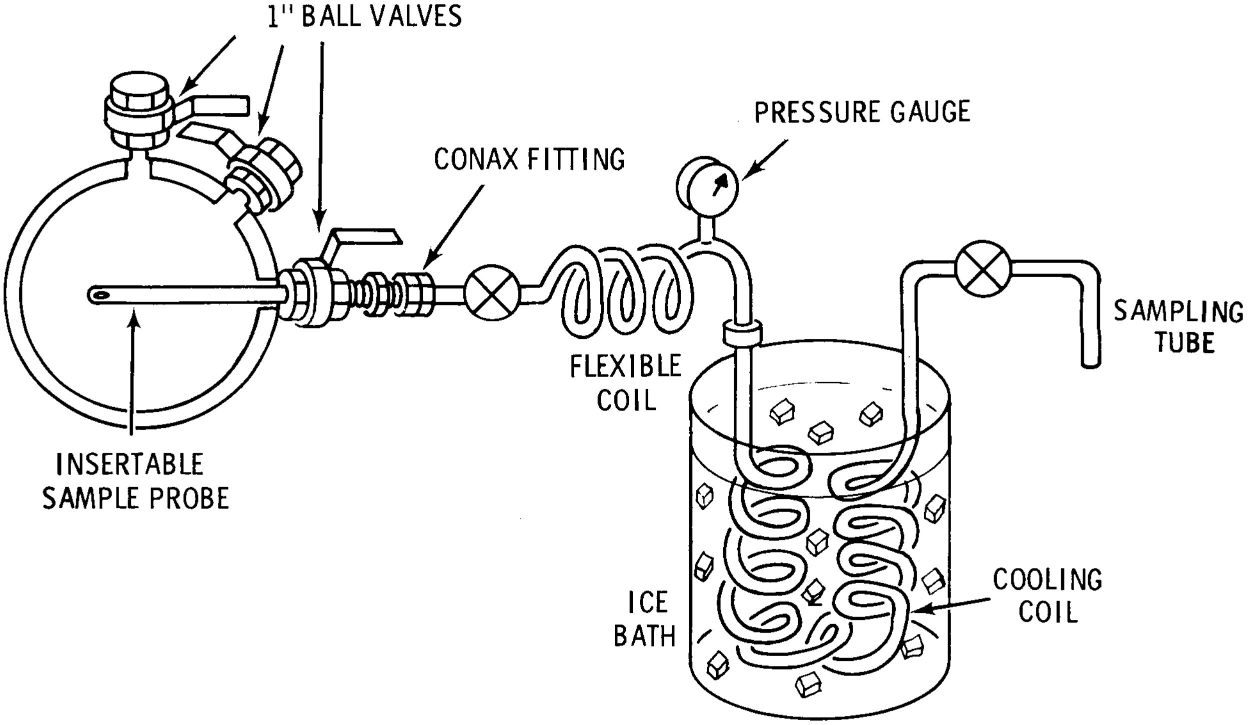
1. Sample points are arranged around the circumference of a pipe. The sample points may be fixed or of the insertable probe type. Fixed sample points have tubes inserted to various depths in the pipe to enable the operator to sample the various phases present in the pipe. Insertable probes accomplish 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 part (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.

EDITION: 7/78

ILLUSTRATION:



CROSS SECTION OF PIPE SHOWING "PORCUPINE" ARRANGEMENT OF BALL VALVES WITH INSERTABLE TRAVERSING PROBE PRESENT (USED IN FIELD TEST)

METHOD TITLE:

Evacuated cylinders

NO. 30-S

SAMPLE TYPE:

Gas and Liquid

SAMPLE POINT:

Wellhead, pipeline, etc.

APPLICATION:

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

REFERENCES:

1)Stoker, A. K. and W. D. Purtyman, "Some Problems Involved With Sampling Geothermal Sources," Las Alamos Scientific Lab, Report LA-UR-75-2335, 1975.

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_2S, 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_2S should be regarded with caution due to the reactive metal environment of the cylinder.

EDITION:

7/78

ILLUSTRATION:

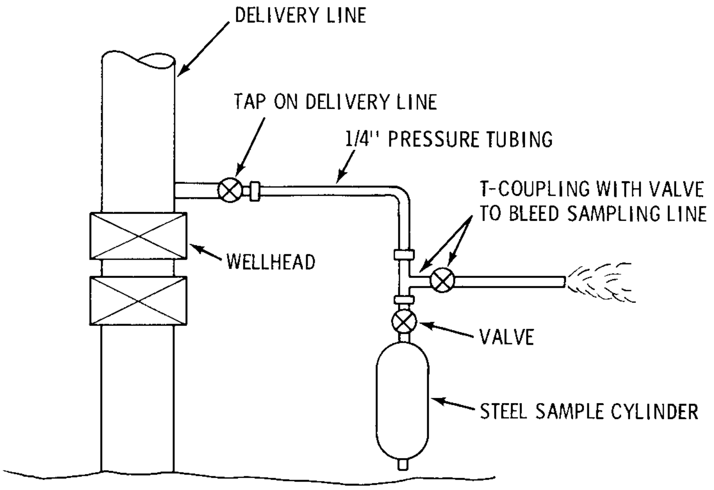


FIG 1. EVACUATED CYLINDER SAMPLING APPARATUS

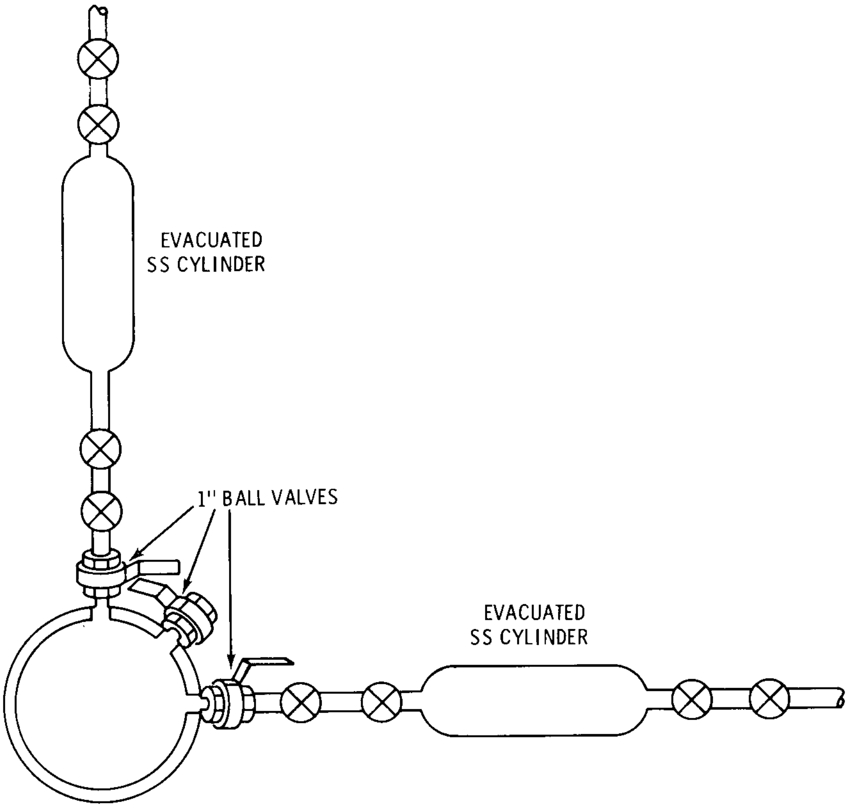


FIG 2. EVACUATED CYLINDER ARRANGEMENT USED IN FIELD TEST

METHOD TITLE:

Evacuated cylinder-storage oven method.

NO. 31-S

SAMPLE TYPE:
Liquid

SAMPLE POINT:
Pipeline

APPLICATION:

Sampling hot pressurized fluid systems.

REFERENCES:

Allen, C.A., J.M. Baldwin and R.E. McAtee, "Status Report. Raft River Project. Sampling Analysis, and Environmental Effects Studies, Allied Chemical Corp., Idaho National Engineering Laboratory, Idaho Falls, Idaho. Proceedings, 2nd Workshop on Sampling and Analyses of Geothermal Effluents, Las Vegas, February 1977.

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.

EDITION:
7/78

ILLUSTRATION:

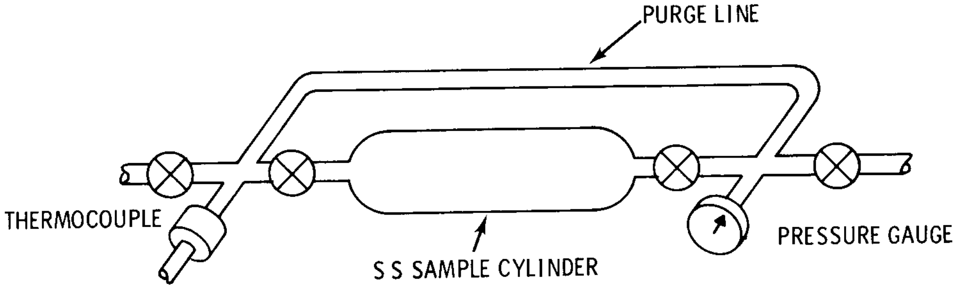


FIG 1. GEOTHERMAL HIGH PRESSURE SAMPLER

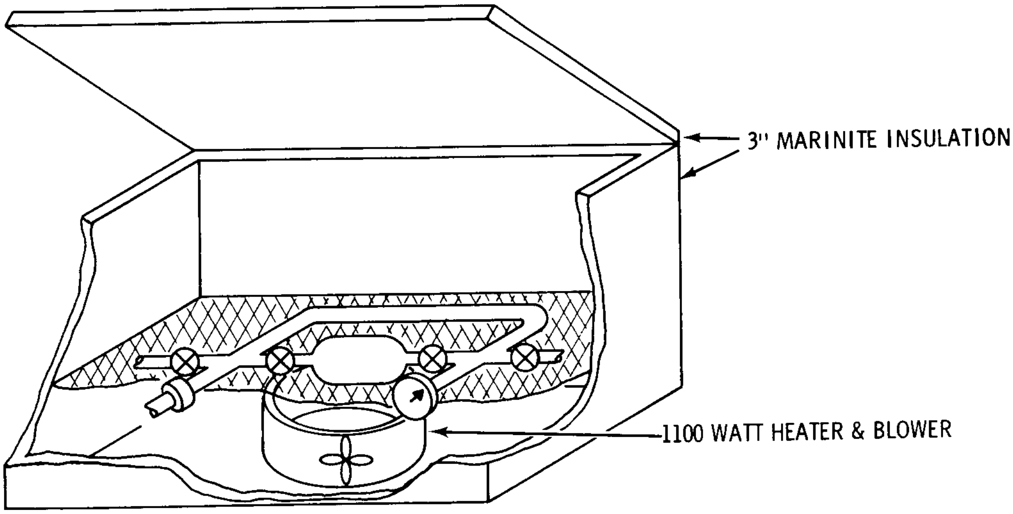


FIG 2. SAMPLE STORAGE OVEN

METHOD TITLE:

Klyen downhole sampler

NO.

32-S

SAMPLE TYPE:

Liquid and Gas

SAMPLE POINT:

Wellbore

APPLICATION:

Downhole sampling of liquid and gas.

REFERENCES:

1. Klyen, L. E. "A Vessel for Collecting Subsurface Water Samples from Geothermal Drillholes," Geothermics, Vol. 2, p. 56-60, 1973.
2. Literature from Kuster Co., P.O. Box 7038, Long Beach, CA 90807.

DESCRIPTION

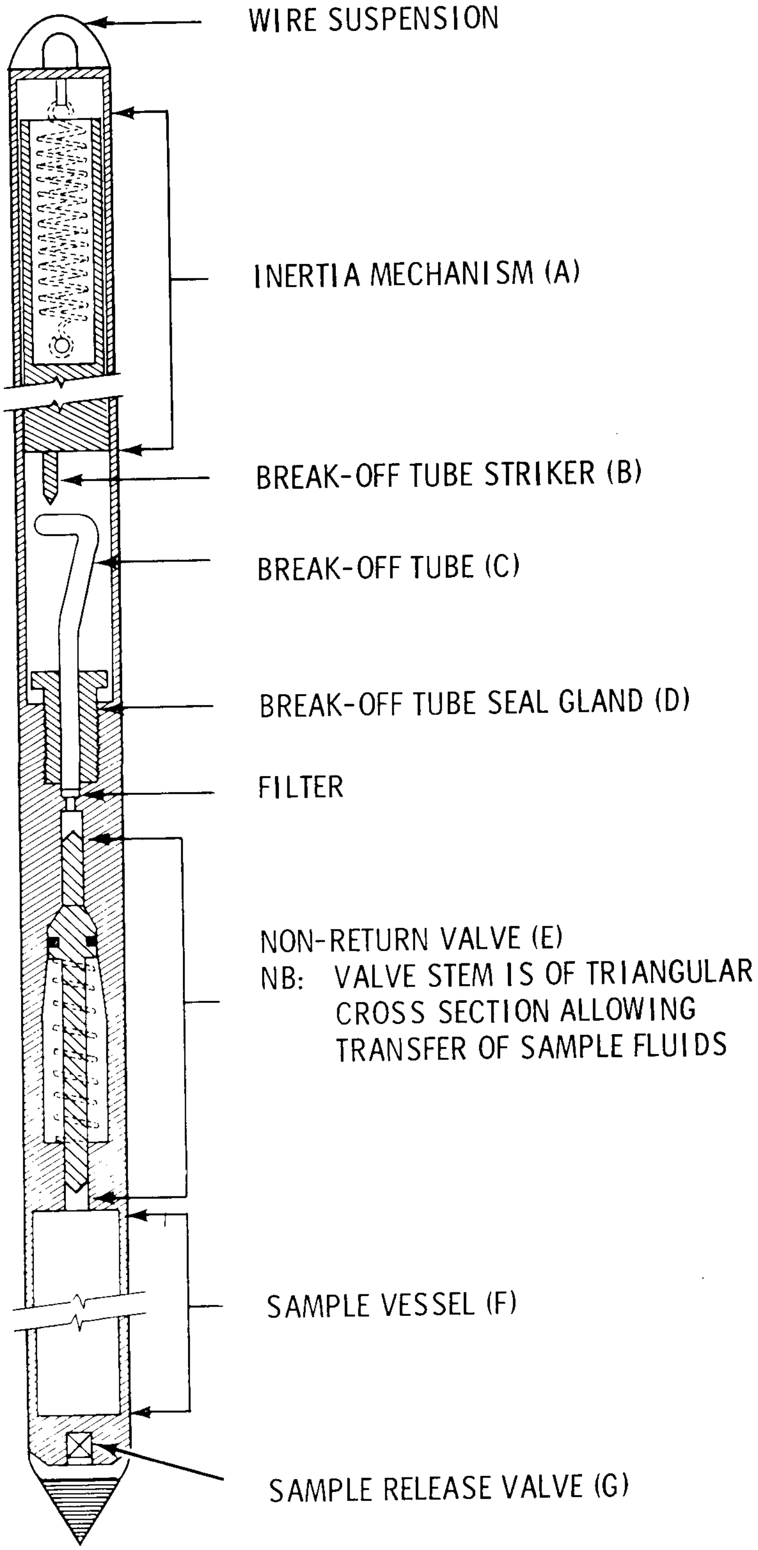
The loaded sampler is shackled to the suspension wire of a suitable winch which must be fitted with a depthometer. It is then lowered into a recovery tube on the top of the borehole, the suspension wire passing over a pulley wheel and through a threaded gland, which is screwed on to the top of the recovery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



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: Fournier, R.O. and J.C. Morgenstern, "A Device for Collecting Down-Hole Water and Gas Samples in Geothermal Wells" U.S.G.S. Prof. Paper, 750-C, p. C151-155, 1971.
Fournier, R.O. and A.H. Truesdell, "A Device for Measuring Down-Hole Pressures and for Sampling Fluids in Geothermal Wells," U.S.G.S. Prof Paper 750-3, p. C146-C150, 1971.
Fournier, R.O. and J.M. Thompson, "Geothermal Down-Hole Sampling Instrumentation," Proceedings, 2nd Workshop on Sampling and Analysis of Geothermal Effluents, Las Vegas, NV, 2/77.

DESCRIPTION

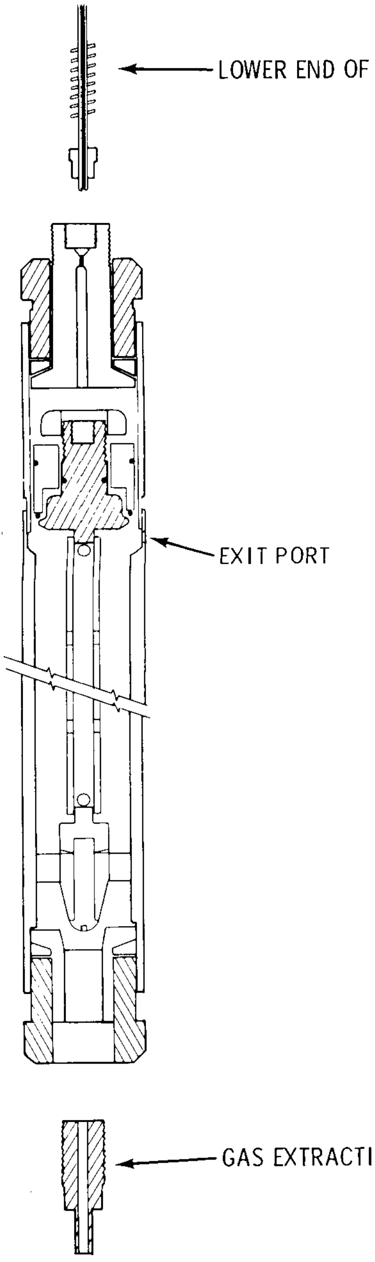
Sampler in open position is lowered using a long flexible stainless steel tube into the wellbore and fluid flows through it during descent. Closure is accomplished by nitrogen gas pressure applied from the surface through the flexible tube to a piston and plunger within the sample chamber. Continued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

COMMENTS:

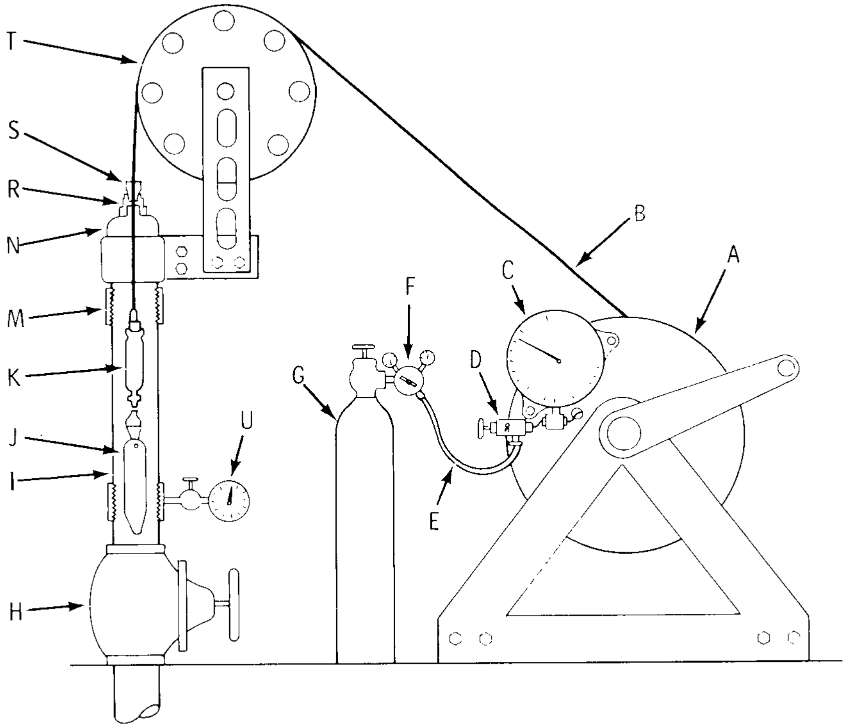
1. All materials are stainless steel except for one teflon o-ring, two viton o-rings, and several other teflon parts.
2. A modification of the lower end of the sampler using a special gas extraction fitting allows the sampler to be used for gas sampling.
3. Sample device can be used at temperatures up to 280°C.

EDITION:
7/78

ILLUSTRATION:



Working drawing of device for collecting down-hole samples of water and gas in geothermal wells.



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 lea 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 t tally the number of revolutions, u, pressure gage f wellhead pressures.

METHOD TITLE:

Evacuated flask method for silencer sampling.

NO. 34-S

SAMPLE TYPE: Gas

SAMPLE POINT: Silencer

APPLICATION:

Sampling of reactive gases (CO_2 and H_2S) from silencers.

REFERENCES:

Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977. (See note V on page B-1)

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.

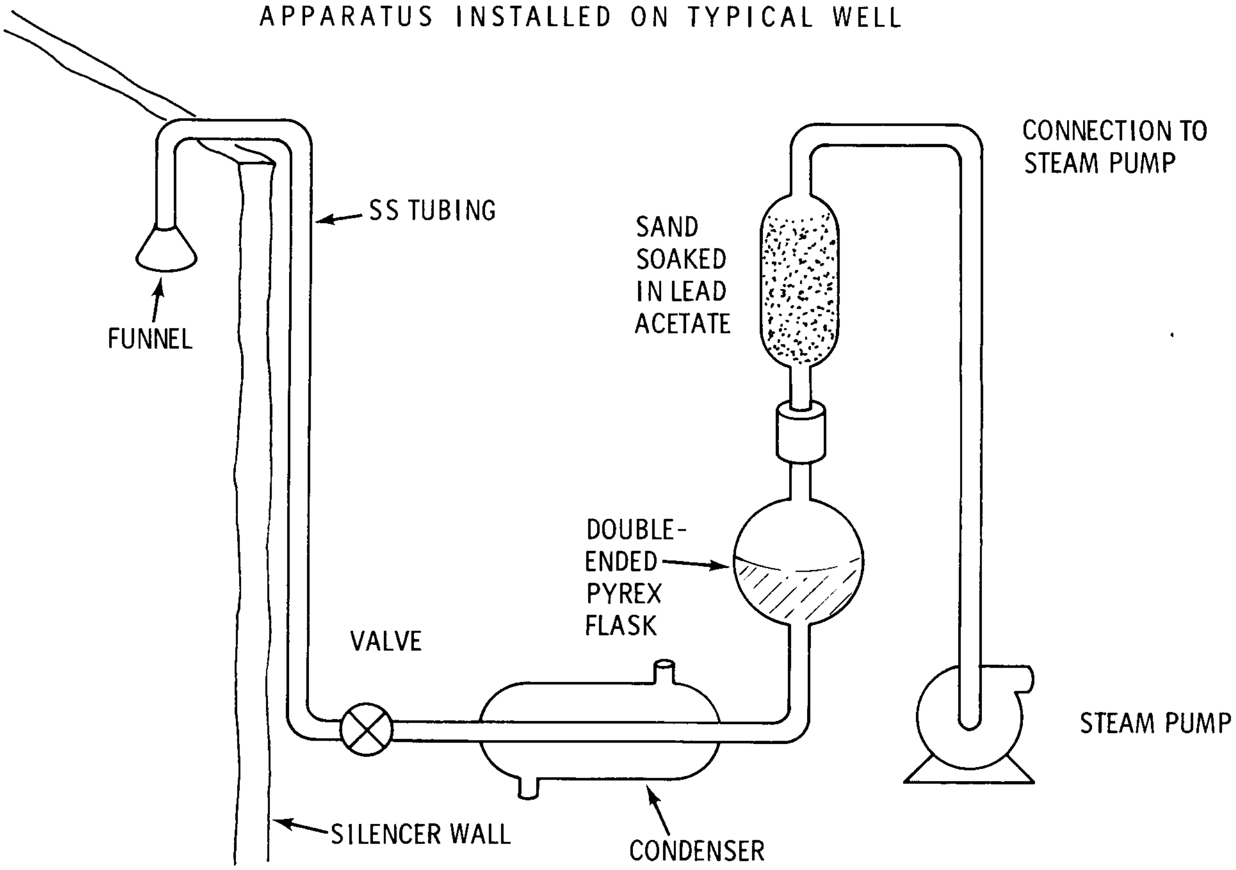
COMMENTS:

The method is not applicable for collecting residual gas (CH_4, N_2, H_2, etc.) samples.

EDITION: 7/78

PAGE: B-36

ILLUSTRATION:



APPARATUS FOR COLLECTING STEAM AND GAS SAMPLES FROM THE SILENCER OF A GEOTHERMAL WELL

METHOD TITLE:	NO. 35-S	
Liquid sampling from unsilenced discharge pipes.	SAMPLE TYPE: Liquid	SAMPLE POINT: Discharge pipe

APPLICATION:	REFERENCES:
Sampling of liquid from discharge pipes.	Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems," Academic Press, New York, 1977. (See note V on page B-1)

DESCRIPTION

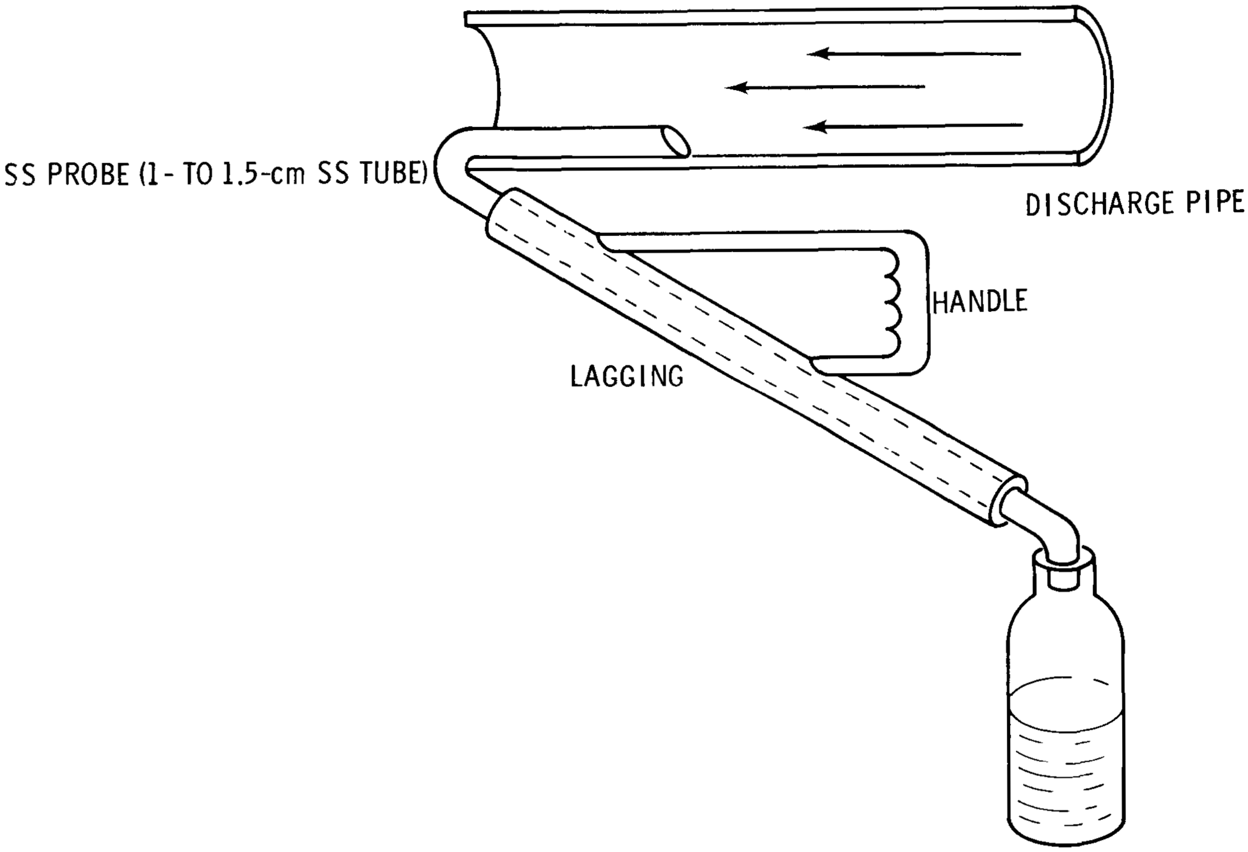
The sampling apparatus is welded to the discharge pipe or held in the hand if the discharge is small. If held in the hand, the sampler should be inserted very slowly into the discharge, preferably toward the bottom of the pipe. Evaporative heat losses are generally small and samples at close to boiling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

EDITION:
7/78

ILLUSTRATION:



APPARATUS FOR COLLECTING WATER SAMPLES FROM THE END OF THE HORIZONTAL DISCHARGE PIPE OF A GEOTHERMAL WELL

METHOD TITLE:

Gas concentration measurement method.

NO. 36-S

SAMPLE TYPE:

Gas

SAMPLE POINT:

Pipeline

APPLICATION:

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

REFERENCES:

1. McDowell, G.D. Geothermics 3, 100 (1974)
2. Ellis, A.J. and W.A.J. Mahon, "Chemistry and Geothermal Systems", Academic Press, New York, 1977. (See note V on page B-1)

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 CO_2 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

$$W(\mathrm{lb}) = \frac{M144P_gV_s}{1545T} \quad \text{and} \quad W(\mathrm{kg}) = \frac{MP_gV_s}{83.13T}$$

where W is pounds of gas per pound of steam or kilograms of gas per kilogram of steam; P_g 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:

EDITION:

7/78

PAGE:

B-38

ILLUSTRATION:

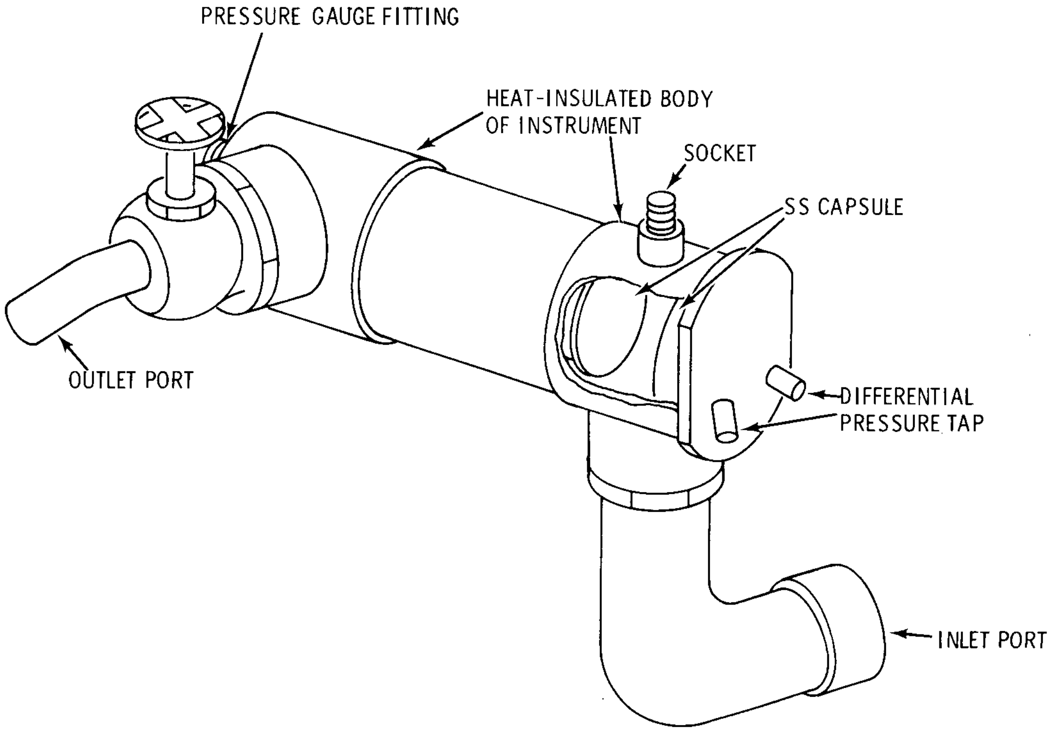


FIG 1. APPARATUS FOR MEASURING THE GAS CONTENT OF THE DISCHARGE FROM A GEOTHERMAL WELL

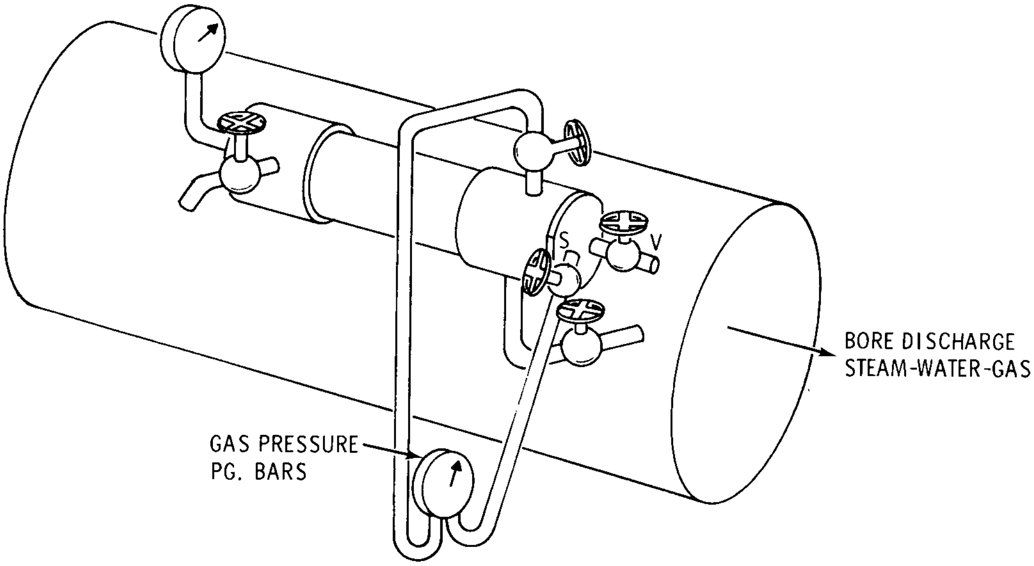


FIG 2. SCHEMATIC ARRANGEMENT OF GAS PROBE IN USE

METHOD TITLE:

Gas sample inlet system for gas chromatograph.

NO. 37-S

SAMPLE TYPE: Gas

SAMPLE POINT:

APPLICATION:

Injecting gas samples into gas chromatograph system.

REFERENCES:

A. H. Truesdell, U.S. Geological Survey, Menlo Park, CA, Personal Communication.

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:

EDITION: 7/78

ILLUSTRATION:

Figure 1

GC INLET SYSTEM

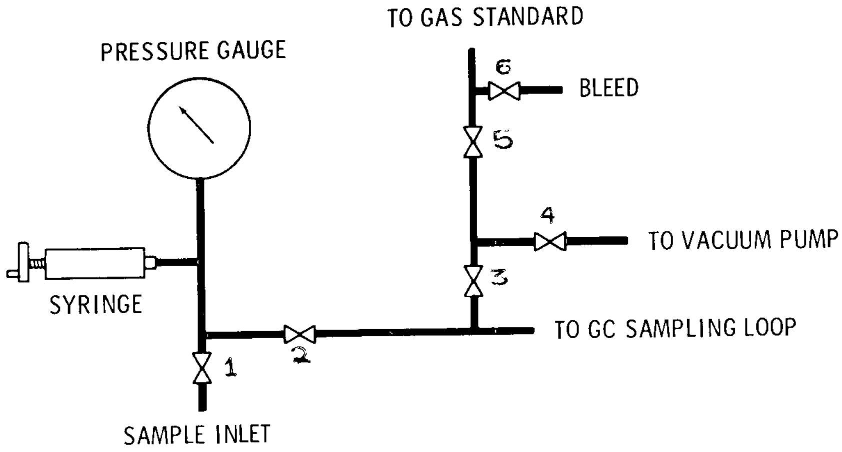


Figure 2

DETAIL OF SYRINGE

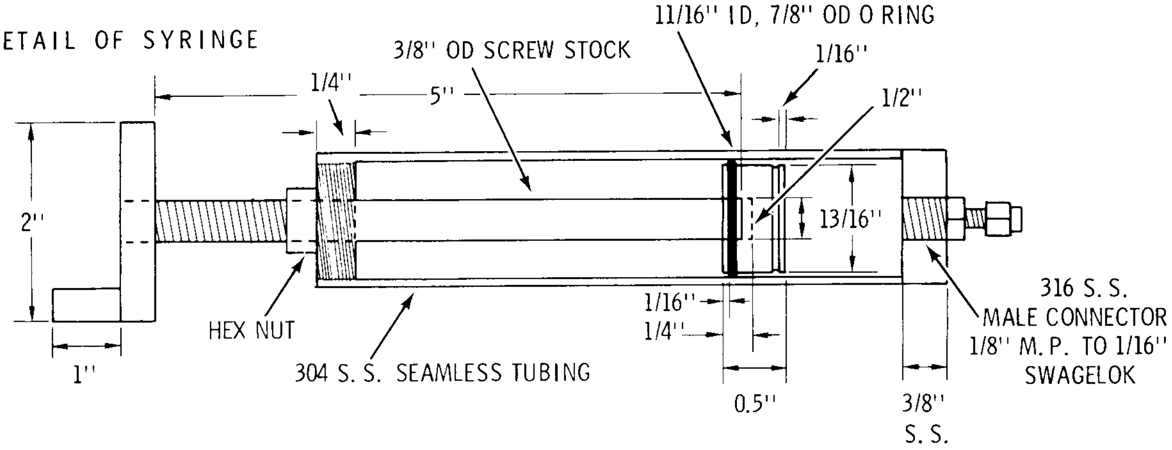
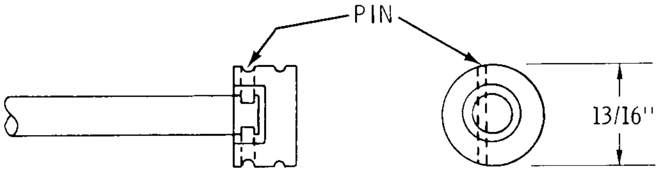


Figure 3

DETAIL OF PISTON



Recommended Analytical Methods for Geothermal Liquids

1. 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: H_2S and 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:

Parameter symbol
and/or name

Analysis: Method Name **No.** Analysis Reference Number

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.

Cross Reference: References, appendices, other sampling numbers, and analyses numbers in this manual	**Literature Reference:** References literature outside this manual - see bibliography for details.
Reagents: Chemicals used in this method	**Equipment:** Required equipment, instrumentation and special apparatus for 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 μ 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 μ membrane filter. Parameters determined using the FA sample were the same as for the RA sample.
5. A 20:1 dilution for silica (SiO_2) using cooled filtered brine and distilled, deionized water for the dilution.
6. A sample was collected for entrained H_2S 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 CO_2 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

Alkalinity

Analysis: Acid Titration

No. 1-A

Method: The sample is titrated with a strong acid (H_2SO_4 or HCl) to separate equivalence points for OH^-, CO_3^{2-}, and HCO_3^-. Equivalence points are determined either potentiometrically or with visual indicators.

Sample Handling: Use RU brine, determine as quickly as possible after sampling to avoid CO_2 losses.

Range: >20 mg/l $CaCO_3$ **Precision:** ±3% **Accuracy:** ±10%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 38-A, 39-A, 61-A, 62-A, 63-A, 64-A, 65-A, 141-A

Literature Reference:

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

Reagents:

Standard HCl or H_2SO_4
Phenolphthalien indicator
Mixed methyl red-bromocresol green indicator or methyl orange indicator
Standard pH buffers

Equipment:

Buret, pH meter and electrodes

Remarks:

1. Interferences: determinations of OH^-, CO_3^{2-}, and HCO_3^- contributions to total alkalinity possible only with absence of other weak bases; residual Cl_2, color, and turbidity affect visual indicator titrations; loss or gain of atm. CO_2 affects results; erratic results obtained when oxidizing or reducing species are present; some constituents may cause buffering at endpoint.
2. Field determination recommended.

Edition:
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Al

Aluminum

Analysis: Atomic Absorption (Direct) **No.** 2-A

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
N_2O burner head

Remarks:

1. High Fe, PO_4, 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.

(cont. on back)

Edition:
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4. If sample shows Tyndall effect, filter through 0.45 μ membrane filter.

Al

Aluminum

Analysis: Atomic Absorption (Graphite Furnace) **No.** 3-A

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.

Range: **Precision:** ±4% **Accuracy:**

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S Analysis Methods: 2-A, 4-A, 5-A	Instrument Manufacturer's Methods Manual
Reagents:	**Equipment:**
Aluminum standards Argon gas	Atomic absorption spectrophotometer Graphite furnace Plastic tip pipets

Remarks: Matrix matching between sample and standards, standard additions and background correction recommended.

Edition:
7/78

Al

Aluminum

Analysis: Atomic Absorption (Extraction) **No.** 4-A

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 N_2O-acetylene burner and the absorption measured at 309.3 nm.

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

Range: **Precision:** ±15% **Accuracy:** ±6%

Cross Reference:

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

Literature Reference:

APHA 301 V (75)
Presser and Barnes, USGS WRI-22-74
Instrument Manufacturer's Standard Methods Manual

Reagents:

Methyl isobutyl ketone or chloroform
Ammonium acetate
Ammonium hydroxide
8-Hydroxyquinoline (8-Quinolinol)
Aluminum standards
Nitrous oxide gas cylinder

Equipment:

Atomic Absorption Spectrophotometer
N_2O burner head
Separatory funnels

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

Al

Aluminum

Analysis: Flame Emission **No.** 5-A

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 HNO_3 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%
>0.5 mg/l±5%

Cross Reference:

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

Literature Reference:

Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 95-116.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

Reagents:

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

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.

Edition:
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(cont. on back)

5. In lab, dilute sample and add 2000 mg/ℓ potassium chloride as an ionization buffer.

Al

Aluminum

Analysis: X-Ray Fluorescence	**No.** 6-A

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

Literature Reference:

Cooper, J.A., Nuc. Inst. and Methods, Vol. 106, pp. 525-538, 1973.

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

Al

Aluminum

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 7-A

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.

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:
"Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System," EPA-600/4-77-032, June 1977.

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.
3. Additional reference: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

Edition:
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(cont. on back)

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

Al

Aluminum

Analysis: Spark Source Mass Spectrometry **No.** 8-A

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:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed. Academic Press, NY (1977).

D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

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.

Edition:
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Al

Aluminum

Analysis: Neutron Activation

No. 9-A

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.

Range:

Precision:

Accuracy:

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

Literature Reference:
Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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

Al

Aluminum

Analysis: Emission Spectrometry

No. 10-A

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 RA 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).

Edition:
7/78

Ammonia

Analysis: Distillation Procedure **No.** 11-A

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: **Precision:** **Accuracy:**

Cross Reference:

Appendix 2

Sampling Methods: 11-S, 29-S

Analysis Methods: 12-A, 13-A, 14-A, 15-A

Literature Reference:

APHA 418A (75)

ASTM 1426-74 (77)

EPA 00610 (76)

Reagents:

- $Na_2B_4O_7$
- NaOH
- Dechlorinating agent (any of the following):
  - Phenylarsine oxide
  - Sodium arsenite
  - Sodium sulfite
  - Sodium thiosulfate
- Sulfuric acid
- Ammonia-free H_2O

Equipment:

- 800-2000 ml pyrex flask
- vertical condenser
- 500 ml receiving flask
- (Micro-distillation equipment may also be used)

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.

Edition:
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NH3

Ammonia

Analysis: Titration **No.** 12-A

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: **Precision:** ±2% **Accuracy:** unknown

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

Literature Reference:

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

Equipment:
KJELDAHL apparatus with flasks, burets.

Remarks: Distillation required before analysis.

Edition:
7/78

NH_3

Ammonia

Analysis: Nesslerization **No.** 13-A

Method: A basic solution of $HgI_2 + KI$ is added to the sample to form $NH_2Hg_2I_3$ 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%

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

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

Reagents:
$ZnSO_4 \cdot 7H_2O$
EDTA or Rochelle salt solution
Nessler reagent ($HgI_2 + KI$)
NaOH
Ammonia standards
Ammonia free H_2O

Equipment:
Spectrophotometer or filter photometer at 450-500 nm
Matched absorbance cells or Nessler tubes
pH meter

Remarks:

1. Interferences: many interferences eliminated by distillation; others (in nondistilled samples) eliminated by addition of basic $ZnSO_4$ to precipitate Ca^{2+}, Fe, Mg^{2+}, and H_2S; addition of EDTA or Rochelle salts prevents Ca^{2+} and Mg^{2+} from precipitating during determinations; S^{2-}, hydrazine, urea, and other hydrolyzable organic amides and amino acids will interfere.
2. Ammonia standards must be prepared fresh daily.

Edition:
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NH_3

Ammonia

Analysis: Automated Colorimetric Phenate

No. 14-A

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

Literature Reference:
EPA 00610 (76)
Technicon Auto Analyzer Industrial Method 98-70W Revised.
Bolleter, W.T., Bushman, C.J. and Tidwell, P.H., Anal. Chem., 33, 592, 1961.

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

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 Hg^{2+}, turbidity (removed by filtration), color absorbing from 630-660 nm.

Edition:
7/78

NH_3

Ammonia

Analysis: Ammonia Selective Electrode | **No.** 15-A

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.

Range: 1-17,000 mg NH_3/l **Precision:** ±3% **Accuracy:** ±3%

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, S^{2-}, 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

NH_3

Ammonia

Analysis: Ion-Exchange Chromatography

No. 16-A

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:

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

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.
2. Additional reference: Small, H., T. S. Stevens, and W. C. Bauman, Anal. Chem. 47 1801 (1975).

Sb

Antimony

Analysis: Atomic Absorption (Direct) **No.** 17-A

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:
Instrument Manufacturer's Method's Manual,
Dean & Rains III (192).

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)

Edition:
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6. Use of a graphite furnace will increase sensitivity.

Sb

Antimony

Analysis: Atomic Absorption (Hydride Evolution)

No. 18-A

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 at $NaBH_4$ to an acid solution of sample containing $SnCl_2$ 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
$SnCl_2$ solution
$NaBH_4$ 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

No. 19-A

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 HNO_3 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

Literature Reference:
Cooper. Nuc. Inst. and Methods, Vol. 106, pp. 525-538, 1973.

Reagents:
Antimony standards

Equipment:
X-ray fluorescence spectrophotometer

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.

Edition:
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Sb

Antimony

Analysis: Inductively Coupled Plasma - Atomic Emission Spectroscopy **No.** 20-A

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:** "Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System," EPA-600/4-77-032, June 1977.
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.
3. Additional references: R.H. Scott and M.L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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(cont. on back)

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.

Antimony

Analysis: Spark Source Mass Spectrometry	**No.** 21-A

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/1 **Precision:** ±25% **Accuracy:** ±25%

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

Literature Reference:
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:
Antimony standards

Equipment:
Spark source mass spectrometer

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

Edition:
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Sb

Antimony

Analysis:	Neutron Activation	**No.**	22-A

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: **Precision:** **Accuracy:**

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

Literature Reference:
Robertson & Carpenter, "Neutron Activation Techniques for the Measurements of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

Reagents:

Equipment:

Neutron source (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 for metals and non-metals.

Edition:
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Sb

Antimony

Analysis: Emission Spectrometry

No. 23-A

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

HNO_3 or $HClO_4$

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 precipited along with SiO_2 in HNO_3 dehydration procedure.
4. Alternatively antimony may be precipitated with $HClO_4$ during dehydration procedure. This method is not applicable where high levels of alkali metals form difficultly dissolved perchlorate salts.

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(over)

5. Large differences in matrix effects will be observed depending on the type of excitation source (flame, AC spark, or DC arc).

As

Arsenic

Analysis: Silver Diethyldithiocarbamate **No.** 24-A

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) USGS Book 5, Chapter A1 (1974)
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.

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As

Arsenic

Analysis: Atomic Absorption (Direct) **No.** 25-A

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.

Range: (linear) 0.7-20 mg/l **Precision:** **Accuracy:**

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

Literature Reference:
Dean & Rains, Flame Emission and Atomic Absorption Spectrometry, Vol III, 1975. pp. 205-208.
Instrument Manufacturer's Standard Methods Manual.

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, Mg, 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.

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4. Use of a graphite furnace will increase sensitivity.

As

Arsenic

Analysis: Atomic Absorption (Hydride Evolution) **No.** 26-A

Method: Arsenic is determined as its hydride by atomic absorption at 193.7 nm in an argon or nitrogen-hydrogen flame after reduction with $SnCl_2$ - 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
$SnCl_2$
Zn slurry (200 mesh Zn)
HCl
Nitrogen or argon bottled gas
Hydrogen bottled gas
$NaBH_4$ 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 $NaBH_4$ 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.

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As

Arsenic

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 27-A

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 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:
Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System EPA-600/4-77-032, June 1977.

Reagents:
Arsenic 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. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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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.

Arsenic

Analysis: Spark Source Mass Spectrometry

No. 28-A

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:
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

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).

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As

Arsenic

Analysis: Neutron Activation **No.** 29-A

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:
Robertson & Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in *Environmental* Samples", NAS-NS-3114, Jan. 1974.

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

Edition:
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As

Arsenic

Analysis: Emission Spectrometry **No.** 30-A

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).

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Ba

Barium

Analysis: Turbidimetric (Absorptometric) **No.** 31-A

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

Sample Handling: Use filtered acidified brine.

Range: **Precision:** **Accuracy:**

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 197-A, 198-A

Literature Reference:
API 3.32 (1968).

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 $CaCO_3$.
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.

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Ba

Barium

Analysis: Atomic Absorption **No.** 32-A

Method: The sample containing barium is aspirated directly into a N_2O-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

Literature Reference:
APHA 303 (75) USGS Book 5, Chapter A1 (1974)
EPA 01007 (76)
Instrument Manufacturer's Standard Methods Manual

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.

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4. If sample shows Tyndall effect, filter through 0.45 μ 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 **No.** 33-A

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 HNO_3 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%
>0.5 mg/l±5%

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

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 33-65.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

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

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 KNO_3 until a 1000-2000 mg/l K background is obtained in both standards and samples.
2. Use of standard additions and matrix matching of alkali and alkalir earth metals recommended.
3. Precipitated $BaSO_4$ may be determined by filtration of brine through 0.45μ filter ashing paper dissolution of $BaSO_4$ with EDTA and ammonia and measurement via FAE.

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

Ba

Barium

Analysis: Inductively Coupled Plasma - Atomic Emission Spectroscopy **No.** 34-A

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.

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:
"Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System" EPA-600/4-77-032, June, 1977.

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.
3. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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

Ba

Barium

Analysis: Spark Source Mass Spectrometry

No. 35-A

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.)
±25%

Accuracy: ±5% (isotope dil.)
±25%

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

Literature Reference:
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

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.
2. Additional references: J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975).
   J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975).
   R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. 41 955 (1969).

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Ba

Barium

Analysis: Neutron Activation

No. 36-A

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.

Range:

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Robertson & Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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Ba

Barium

Analysis: Emission Spectrometry **No.** 37-A

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).

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HCO_3, CO_3

Bicarbonate, Carbonate

Analysis: Acid Titration **No.** 38-A

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. Specie 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
Analysis Methods: 1-A, 39-A, 61-A, 62-A, 63-A, 64-A, 65-A, 141-A

Literature Reference:
APHA 407 B(75)
ASTM D513-71C (77)
USGS Book 5, Chapter A1 (1974)

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

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).

Edition: 2. CO_3^{2-}, HCO_3^-, and H_2CO_3 concentrations may be determined by this method.

7/78 3. Determine bicarbonate and carbonate on site whenever possible on fresh raw unacidified brine.

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4. HCl may be standardized with Na_2CO_3. Dry Na_2CO_3 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.

HCO_3, CO_3

Bicarbonate, Carbonate

Analysis: Calcium Carbonate Saturation Calculation **No.** 39-A

Method: By determining the sample pH and calcium ion concentration and with the values of the solubility product of $CaCO_3$ (K_S) and the second proton dissociation constant of H_2CO_3 (K_2), bicarbonate may be determined from the equation: $\log(HCO_3^-) = -\log(Ca^{2+}) - \log(K_2/K_S) - pH$ and carbonate from the equation: $(CO_3^{2-}) = \frac{K_2(HCO_3^-)}{(H^+)}$

Sample Handling: Use RU brine for pH measurement and RA or FA brine for Ca^{2+} determination.

Range:

Precision:

Accuracy:

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 1-A, 38-A, 61-A, 62-A, 63-A, 64-A, 65-A, 141-A

Literature Reference:
APHA 203 (75)

Reagents:
Use appropriate reagents for pH and Ca^{2+} determinations.

Equipment:
Use equipment appropriate to pH, Ca^{2+}, and TDS determinations.

Remarks:

1. pH, Ca^{2+} 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.

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Boron

Analysis: Carmine Colorimetric **No.** 40-A

Method: Carmine in concentrated H_2SO_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.

Range: 2-20 μg **Precision:** 4 μg ±10% higher conc. ±5% **Accuracy:** 4 μg ±10%, higher conc. ±5%

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 A1 (1974)

Reagents:
Boron standards
HCl
H_2SO_4
Carmine N.F. or carminic acid
NaOH

Equipment:
UV-Vis spectrophotometer at 585 nm.

Remarks: 1. Interferences: F^-, SiO_2 and PO_4^{3-} create slight interference.
2. Range may be expanded by dilution or evaporation of sample.

Edition:
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Boron

Analysis: Curcumin Colorimetric

No. 41-A

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

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

Reagents:
Boron standards
Curcumin reagent
Ethyl or isopropyl alcohol
HCl
Oxalic acid
NaOH or Na_2CO_3

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 NO_3^-; >100 mg/l Ca^{2+} and Mg^{2+} may be removed by precipitating with NaOH or Na_2CO_3 and filtering.
2. Close control of evaporating times, volumes and other variables required.
3. Range may be expanded by sample dilution or concentration.

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B

Boron

Analysis: Flame Emission **No.** 42-A

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.

Range: >2 mg/l low brine
>20 mg/l high brine

Precision: ±10-25%

Accuracy: ±10-25%

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

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 95-116.
W.Snelleman, Spectrochim. Acta, 23B, 403 (1968).

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

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) ispropanal.

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Boron

Analysis: Inductively Coupled Plasma - Atomic Emission Spectroscopy

No. 43-A

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: 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:
"Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System", EPA-600/4-77-032, June, 1977.

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.
3. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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(cont. on back)

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

Boron

Analysis: Spark Source Mass Spectrometry **No.** 44-A

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.) ±25% **Accuracy:** ±5% (isotope dil.) ±25%

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

Literature Reference:
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:
Boron standards

Equipment:
Spark source mass spectrometer

Remarks:

1. Spark source mass spectrometry provides simultaneous, multi-element determination for selected metals and non-metals.
2. Additional references: J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975). J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975). R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. <u>41</u> 955 (1969).
3. Since boron is a volatile element, evaporation to complete dryness may volatilize boron (Rowe, Fournier, and Morey, 1973, USGS Bulletin #1303).

Edition:
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Boron

Analysis: Emission Spectrometry **No.** 45-A

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;
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Br

Bromide

Analysis: Hypochlorite Oxidation - Titration

No. 46-A

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 71870 (76)

USGS Book 5, Chapter A1 (1974)

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 molybdate
- Sodium thiosulfate or 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:

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Br

Bromide

Analysis: Chromic Acid Oxidation - Extraction **No.** 47-A

Method: Bromide is oxidized by chromic acid to bromine, then extracted from the aqueous phase with CCl_4. The CCl_4 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
±15% @ 40 mg/l **Accuracy:** ±3-4% @ 200-40
12% @ 40 mg/l

Cross Reference:

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

Literature Reference:

API 3.14 (68)

Reagents:

Sulfuric acid
Chromium trioxide
Carbon tetrachloride

Equipment:

UV-Vis spectrophotometer at 417 nm
Separatory funnels
Filtering apparatus

Remarks:

1. Chloride and iodide do not interfere in this method.
2. Large precipitates may form upon addition of H_2SO_4 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 our required for high solids brines during the extraction step.

Edition:
7/78

Br

Bromide

Analysis: Colorimetric (Iodine-Permanganate) **No.** 48-A

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)
USGS Book 5, Chapter A1 (1974)

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_2^{2} >1mg/l, $S_2O_3^{-3}$ >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

Br

Bromide

Analysis: Phenol Red - Colorimetric **No.** 49-A

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

Literature Reference:

APHA 406 (75)

Reagents:

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

Equipment:

UV-Vis spectrophotometer to measure at 590 nm.

Remarks:

1. Interferences: Cl_2 forms during reaction, may be removed by addition of $Na_2S_2O_3$.
2. Glassware must be cleaned using dilute HNO_3 to remove traces of bromide.
3. High salinity may affect consistency of results.

Edition;
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Analysis:	Bromide Specific Electrode	**No.**	50-A

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 **Precision:** ±2% **Accuracy:**

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

Literature Reference:

Electrode Manufacturer's Literature

Reagents:

Ionic strength adjustor ($NaNO_3$)
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 $NaNO_3$ per 100 ml solution.

Edition:
7/78

Br

Bromide

Analysis: X-Ray Fluorescence	**No.** 51-A

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:	**Literature Reference:**
Appendix 2 Sampling Methods; 11-S, 29-S	Cooper, J.A. , Nuc. Inst. and Methods., Vol. 106, pp. 525-538, 1973.
Reagents:	**Equipment:**
Bromide standards	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

Br

Bromide

Analysis: Ion-Exchange Chromatography **No.** 52-A

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

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).

Reagents:

Na_2CO_3
$NaHCO_3$
Standard bromide solutions

Equipment:

Dionex Ion Chromatograph
75-120 psi air supply

Remarks:
1. Bromide may be determined simultaneously with fluoride, nitrate, and sulfate by this method.
2. Additional reference: Small, H., T. S. Stevens and W. C. Bauman, Anal. Chem. 47, 1801 (1975).

Edition:
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Br

Bromide

Analysis: Spark Source Mass Spectrometry

No. 53-A

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

Literature Reference:
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:
Bromide standards

Equipment:
Spark source mass spectrometer

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

Br

Bromide

Analysis: Neutron Activation **No.** 54-A

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:

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

Literature Reference:

Robertson & Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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:
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Ca

Calcium

Analysis: EDTA Titrimetric **No.** 55-A

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: **Precision:** ±5% **Accuracy:** ±3%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 92-A, 93-A, 124-A

Literature Reference: ASTM D511-76B (1977)
APHA 306C (1975)
USGS Book 5, Chapter A1 (1974)
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

No. 56-A

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)
USGS, Book 5 Chapter A1, (1974).
APHA 301A (1975)
ASTM D2576-70, D511-76C (1977).
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains; 1975, Vol. III, pp. 33-64.

Reagents:

Ca stock solution, 1000 ppm, may be prepared from $CaCO_3$ and HCl
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, $SO_4^{=}$, 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) La^{+3} or Sr^{+2} to minimize interferences from Si, Al, PO_4, SO_4, Ti, and Zr.
3. If sample shows Tyndall effect, filter through a 0.45μ membrane filter.

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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.

Ca

Calcium

Analysis: Flame Emission

No. 57-A

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 HNO_3 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% >0.5 mg/l±5%

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

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 33-65.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

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.

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Ca

Calcium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy **No.** 58-A

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: 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:
Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA 600/4-77-032, June 1977.

Reagents:
Calcium standard solution; prepared from $CaCO_3$ and 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 affect vaporization characteristics. Background correction and standard additions method recommended. ICP-AES is a simultaneous multi-element technique for metal ions.
2. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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3. Upper limit of concentration range may be extended by using alternate spectral lines.

Analysis: Neutron Activation	**No.** 59-A

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.

Range: **Precision:** **Accuracy:**

Cross Reference: Appendix 2 Sampling Methods: 11-S, 29-S	**Literature Reference:** Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.
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:
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Ca

Calcium

Analysis: Emission Spectrometry **No.** 60-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 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:
Calcium 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:
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CO_2

Carbon Dioxide

Analysis: Titrimetric

No. 61-A

Method: The sample is titrated with a strong acid (H_2SO_4 or HCl) to separate equivalence points for CO_3^{2-}, HCO_3^-, and OH^-. Equivalence points are determined either potentiometrically or with visual indicators. The molar concentration of CO_2 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:

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
Analysis Methods: 1-A, 38-A, 39-A, 62-A, 63-A, 64-A, 65-A, 141 A

Literature Reference: ASTM D513-71 C,D,E (1977) The following procedure which applies to free CO_2 can be used for total CO_2: APHA 407B (1975)

Reagents:
Hydrochloric or sulfuric acid
Sodium carbonate or sodium hydroxide
Bromcresol green-methyl red indicator
Phenolphthalein indicator

Equipment:
Buret
pH meter

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 parts.
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.

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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.

CO_2

Carbon Dioxide

Analysis: Strontium Gravimetric

No. 62-A

Method: Sample is pretreated with phosphoric acid in a glass bubbler apparatus using a nitrogen atmosphere and boiled to remove all the CO_2 from sample. The CO_2 is trapped in a sodium hydroxide solution and is then determined gravimetrically by adding strontium nitrate solution, filtering, ashing and weighing the $SrCO_3$ 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).

Range:

Precision: ±10%

Accuracy:

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

Analysis Methods: 1-A, 38-A, 39-A,61-A 63-A, 64-A, 65-A, 141-A

Literature Reference:

Reagents:

Phosphoric acid
Sodium hydroxide
Strontium nitrate
Sodium carbonate
Nitrogen gas - CO_2 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 CO_2 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).

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CO_2

Carbon Dioxide

Analysis: Precise Evolution **No.** 63-A

Method: CO_2 is liberated by acidifying and boiling the sample in a closed system. The liberated CO_2 is trapped by bubbling into a $Ba(OH)_2$ solution; excess $Ba(OH)_2$ is then titrated with standard HCl and the CO_2 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
Analysis Methods: 1-A, 38-A, 39-A, 61-A, 62-A, 64-A, 65-A, 141-A

Literature Reference:
ASTM D513-71A, B (1977)

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 - Titrimetric".
3. Alternatively, the CO_2 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.)

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CO_2

Carbon Dioxide

Analysis: Calculation **No.** 64-A

Method: By determining the sample pH and calcium ion concentration and with the values of the solubility product of $CaCO_3$ (K_S) and the second proton dissociation constant of H_2CO_3 (K_2), bicarbonate may be determined from the equation: $\log(HCO_3^-) = -\log(Ca^{2+}) - \log(K_2/K_S) - pH$ and carbonate from the equation: $(CO_3^{2-}) = \frac{K_2(HCO_3^-)}{(H^+)}$. The amount of CO_2 is determined by the relation mg/l total CO_2 = mg/l free CO_2 + 0.88(A+B) where A = mg/l bicarbonate alkalinity and B = 1/2(mg/l carbonate alkalinity). Free CO_2 is determined titrimetrically or nomographically.

Sample Handling: Use RU or FU brine for pH and alkalinity measurements and RA or FA brine for Ca^{2+} determination.

Range:

Precision:

Accuracy:

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
Analysis Methods: 1-A, 38-A, 39-A,
61-A, 62-A, 63-A, 65-A, 141-A

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

Reagents:

Use appropriate reagents for pH, alkalinity, and Ca^{2+} determinations.

Equipment:

Use equipment appropriate to pH, Ca^{2+}, and titrimetric determinations.

Remarks:

1. pH, Ca^{2+}, 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:
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CO_2

Carbon Dioxide

Analysis: Carbon Analyzer (Infrared) **No.** 65-A

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: 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 Analysis Methods: 1-A, 38-A, 39-A, 61-A, 62-A, 63-A, 64-A, 141-A	**Literature Reference:** EPA 00680 (1976)
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 - Titrimetric".

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Cs

Cesium

Analysis: Atomic Absorption

No. 66-A

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:
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains; 1975, Vol. III, pp. 2-32.

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.

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(cont. on back)

5. Some difficulties in balancing signals when using red filters and background correction simultaneously have been reported.

Cs

Cesium

Analysis: Flame Emission **No.** 67-A

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 HNO_3 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% >0.5 mg/l±5%

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

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 1-33.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

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.

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(cont. on back)

5. Calcium interference may be removed by treating with ammonium oxalate, ammonium hydroxide and filtering.

Cs

Cesium

Analysis: Neutron Activation

No. 68-A

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.

Range: **Precision:** **Accuracy:**

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

Literature Reference:
Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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Cesium

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 by required.

Range:

Precision:

Accuracy:

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

Literature Reference:
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains;1975 , Vol. III, pp. 2-32.
Instrument Manufacturer's Literature.

Reagents:

Cesium 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).

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Cl

Chloride

Analysis: Silver Nitrate Titration **No.** 70-A

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:
APHA 408A (1975)
ASTM D512-67B (1977)
API 2.8 (1968)
USGS Book 5, Chapter A1, (1974)
Fischer and Peters, Quantitative Chemical Analysis, p. 375.

Reagents:
Potassium chromate indicator
Standardized NaCl solution
Standardized $AgNO_3$ titrant solution

Equipment:
Burette
Magnetic stirrer and teflon-coated stirbar

Remarks:

Possible interferences: 1. Bromide, iodide, CN^-, and $S^=$ 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 Ca^{+2} and/or Mg^{+2} content samples may form ppt. when pH is raised to 8.3. Dilution or separation of Ca and/or Mg may be necessary.

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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.

Analysis: Mercuric Nitrate Titration **No.** 71-A

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.

Range: 0.2-100 mg/l **Precision:** ±2% **Accuracy:** ±5%

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

Literature Reference: EPA 00940 (1976)
APHA 408B (1975)
ASTM D512-67A (1977)
USGS Book 5, Chapter A1 (1974)

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

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.

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Chloride

Analysis: Titrimetric (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:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 70-A, 71-A, 73-A, 74-A

Literature Reference:
Fischer and Peters, Quantitative Chemical Analysis; p. 742.

Reagents:
Sodium chloride standard solution
Silver nitrate standard solution

Equipment:
Conductivity cell

Remarks: 1. A variation of this procedure involves plotting volume of $AgNO_3$ added vs potential using an Ag electrode and reference electrode (U.S. Geological Survey Method).

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Chloride

Analysis: Gravimetric

No. 73-A

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

Literature Reference:

Fischer and Peters, Quantitative Chemical Analysis; p. 181.

"Determination of Chloride in Soluble Chlorides", I.M. Kolthoff, E.B. Sandell, Textbook of Quantitative Inorganic Analysis, 34d Ed.; 1952, p. 303.

Reagents:

$AgNO_3$ standard solution
Nitric acid
Hydrochloric acid

Equipment:

Filtration apparatus
Drying oven
Analytical balance

Remarks:

1. Interferences: anions which form insoluble salts with Ag^+, e.g., S^{2-}, Br^-, I^-, $S_2O_3^=$, SCN^-, CN^-, precipitate may contain occluded materials from mother liquor; AgCl precipitate subject to photodecomposition (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.

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Cl

Chloride

Analysis: Chloride-Specific Electrode **No.** 74-A

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:**

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 50-A, 72-A, 89-A
101-A

Literature Reference:
Silver Halide Electrode Instruction Manual, Form 94H1678, Orion Research Inc., Cambridge, MA (1976).

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
pH meter with expanded mV scale or specific ion meter

Remarks:
1. Bromide ratio above 2×10^{-3} and iodide ratio above 5×10^{-7} will interfere.
2. The ionic strength adjustor solution consisted of the addition of 2 ml of 5 M $NaNO_3$ per 100 ml of solution.

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Cl

Chloride

Analysis: X-Ray Fluorescence **No.** 75-A

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

Literature Reference:

Cooper, J.A., Nuc. Inst. and Methods., Vol. 106, pp. 525-538, 1973.

Reagents:

Chloride standards
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, $CdNO_3$ solution added: sample first freed of any free H_2S by bubbling argon through liquid. Sample may be diluted to extend range.

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Cl

Chloride

Analysis: Ion-Exchange Chromatography **No.** 76-A

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

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)

Reagents:

Standard chloride solutions
Sodium carbonate/sodium bicarbonate eluent

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.
2. Additional reference: Small, H., T. S. Stevens and W. C. Bauman, Anal. Chem., 47, 1801 (1975).

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Cl

Chloride

Analysis: Neutron Activation

No. 77-A

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.

Range:

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

Reagents:

Standards containing chloride

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.

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CONDUCTIVITY

Analysis: Conductivity Meter

No. 78-A

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:

USGS Book 5, Chapter A1 (1974).
APHA 205 (75)
ASTM D1125-77A,B,C, (1977)
API 2.91 (68)
EPA 00095 (76)

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.

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6. Specific conductivity will change as sample ages according to CO_2 concentration and oxidation of ion's (iron and manganese) and H_2S occurs.

Cu

Copper

Analysis: Atomic Absorption **No.** 79-A

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 HNO_3 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

Literature Reference:

EPA 01042 (1976)
USGS Book 5, Chapter A1, (1974)
APHA 301 (1975)
ASTM D2576-70, D1688D (1977)
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains; 1975 Vol. III pp. 65-94.

Reagents:

Cu stock solution, (purchased or prepared from metallic copper in 1:1 HNO_3)

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.

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5. Use of standard additions recommended.

Cu

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.

Range:

Precision: ∓10%

Accuracy: ±5%

Cross Reference:

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

Literature Reference:

USGS Book 5 Chapter A1 (1974).

Reagents:

Ammonium pyrrolidine dithiocarbamate
Methyl isobytyl 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)).

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Cu

Copper

Analysis: X-ray Fluorescence **No.** 81-A

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, 29-S

Literature Reference:

Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

Reagents:

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

Equipment:

X-ray fluorescence spectrophotometer

Remarks:

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Cu

Copper

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 82-A

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.

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:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

Reagents:

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

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:

   R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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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	**No.** 83-A

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:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S	Trace Analysis by Mass Spectrometry, A.J. Aheard, ed. Academic Press, NY (1977). D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).
Reagents:	**Equipment:**
Solid copper standard sample	Spark source mass spectrometer

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

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Cu

Copper

Analysis: Neutron Activation

No. 84-A

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:

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

Literature Reference:

Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

Reagents:

Standards containing copper

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-Copper may be measured simultaneously with other elements of interest.

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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).

Analysis: Alizarin (Pre-distillation) **No.** 86-A

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 **Precision:** ±15% **Accuracy:** ±5%

Cross Reference:

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

Literature Reference:

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

Reagents:

Sulfuric acid; cone
Hydrochloric acid; cone
Fluoride standard solutions; prepared from KF
Zirconyl-alizarin reagent; Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$)
3-alizarinsulfuric acid (alizarin red S)
Sodium arsenite

Equipment:

Nessler tubes for visual comparison

Remarks: Interferences from Al(III), Cl^-, Fe(III), hexametaphosphate, PO_4^{3-}, SO_4^{2-}, color and turbidity removed by distillation, which is quantitative within the accuracy and precision of the Alizarin method.

Procedure is time consuming. The still must be flushed by distilling with pure H_2O before and after distilling HF. One hour is required for development of zirconium hexafluoride species.

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Fluoride

Analysis: Colorimetric (Spadns)

No. 87-A

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.

Range: 25-200 mg/l **Precision:** ±16% **Accuracy:** ±20%

Cross Reference:

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

Literature Reference:

APHA 414 C. (1975)
ASTM D1179-72 A (1977)
EPA 00950, 00951 (1976)

Reagents:

Standard fluoride solutions
Spadns solution
Sodium arsenite
Zirconyl chloride octahydrate
Hydrochloric acid, conc.

Equipment:

Spectrophotometer to measure at 570 nm.

Remarks: 1. No known interferences.

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Analysis: Amadac F Colorimetric **No.** 88-A

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.

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Analysis: Fluoride Specific Electrode **No.** 89-A

Method: Fluoride concentration is measured with a fluoride specific electrode containing a lanthanum fluoride crystal and an electrometer or pIon 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

Literature Reference:
APHA 414B (1975)
ASTM D1179-72B (1977)
USGS Book 5, Chapter A1 (1974)

Reagents:
Stock fluoride solution
Fluoride standards: 1-10 μg/ml
Total ionic strength adjustment buffer (TISAB)

Equipment:
Fluoride electrode
Calamel 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, Fe^{+3}, 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.

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3. Recovery values from spiked samples may be high.

Fluoride

Analysis: Ion-Exchange Chromatography **No.** 90-A

Method: Anion components are separated on sulfonated cation exchange colums 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

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)

Reagents:

Standard fluoride solution
Sodium carbonate/sodium bicarbonate eluent

Equipment:

Dionex Ion Chromatograph
75-120 psi air supply

Remarks:

1. May be analyzed simultaneously with bromide, nitrate, and sulfate.
2. Additional reference: Small, H., T. S. Stevens, and W. C. Bauman, Anal. Chem. 47, 1801 (1975).

Edition:
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F

Fluoride

Analysis: Spark Source Mass Spectrometry **No.** 91-A

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.

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
Anal. Letters, 10(5) 371-379 (1977).
Trace Analysis by Mass Spectrometry, A. J. Aheard, ed., Academic Press, NY (1977).

Reagents:

Sodium fluoride or other fluoride std.

Equipment:

Spark source mass spectrometer

Remarks:

Edition:
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HARDNESS

Hardness

Analysis: EDTA Titration

No. 92-A

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/1 **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)
USGS Book 5, Chapter A1 (1974)
ASTM D 1126-67B (1977)
EPA 00900 (1976)

Reagents:

Ammonium chloride
Ammonium hydroxide
EDTA-Mg salt or
  EDTA-disodium salt
Sodium cyanide
Sodium sulfide
Hydroxylamine hydrochloride
Ethanol or isopropanol
Eriochrome Black T dye
Calcium carbonate
Hydrochloric acid

Equipment:

Burets

Remarks:

1. Highly colored and strong brines interfere (Al >20 ppm, CO_3 >1000 ppm, Cl >10,000 ppm, SO_4 >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 Mg^{+2} and Na_2-EDTA in approximate equivalence for best results.

Edition:
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HARDNESS

Analysis: Calculation

No. 93-A

Method: Hardness is determined as mg/l $CaCO_3$ 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 $CaCO_3$.

Sample Handling: Use RA or FA brine for the metal determinations.

Range:

Precision:

Accuracy:

Cross Reference:

Appendix 2

Sampling Methods: 11-S, 29-S

Analysis Methods: 55-A, 92-A, 105-A, 124-A

Literature Reference:

APHA 309 (75)

USGS Book 5, Chapter A1 (1974)

Reagents:

Use reagents required for metals determinations

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:

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H_2S

Hydrogen Sulfide

Analysis: Titrimetric (Iodine)

No. 94-A

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 $S^=$ >10 mg/l

Accuracy: ±5% on $S^=$ >10 mg/l

Cross Reference: Appendix 2
Sampling Methods:
4-S, 11-S, 12-S, 29-S, 34-S
Analysis Methods: 202-A

Literature Reference:
APHA 428 D (1975)
API 3.10.1 (1968)
USGS Book 5, Chapter A1 (1974)
EPA 00746 (1976)

Reagents:
Zinc acetate
Sodium thiosulfate
Starch
Iodine
Hydrochloric acid

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.

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(cont. on back)

4. H_2S 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 N_2 gas free of H_2S for purging H_2S out of original trapping solution.

H_2S

Hydrogen Sulfide

Analysis: Colorimetric (Methylene Blue)

No. 95-A

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

Literature Reference:
APHA 428 C (1975)
API 3.10.2 (1968)

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
Iodine
Potassium Iodide
Sodium Thiosulfate
Hydrochloric acid
Sodium Hydroxide
Starch

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).

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(cont. on back.)

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) **No.** 96-A

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)
USGS Book 5, Chapter A1 (1974)

Reagents:

Acetic acid
Bromine water
Calcium carbonate
Calcium oxide
Hydrochloric acid
Methyl red indicator
Potassium fluoride
Hypochlorite solution
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:
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Analysis: Colorimetric (Arsenious-Ceric-Ferric thiocyanate) **No.** 97-A

Method: Procedure is similar to the arsenious-ceric colorimetric method, except the reaction of Ce(IV) with the arsenious 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.

Edition:
7/78

Analysis: Leuco Crystal Violet Method **No.** 98-A

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

Literature Reference:
APHA 415A (1975)

Reagents:
Potassium iodide
Citric acid
Ammonium hydroxide
Ammonium dihydrogen phosphate
Leuco crystal violet indicator
Mercuric chloride
Sulfuric acid
Potassium peroxymonosulfate
Sodium thiosulfate
Oxone
Calcium oxide

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.

Edition:
7/78

Analysis: Colorimetric (Arsenious-Ceric) **No.** 99-A

Method: The iodide concentration affects the first order reaction rate of AsO_3 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)
USGS Book 5, Chapter A1 (1974)

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

No. 100-A

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/1

Precision: ±1-2% at 10-50 mg/1

Accuracy: ±1-2% at 10-50 mg/1

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 97-A, 98-A, 99-A

Literature Reference:

API 3.15 (1968)

Reagents:

Bromophenol blue
Sulfuric acid
Carbon tetrachloride
Potassium iodide
Potassium nitrate

Equipment:

Spectrophotometer to measure at 517 nm

Remarks: Hydrogen sulfide can interfere. May be removed by boiling acidified brine.

Edition:
7/78

Analysis: Iodide-Specific Electrode **No.** 101-A

Method: Iodide concentration is measured directly using a silver iodide electrode and an electrometer

Sample Handling: Use unacidified brine sample

Range: 0.1-100 mg/l **Precision:** ±2% **Accuracy:**

Cross Reference:
Appendix 2
Sampling Methods: 11-S,29-S
Analysis Methods: 50-A, 74-A, 89-A

Literature Reference:
"Instruction Manual; Halide Electrode", Orion Research Co., 1976.

Reagents:
Iodide standard solutions; prepared from potassium iodide
Sodium nitrate, reagent grade

Equipment:
Silver iodide electrode, Orion model 94-53
Specific ion meter or pH meter with millivolt scale
Magnetic stirrer and stirbar
Reference electrode

Remarks:
1. Sulfide interference at 10^{-6} ratio level.[1]
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 $NaNO_3$ per 100 ml of solution.

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[1] Manufacturer's specifications.

Edition:
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Analysis: X-Ray Fluorescence

No. 102-A

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

Literature Reference:

Cooper, J. A., Nuc. Inst. and Methods., Vol. 106, pp. 525-538, 1973.

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

Analysis: Spark Source Mass Spectrometry **No.** 103-A

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/1 **Precision:** ±25% **Accuracy:** ±25%

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S	Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977). D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).
Reagents:	**Equipment:**
Solid iodide standard sample	Spark source mass spectrometer

Remarks: Other elements may be determined simultaneously with iodide.

Edition:
7/78

Analysis: Neutron Activation

No. 104-A

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:

Appendix 2

Sampling Methods: 11-S, 29-S

Literature Reference:

Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

Reagents:

Standards containing iodide

Equipment:

Reactor

Multichannel analyzer

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

No. 105-A

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.

Range: 0.05-3 mg/l **Precision:** **Accuracy:**

Cross Reference:

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

Literature Reference:

APHA 310A (1975)
ASTM D1068-77A (1977)

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.

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.

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(cont. on back)

5. If noticeable color is present evaporate sample, gently ash residue and redissolve in acid.

Fe

Iron

Analysis: Atomic Absorption **No.** 106-A

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

Literature Reference:

EPA 01045 (1976)
USGS Book 5, Chapter A1, (1974)
APHA 301 A II. (1975)
Flame Emission and Atomic Absorption Spectrometry; Dean and Rains; 1975 Vol. III pp. 216-246.
~~ASTM 2576-70F~~, D1068-77C (1977)

Reagents:

Iron stock solution,
prepared from iron wire and 1:1 HCl
Nitrous oxide gas cylinder (option)
Potassium chloride (option)

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 (D_2 lamp).

Edition:
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(over)

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.

Fe

Iron

Analysis: Atomic Absorption (MIBK Extraction) **No.** 107-A

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

Literature Reference:

APHA 301-A-III (1975)

Reagents:

Ammonium pyrrolidine dithiocarbamate
Methyl isobutyl ketone
Iron standard solutions, prepared from iron and hydrochloric acid

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)).

Edition:
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Fe

Iron

Analysis: Flame Emission

No. 108-A

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 HNO_3 per liter of sample.

Range:		Precision:		Accuracy:	
	>0.05 mg/l low brine		<0.5 mg/l ±25%		<0.5 mg/l ±25%
	>0.5 mg/l high brine		>0.5 mg/l ±5%		>0.5 mg/l ±5%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 106-A, 107-A

Literature Reference:

Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975 pp.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

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

Fe

Iron

Analysis: X-ray Fluorescence **No.** 109-A

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, 29-S

Literature Reference:

Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

Reagents:

Iron standards

Equipment:

X-ray fluorescence spectrophotometer

Remarks:

Edition:
7/78

Fe

Iron

Analysis:	Inductively Coupled Plasma- Atomic Emission Spectroscopy	**No.**	110-A

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: 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:
"Evaluation of an Inductively Coupled Plasma Multichannel Spectrometric Analysis System", EPA-600/4-77-032, June 1977.

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.

(cont. on back)

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4. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

Fe

Iron

Analysis: Spark Source Mass Spectrometry

No. 111-A

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.

Range: 0.1-1000 mg/l

Precision: ± 5% (isotope Dil.)
±25%

Accuracy: ± 5% (isotope Dil.)
±25%

Cross Reference:

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

Literature Reference:

D.L. Donohue, J.A. Carter and J.C. Franklin
Anal. Letters, 10(5) 371-379 (1977).
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).

Reagents:
Iron standards

Equipment:
Spark source mass spectrometer

Remarks: 1. Additional References:

J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975).

J. D. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 345 (1975).

R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. 41 955 (1969).

Edition:
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Fe

Iron

Analysis: Neutron Activation

No. 112-A

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:

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

Literature Reference:

Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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:
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Fe

Iron

Analysis: Emission Spectrometry **No.** 113-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 iron emission line is measured against standards.

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

Range: 0.5-2 mg/l **Precision:** ±10% **Accuracy:**

Cross Reference: Appendix 2 Sampling Methods: 11-S, 29-S	**Literature Reference:** Instrument Manufacturer's Literature
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:
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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 HNO_3 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)
ASTM D2576-70, D3559-77A (1977)
1)APHA 301A II (1975)
2)Flame Emission and Atomic Absorption Spectrometry, Dean and Rains; 1975 Vol. III pp. 183-202.

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 PO_4, CO_3, 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)

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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.

Pb

Lead

Analysis: Atomic Absorption (MIBK Extraction)	**No.** 115-A

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	**Literature Reference:** APHA 301-A-III (1975) USGS Book 5, Chapter A1 (1974)
Reagents: Ammonium pyrrolidine dithiocarbamate solution Methyl isobutyl ketone Lead standard solutions, prepared from lead and dilute HNO_3	**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)).

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Pb

Lead

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 116-A

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

Literature Reference:

"Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System" EPA-600/4-77-032, June 1977.

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.
3. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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Pb

Lead

Analysis: Spark Source Mass Spectrometry

No. 117-A

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.

ange: 0.1-1000 mg/l

Precision: ±5% (isotope dil.)
±25%

Accuracy: ±5% (isotope dil.)
±25%

Cross Reference:

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).

D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Solid lead
standard sample

Equipment:

Spark source mass spectrometer

Remarks:

1. Other elements may be determined simultaneously with lead.
2. Additional references:

J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975).

J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975).

R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. 41 955 (1969).

Edition:
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Pb

Lead

Analysis: Emission Spectrometry **No.** 118-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 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).

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Li

Lithium

Analysis: Atomic Absorption

No. 119-A

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/1 **Precision:** ±5% **Accuracy:** ±10%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 120-A

Literature Reference:

Flame Emission and Atomic Absorption Spectrometry, Dean and Rains, 1975, Vol. III, pp. 2-32.
USGS Book 5, Chapter A1 (1974)
ASTM D3561-77 (1977)

Reagents:

Lithium standard solutions; prepared from Li_2CO_3 and hydrochloric acid
Potassium chloride

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:
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Li

Lithium

Analysis: Flame Emission

No. 120-A

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 HNO_3 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%
>0.5 mg/l±5%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 119-A

Literature Reference:

Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975.
W. Snelleman, Spectrochim. Acta, 23B, 403 (1968).

Reagents:

Lithium atomic absorption standard solutions or lithium carbonate
Hydrochloric acid (to dissolve lithium carbonate)
Potassium chloride or potassium nitrate

Equipment:

Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer

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

Li

Lithium

Analysis: Ion-Exchange Chromatography

No. 121-A

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.

Range: **Precision:** ±1.35% **Accuracy:** ±5%

Cross Reference:

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

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)

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.
2. Additional reference: Small, H., T. S. Stevens and W. C. Bauman, Anal. Chem., 47 1801 (1975).

Edition:
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Li

Lithium

Analysis: Spark Source Mass Spectrometry

No. 122-A

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed. Academic Press, NY (1977).
D.L. Donohue, J.A. Carter, and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Solid lithium standard sample

Equipment:

Spark source mass spectrometer

Remarks:

Edition:
7/78

Li

Lithium

Analysis: Emission Spectrometry

No. 123-A

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.

Range: Dilute to ≤ 1.0 mg/l

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Instrument Manufacturer's Literature

Reagents:

Lithium stock solution; may be prepared from Li_2CO_3 and HCl

Equipment:

Emission spectrometer

Remarks:

1. Some flames (e.g. O_2-H_2-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).

Edition:
7/78

Mg

Magnesium

Analysis: EDTA Titrimetric **No.** 124-A

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

Literature Reference:

APHA 313C (1975)
ASTM D 511-76B (1977)
API 2.4 (1968)
USGS Book 5, Chapter A1 (1974)

Reagents:

Murexide (ammonium purpurate)
Sodium hydroxide (4N)
EDTA
Ammonium chloride-ammonium hydroxide buffer
Calcium standard
Magnesium standard
Eriochrome Black T
Hydroxylamine hydrochloride

Equipment:

Buret

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

Edition:
7/78

Mg

Magnesium

Analysis: Atomic Absorption

No. 125-A

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 HNO_3 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

Literature Reference:

EPA 00927 (1976)
USGS Book 5, Chapter A1, (1974)
APHA 301 A. II (1975)
ASTM D2576-70, D511-76C (1977)
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains, 1975, Vol. III, pp. 33-64.

Reagents:

Magnesium stock solution, may be prepared by dissolving magnesium ribbon in 1:1 HCl
Potassium chloride
Nitrous oxide gas cylinder (option)
Lanthanum chloride

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

Mg

Magnesium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 126-A

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: 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:

"Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System", EPA-600/4-77-032, June 1977.

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.

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5. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

Mg

Magnesium

Analysis: Spark Source Mass Spectrometry

No. 127-A

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/1 **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
Anal. Letters, 10(5) 371-379 (1977).
Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).

Reagents:

Magnesium standards

Equipment:

Spark source mass spectrometer

Remarks:

Edition:
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Mg

Magnesium

Analysis: Neutron Activation

No. 128-A

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.

Range:

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

Reagents:

Standards containing magnesium

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 analyzed simultaneously with magnesium.

Edition:
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Mg

Magnesium

Analysis: Emission Spectrometry

No. 129-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 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

Literature Reference:

Instrument Manufacturer's Literature

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).

Edition:
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Mn

Manganese

Analysis: Atomic Absorption

No. 130-A

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 HNO_3 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

Literature Reference:

EPA 01055 (1976)
USGS Book 5, Chapter A1, (1974)
APHA 129 (1975)
ASTM D2576-70, D858-77B (1977)
Flame Emission and Atomic Absorption Spectrometry, Dean and Rains, 1975, Vol. III.

Reagents:

Mn stock solution, 1000 ppm purchased or prepared from metallic manganese in 1:1 nitric acid
Nitrous oxide gas cylinder (option)

Equipment:

Atomic Absorption Spectrophotometer
Nitrous oxide burner head (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.
2. If sample shows Tyndall effect, filter through a 0.45 μ membrane filter.

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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.

Mn

Manganese

Analysis: Atomic Absorption (MIBK Extraction) **No.** 131-A

Method: Manganese is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into methyl isobutyl keton (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: **Precision:** ±10% **Accuracy:** ±10%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 130-A

Literature Reference:
ASTM 858-77C (1977)
USGS Book 5, Chapter A1 (1974)

Reagents:
Ammonium pyrrolidine dithiocarbamate solution
Methyl isobutyl ketone
Manganese standard solutions, prepared from manganese metal in dilute nitric acid

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:
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Mn

Manganese

Analysis: X-ray Fluorescence

No. 132-A

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, 29-S

Literature Reference:

Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

Reagents:

Manganese standards

Equipment:

X-ray fluorescence spectrophotometer

Remarks:

Edition:

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Mn

Manganese

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 133-A

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

Literature Reference:

"Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System", EPA-600/4-77-032, June 1977.

Reagents:

Manganese standard solution, prepared from metallic manganese 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.
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.

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5. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

Mn

Manganese

Analysis: Spark Source Mass Spectrometry | **No.** 134-A

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed. Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Solid manganese standard sample

Equipment:

Spark source mass spectrometer

Remarks: Several elements of interest may be analyzed simultaneously with this instrumentation.

Edition:
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Mn

Manganese

Analysis: Neutron Activation

No. 135-A

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:

Robertson, D.E. & Carpenter, R., "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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:
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Mn

Manganese

Analysis: Emission Spectrometry

No. 136-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 manganese emission line is measured against standards.

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

Range: 0.06-2 mg/1 **Precision:** ±10% **Accuracy:**

Cross Reference:

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

Literature Reference:

Instrument Manufacturer's Literature

Reagents:

Manganese 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:
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Hg

Mercury

Analysis: Cold Vapor Atomic Absorption

No. 137-A

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

Literature Reference:

ASTM D3223-73 (1977)
EPA 71900 (1976)
APHA 301 A (1976)

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.

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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.

Hg

Mercury

Analysis: X-Ray Fluorescence **No.** 138-A

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:
Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

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.

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Hg

Mercury

Analysis: Neutron Activation

No. 139-A

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:

Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NA-3114, Jan. 1974.

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).

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Hg

Mercury

Analysis: Emission Spectrometry

No. 140-A

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

Literature Reference:

Instrument Manufacturer's Literature

Reagents:

Mercury standards

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).

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pH

pH

Analysis: pH meter

No. 141-A

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
Analysis Methods: 1-A, 38-A, 39-A, 61-A, 62-A, 63-A, 64-A, 65-A

Literature Reference: USGS Book 5, Chapter A1 (1974)
APHA 424 (75)
ASTM D1293-65 (77)
API 2.1 (68)
EPA (76)

Reagents:

Distilled water pH buffers

Equipment:

pH meter
Glass electrode
Reference electrode

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.

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4. Oxidation of various ions such as iron or manganese can influence pH.
5. The reaction $2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^=$ increases pH.

PO_4

Phosphate

Analysis: Colorimetric (Stannous Chloride) **No.** 142-A

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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3. Alternatively the orthophosphate phosphorous is extracted selectively as phosphomolybdic acid into methyl isobutyl ketone from a 2 M $HClO_4$ 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.

PO_4

Phosphate

Analysis: Colorimetric (Ascorbic Acid Reduction)

No. 143-A

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

Literature Reference:

APHA 425 F (1975)
ASTM D515-72 A (1977)
EPA 70507 (1976)
USGS Book 5, Chapter A1 (1974)
API 3.9 (1968)

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)).

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5. Arsenic must be reduced first to avoid significant interference.

PO_4

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

Literature Reference:

D. F. Boltz, "Colorimetric Determination of Non-Metals", Interscience Publishers, Inc., New York, 1958, pp. 38-39.

Reagents:

Potassium dihydrogen phosphate reagent grade KH_2PO_4
Sodium molybdate reagent grade $Na_2MoO_4 \cdot 2H_2O$
1-Butanol - reagent grade
Chloroform reagent grade

Equipment:

Spectrophotometer for use at 310 nm
Absorption cells 1 cm light path

Remarks: The selective extraction of molybdophosphoric acid eliminates interference due to silicate, arsenate, and germanate.

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PO_4

Phosphate

Analysis: X-Ray Fluorescence **No.** 145-A

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:
Nuc. Inst. and Methods, Vol. 106, pp. 525-538, (1973).

Reagents:
Potassium dihydrogen phosphate or other phosphate standard

Equipment:
X-ray fluorescence spectrophotometer

Remarks: 1. Analysis gives result as phosphorous concentration. To obtain the phosphate concentration multiply by the gravimetric factor $\frac{PO_4}{P}$ (i.e., $[PO_4^{-3}] = [P] \times 3.07$).

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PO$_4$

Phosphate

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 146-A

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.

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:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

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.
2. Additional references: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).
3. Background correction and standard additions method recommended.

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(over)

4. Analysis gives result as phosphorous concentration. To obtain the phosphate concentration multiply by the gravimetric factor $\frac{PO_4}{p}$ (i.e., $[PO_4^{-3}] = [P] \times 3.07$).

PO_4

Phosphate

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.

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

Cross Reference:

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

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 $\frac{PO_4}{P}$ (i.e., $[PO_4^{-3}] = [P] \times 3.07$).

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K

Potassium

Analysis: Specific Ion Electrode | **No.** 148-A

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: >0.04 mg/l **Precision:** **Accuracy:**

Cross Reference: Appendix 2 Sampling Methods: 11-S, 29-S Analysis Methods: 182-A	**Literature Reference:** Orion Research Inc., Literature
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.

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K

Potassium

Analysis: Atomic Absorption **No.** 149-A

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)

USGS Book 5, Chapter A 1 (1974)

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.

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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.

K

Potassium

Analysis: Flame Emission **No.** 150-A

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 HNO_3 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% >0.5 mg/l ±5%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 149-A

Literature Reference:

Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 2-27.
W. Snelleman, Spectrochim. Acta, 1975 23B 403 (1968)

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.

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K

Potassium

Analysis: X-Ray Fluorescence **No.** 151-A

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, 29-S

Literature Reference:

Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

Reagents:

Potassium chloride or other potassium standard

Equipment:

X-ray fluorescence spectrophotometer

Remarks:

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K

Potassium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy	**No.** 152-A

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:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

Reagents:

Potassium chloride or other potassium standard

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: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).
3. Background correction and standard additions method recommended.

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Analysis: Ion Exchange Chromatography **No.** 153-A

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

Literature Reference:

Dionex Corp., Sunnyvale, CA, Literature
Anal. Chem., 47 (11), 1801 (1975).
Microchem. J., 22, 45 (1977).
Anal. Chem., 49 (3), 401 (1977).

Reagents:

Potassium chloride or other potassium standard
Nitric acid

Equipment:

Ion exchange chromatograph

Remarks:

1. High rubidium concentrations cause interference because rubidium elutes at the same time as potassium.
2. Additional reference: Small, H., T. S. Stevens and W. C. Bauman, Anal. Chem., 47 1801 (1975).

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K

Potassium

Analysis: Spark Source Mass Spectrometry **No.** 154-A

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.) ±25% **Accuracy:** ±5% (isotope dil.) ±25%

Cross Reference:

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Potassium chloride or other potassium standard.

Equipment:

Spark source mass spectrometer

Remarks: 1. Additional references: J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975). J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975). R. Alvarez, B.J. Paulsen, and D.E. Kelleher, Anal. Chem. 41 955 (1969).

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Analysis: Neutron Activation | **No.** 155-A

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.

Range: **Precision:** **Accuracy:**

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

Literature Reference:
Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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K

Potassium

Analysis: Emission Spectrometry **No.** 156-A

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.

Range:	**Precision:**	**Accuracy:**
Dilute to ≤ 1.0 mg/l		

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S	Instrument Manufacturer's Literature

Reagents:	**Equipment:**
Potassium chloride or other potassium standard	Emission spectrometer

Remarks:

1. Some flames (e.g. O_2-H_2-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).

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RADIOACTIVE ISOTOPES

Analysis: Gamma Spectrometry	**No.** 157-A

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: Appendix 2 Sampling Methods: 11-S, 29-S	**Literature Reference:** Procedures Manual Health and Safety Lab, ERDA-NY HASL-300
Reagents: Nuclear reference solutions	**Equipment:** Gamma detector system [Ge(Li)-semiconductor] Multichannel analyzer Merinelli flask Planchet for solid residue

Remarks: Precipitates are analyzed by filtering the samples and analyzing the residue on planchets.

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RADIOACTIVE ISOTOPES

Analysis: Lead-210 **No.** 158-A

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 HNO_3 and allowed to equilibrate with stable carriers.

Range: >0.1 pCi/ml (liter sample) **Precision:** ±10% **Accuracy:** ±20%

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

Literature Reference: 1. "Collected Radiochemical Procedures", edited by Helen L. Smith; LA-1721, 4th Ed.; UC-4, Chemistry Issued: April 1975.
2. W. M. Gibson, "The Radiochemistry of Lead", NAS-NS 3040, August 1961.

Reagents:

Standardized Bi carrier
Pb carrier (10 mg/ml)
Thioacetamide
Normal acids and bases of varying molarities

Equipment:

Normal glassware
Hot water bath
Centrifuge
Filtering apparatus
Low-background beta proportional counter

Remarks:

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RADIOACTIVE ISOTOPES

Analysis: Ra-226 (Radon Emanation Method) **No.** 159-A

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 SO_3. 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

Literature Reference:

APHA 705 (1975)
ASTM D3454-75T (1977)
Procedures Manual HASL-300 (1974)

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.

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RADIOACTIVE ISOTOPES

Analysis: Ra-226 **No.** 160-A

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 HNO_3 and allowed to equilibrate with carriers and tracer.

Range: $>1 \times 10^{-3}$ pCi/ml (liter sample) **Precision:** ±10% **Accuracy:** ±20%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 159-A

Literature Reference:
(See remarks)

Reagents:
Ba-133 tracer
Ba carrier, 10 mg/ml
Pb carrier, 10 mg/ml
0.25 EDTA solution
98% HNO_3
Normal acids

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

1. Radium-226 Analysis Principles, Interference and Practice, National Lead Co., Inc. WIN-112 February 1, 1960.
2. P. E. Trujillo, Jr., "Analytical Procedures for the Determination of Radionuclides in Air Filters, Water, and Soils", Los Alamos Scientific Laboratory, H8-MR-72-3 May, 1972.
3. Harley, J. R., Editor, "HASL Procedures Manual", Health and Safety Laboratory, HASL-300, August 1974.
4. APHA 705 (1975), ASTM D2460-70 (1977).

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5. Large precipitates may form upon H_2SO_4 addition and may not completely dissolve in EDTA, This material should be analyzed separately for activity.

RADIOACTIVE ISOTOPES

Radioactive Isotopes

Analysis: Thorium Isotopes **No.** 161-A

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 thenoyltrifluoro-acetene-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 HNO_3 and allowed to equilibrate with carriers and tracers.

Range: >1 x 10^{-3} pCi/ml (liter sample) **Precision:** ±10% **Accuracy:** ±20%

Cross Reference:

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

Literature Reference:

F. L. Moore, "Radiochemical Determination of Ionium in Uranium Fluorination Ash", Anal. Chem. 30, 1020 (1958).

Reagents:

Thorium-234 tracer
Praseodymium, 5 mg/ml
0.5 Mthenoyltrifluoreacetone in xylene
0.4 M $K_2Cr_2O_7$
2 M $Al(NO_3)_3$
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

Remarks:

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RADIOACTIVE ISOTOPES

Analysis: Uranium Isotopes **No.** 162-A

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 HNO_3 and allowed to equilibrate with the tracer.

Range: $>1 \times 10^{-3}$ pCi/ml (liter sample) **Precision:** ±10% **Accuracy:** ±20%

Cross Reference:

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

Literature Reference: 1. James E. Grindler, "The Radiochemistry of Uranium", NAS-NS 3050, March 1962. 2. Editor, Frederick D. Johns, "Handbook of Radiochemical Methods", EPA-680/4-75-001, February 1975.

Reagents:

Standardized U-232 tracer
Dowex 1-x4 (50-100 mesh) anion resin
2.8 M $Al(NO_3)_3$
Normal acids

Equipment:

Resin column
Vortex mixer
Centrifuge
Normal glass ware
40 ml screw-cap vials

Remarks:

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Rb

Rubidium

Analysis: Atomic Absorption **No.** 163-A

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

Literature Reference:

Instrument Manufacturer's Std. Methods Manual
Dean & Rains, <u>Flame Emission and Atomic Absorption Spectrometry,</u> Vol. III, 1975 pp. 2-27.

Reagents:

Rubidium atomic absorption standard solution or rubidium chloride
Sodium chloride
Potassium chloride or potassium nitrate
Ammonium oxalate (option)
Ammonium hydroxide (option)

Equipment:

Atomic absorption spectrophotometer

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.

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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.

Rb

Rubidium

Analysis: Flame Emission	**No.** 164-A

Method: 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.

Sample Handling: Use filtered acidified or raw acidified brine. Sample may be stabilized by diluting with 9 parts distilled water and adding 5 ml HNO_3 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% >0.5 mg/l ±5%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 163-A

Literature Reference:

Dean & Rains, <u>Flame Emission and Atomic Absorption Spectrometry</u>, Vol. III, 1975, pp. 2-27.
W. Snelleman, Spectrochim. Acta, <u>23B</u> 403 (1968).

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.

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Rb

Rubidium

Analysis: Spark Source Mass Spectrometry **No.** 165-A

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:** ±5% (isotope dil.) ±25% **Accuracy:** ±5% (isotope di ±25%

Cross Reference:

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Rubidium chloride or other rubidium standard

Equipment:

Spark source mass spectrometer

Remarks: 1. Additional references: J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975). J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975). R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. <u>41</u> 955 (1969).

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Rb

Rubidium

Analysis: Neutron Activation

No. 166-A

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.

Range:

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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Rb

Rubidium

Analysis: Emission Spectrometry

No. 167-A

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:

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

Literature Reference:

Instrument Manufacturer's Literature

Reagents:

Rubidium chloride or other rubidium standard

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).

Edition:
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SiO_2

Silica

Analysis: Gravimetric **No.** 168-A

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 SiO_2.

Edition:
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SiO_2

Silica

Analysis: Colorimetric (Heteropoly Blue) **No.** 169-A

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 $SiO_2 > 100$ ppm.

Range: >1 mg/l **Precision:** ±15% **Accuracy:** ±15%

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S Analysis Methods: 170-A	APHA 426 C (1975) ASTM D859-68 B, C (1977) EPA 00955 (1976) USGS Book 5, Chapter A1 (1974)
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 $SiO_2 > 100$ 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:
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SiO_2

Silica

Analysis: Colorimetric (Molybdosilicate) **No.** 170-A

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 $SiO_2 > 100$ 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 meta silicate
Sodium bicarbonate

Equipment:

Spectrophotometer to measure at 410 nm.

Remarks:

1. If $SiO_2 > 100$ dilute 1/10 with distilled water.
2. Avoid use of glassware or reagents which may contain silica.
3. Iron, color, turbidity, sulfide interfere. Phosphate removed by oxalic acid.
4. Any silica present as "molybdate-unreactive" silica must be pretreated by digesting with $NaHCO_3$ on a steam bath for one hour.

Edition:
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SiO_2

Silica

Analysis: Atomic Absorption

No. 171-A

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 - $SiO_2/Si = 2.14$.

Sample Handling: Use filtered acidified or raw acidified brine. Sample should be diluted in field if $SiO_2 > 250$ 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

Literature Reference:

APHA 301-A (1975)
Instrument Manufacturer's Std. Methods Manual
USGS Book 5, Chapter A1 (1974).

Reagents:

Silicon atomic absorption standard solution or sodium metasilicate
Nitrous oxide gas cylinder

Equipment:

Atomic absorption spectrophotometer
Nitrous oxide burner head

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.

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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.

SiO_2

Silica

Analysis: Flame Emission

No. 172-A

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 $SiO_2/Si = 2.14$.

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).

Range:

Precision:

Accuracy:

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 171-A

Literature Reference:

Dean & Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 136-154.

W. Snelleman, Spectrochim. Acta, 23B 403 (1968).

Reagents:

Silicon atomic absorption standard solution or sodium metasilicate
Nitrous oxide cylinder

Equipment:

Atomic absorption spectrophotometer with emission mode or flame emission spectrophotometer.
Nitrous oxide burner head

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.

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SiO_2

Silica

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 173-A

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 288.16 nm or alternate wavelength.

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).

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:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

Reagents:

Sodium metasilicate or other silica standard

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: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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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 $\frac{SiO_2}{Si}$ (i.e., $[SiO_2] = [Si] \times 2.14$).

SiO_2

Silica

Analysis: Spark Source Mass Spectrometry **No.** 174-A

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:

Trace Analysis by Mass Spectrometry, A.J. Aheard, ed., Academic Press, NY (1977).
D.L. Donohue, J.A. Carter and J.C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

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 $\frac{SiO_2}{Si}$ (i.e., $[SiO_2] = [Si] \times 2.14$).

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SiO_2

Silica

Analysis: Emission Spectrometry	**No.** 175-A

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 $SiO_2 > 100$ mg/l (10:1 dilution suggested).

Range: 0.2-2 mg/l (as Si) **Precision:** ±10% **Accuracy:**

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S	Instrument Manufacturer's Literature
Reagents:	**Equipment:**
Sodium metasilicate or other silica standard Vanadium internal standard	Emission spectrometer Photo processor Microphotometer

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).

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Ag

Silver

Analysis: Atomic Absorption | **No.** 176-A

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 HNO_3 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

Literature Reference:

EPA 01077 (1976)
APHA 301-A (1975)
Instrument Manufacturer's Std. Methods Manual

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.

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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: Atomic Absorption using APDC and MIBK Extraction

No. 177-A

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

Literature Reference:

APHA 301 A (1975)
USGS Book 5, Chapter A1 (1974)

Reagents:

- Silver atomic absorption standard solution or silver nitrate
- Methyl isobutyl ketone
- Ammonium pyrrolidine dithiocarbamate

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 elminated by using a deuterium arc background correction system.
4. Use of standard additions recommended.

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Ag

Silver

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 178-A

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 328.07 nm or at alternate spectral line.

Sample Handling: Use filtered acidified or raw 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

Literature Reference:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

Reagents:

Silver nitrate or other silver standard

Equipment:

Inductively coupled plasma-atomic emission spectrometer.

Remarks:

1. External standards using NaCl concentrations equivalent to sample concentrations of NaCl are required.
2. Additional reference: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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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.

Ag

Silver

Analysis: Spark Source Mass Spectrometry **No.** 179-A

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.

Sample Handling: Use filtered acidified, raw acidified, filtered unacidified, or raw unacidified brine. Evaporate brine 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:

Trace Analysis by Mass Spectrometry, A. J. Aheard, ed., Academic Press, NY (1977).
D. L. Donohue, J. A. Carter and J. C. Franklin Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Silver nitrate or other silver standard

Equipment:

Spark source mass spectrometer

Remarks:

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Ag

Silver

Analysis: Neutron Activation

No. 180-A

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:

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

Literature Reference:

Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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Ag

Silver

Analysis: Emission Spectrometry

No. 181-A

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).

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Na

Sodium

Analysis: Specific Ion Electrode **No.** 182-A

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:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S Analysis Methods: 148-A	ASTM D2791-77A (1977) Orion Research Inc., Literature
Reagents:	**Equipment:**
Sodium standard solutions or sodium chloride Ammonium chloride Ammonium hydroxide	Sodium specific ion electrode Specific ion meter Magnetic stirrer

Remarks:

1. Interferences are from Ag^+, Li^+, H^+, K^+, NH_4^+. 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:
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Na

Sodium

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.

Range: (linear) 0.02-1 mg/l **Precision:** ±5% **Accuracy:** ±10%

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 11-S, 29-S Analysis Methods: 184-A	EPA 00929 (1976) USGS Book 5, Chapter A1 (1974). Instrument Manufacturer's Std. Methods. Manual ASTM D3561-77 (1977)
Reagents:	**Equipment:**
Sodium atomic absorption standard solution or sodium chloride Potassium chloride or potassium nitrate	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.

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4. Use of standard additions recommended.

5. All glass and plasticware should be acid washed and thoroughly rinsed to prevent sodium contamination.

Na

Sodium

Analysis: Flame Emission

No. 184-A

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 HNO_3 per liter.

Range: >0.05 mg/l

Precision:
<0.5 mg/l ±25%
>0.5 mg/l ±5%

Accuracy:
<0.5 mg/l ±25%
>0.5 mg/l ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 183-A

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, pp. 2-27.
W. Snelleman, Spectrochim. Acta, 23B 403, (1968).

Reagents:
Sodium atomic absorption standard solution or sodium chloride
Potassium chloride or potassium nitrate

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).

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Na

Sodium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 185-A

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:

Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

Reagents:

Sodium chloride or other sodium standard

Equipment:

Inductively coupled plasma-atomic emission spectrometer

Remarks:

1. Additional reference: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", <u>Anal. Chim. Acta</u> <u>75</u>, 257-270 (1975).
2. Background correction and standard additions method recommended.

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Na

Sodium

Analysis: Ion Exchange Chromatography **No.** 186-A

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

Literature Reference:

Dionex Corp., Sunnyvale, CA, Literature
Anal. Chem., 47 (11), 1801 (1975).
Microchem. J., 22, 45 (1977).
Anal. Chem., 49 (3), 401 (1977).

Reagents:

Sodium chloride or other sodium standard
Nitric acid

Equipment:

Ion exchange chromatograph

Remarks: 1. Additional reference: Small, H., T. S. Stevens, and W. C. Bauman, Anal. Chem. 47, 1801 (1975).

Edition:
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Na

Sodium

Analysis: Spark Source Mass Spectrometry **No.** 187-A

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 uncaidified 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:

Trace Analysis by Mass Spectrometry, A. J. Aheard, ed., Academic Press, NY (1977).
D. L. Donohue, J. A. Carter and J. C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Sodium chloride or other sodium standard

Equipment:

Spark source mass spectrometer

Remarks:

Edition:
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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:

Precision:

Accuracy:

Cross Reference:

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

Literature Reference:

Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114. Jan. 1974.

Reagents:

Equipment:

Reactor (neutron source)
Multichannel analyzer

Remarks:

Edition:
7/78

Na

Sodium

Analysis: Emission Spectrometry **No.** 189-A

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: Dilute to $\leq$ 1.0 mg/l **Precision:** **Accuracy:**

Cross Reference:

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

Literature Reference:

Instrument Manufacturer's Literature

Reagents:

Sodium chloride or other sodium standard

Equipment:

Emission spectrometer

Remarks:

1. Some flames (e.g. O_2-H_2-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).

Edition:
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Sr

Strontium

Analysis: Atomic Absorption

No. 190-A

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 of 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

Literature Reference:

USGS Book 5, Chapter A1 (1974)
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

Equipment:

Atomic absorption 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).

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

5. Use of a graphite furnace will increase sensitivity.

y. Use of standard additions recommended.

Sr

Strontium

Analysis: Flame Emission **No.** 191-A

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 HNO_3 per liter.

Range: >0.05 mg/l

Precision: <0.5 mg/l ±25%
>0.5 mg/l ±5%

Accuracy: <0.5 mg/l ±25%
>0.5 mg/l ±5%

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 190-A

Literature Reference:
Dean and Rains, Flame Emission and Atomic Absorption Spectrometry, Vol. III, 1975, p. 33-65.

Reagents:
Strontium atomic absorption standard solution or strontium nitrate
Potassium chloride or potassium nitrate
Nitrous oxide gas cylinder (option)

Equipment:
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).

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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.

Sr

Strontium

Analysis: X-Ray Fluorescence **No.** 192-A

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, 29-S	**Literature Reference:** *Nuc. Inst. and Methods,* Vol. 106, pp. 525-538 (1973).
Reagents: Strontium nitrate or other strontium standard	**Equipment:** X-ray fluorescence spectrophotometer

Remarks:

Edition:
7/78

Sr

Strontium

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 193-A

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.

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:
Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

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.
2. Additional reference: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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3. Background correction and standard additions method recommended.
4. Upper limit of concentration ragne may be extended by using alternate spectral lines.

Sr

Strontium

Analysis: Spark Source Mass Spectrometry **No.** 194-A

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

Literature Reference:
J. A. Carter, D. L. Donohue, and J. C. Frankling, Trace Substances in Environmental Health-IX, U. of Missouri, 303 (1975).

Reagents:
Strontium nitrate or other strontium standard

Equipment:
Spark source mass spectrometer

Remarks: 1. Additional references: J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Conf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975).
R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. 41 955 (1969).

Edition:
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Sr

Strontium

Analysis: Neutron Activation **No.** 195-A

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.

Range: **Precision:** **Accuracy:**

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

Literature Reference:
Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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:
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Sr

Strontium

Analysis: Emission Spectrometry **No.** 196-A

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

Literature Reference:
Instrument Manufacturer's Literature

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).

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SO_4

Sulfate

Analysis: Gravimetric **No.** 197-A

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 $BaSO_4$.

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) EPA 00945 (1976)
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.

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3. A modification to this procedure for high SiO_2 brines involves addition of $BaCl_2$ 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 Na_2CO_3 and Na_2O_2. 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 $BaCl_2$. Precipitate is filtered and ashed at 800°C and resulting solid weighed as $BaSO_4$. (John Bricarello, 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 $BaCl_2$ - 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.

SO_4

Sulfate

Analysis: Turbidimetric **No.** 198-A

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

Literature Reference:

APHA 427-C (1975)
ASTM D516-68 B (1977)
API 2.72 (1968)
EPA 00945 (1976)

Reagents:

Glycerol
Hydrochloric acid
Ethyl alcohol (95%) or isopropyl alcohol
Sodium chloride
Barium chloride
Sulfuric acid
Sodium sulfate
Gylcerol (option)

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.

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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 $BaCl_2$, stirring time, and loose time between adding $BaCl_2$ crystals and spectrophotometric reading.

SO_4

Sulfate

Analysis: Atomic Absorption **No.** 199-A

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: **Precision:** **Accuracy:**

Cross Reference:
Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 32-A, 200-A

Literature Reference:
Instrument Manufacturer's Std. Methods Manual

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

Equipment:
Atomic absorption spectrophotometer
Filtration apparatus
Nitrous oxide burner head

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.

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SO_4

Sulfate

Analysis: Flame Emission - Indirect

No. 200-A

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

Literature Reference:

Cullum, D. C., and D. B. Thomas, Analyst 85, 1960, 668.

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

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).

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SO_4

Sulfate

Analysis: Ion Exchange Chromatography **No.** 201-A

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

Literature Reference:

Dionex Corp., Sunnyvale, CA Literature.
Anal. Chem., 47 (11), 1801 (1975).
Microchem. J., 22, 45 (1977).
Anal. Chem., 49 (3), 401 (1977).

Reagents:

Sulfuric acid, sodium sulfate, or other sulfate standard
$NaHCO_3$
Na_2CO_3

Equipment:

Ion exchange chromatograph

Remarks: 1. Additional reference: Small, H., T. S. Stevens, and W. C. Bauman, Anal. Chem., 47, 1801 (1975).

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Sulfide

Analysis: Titrimetric (Iodine) **No.** 202-A

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: Appendix 2
Sampling Methods:
4-S, 11-S, 12-S, 29-S, 34-S
Analysis Methods: 94-A

Literature Reference:

API 3.10.1 (1968)
USGS Book 5, Chapter A1 (1974)
EPA 00746 (1976)

Reagents:

Zinc acetate
Inert gas (N_2 or CO_2)
Potassium iodide
Hydrochloric acid
Sodium thiosulfate
Starch
Sodium hydroxide
Iodine

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.
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:
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Analysis:	Antimony Test (Qualitative)	**No.**	203-A

Method: The sample is treated with potassium antimony tartrate in the presence of hydrochloric acid. Yellow antimony sulfide, Sb_2S_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 **Precision:** **Accuracy:**

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S	APHA 428 (1975)
Reagents:	**Equipment:**
Potassium antimony tartrate Hydrochloric acid	

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:
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Analysis: Colorimetric (Methylene Blue)

No. 204-A

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.

Range: 0.01-1.0 mg/l
0.2-400 μg/l (Lauth's Violet)

Precision:

Accuracy:

Cross Reference: Appendix 2
Sampling Methods: 4-A, 11-S, 12-A, 29-S, 34-S
Analysis Methods: 95-A

Literature Reference:
APHA 428 C (1975)
API 3.10.2 (1968)

Reagents:
Zinc acetate
Sodium carbonate
N,N-dimethyl-phenylene-diamine oxalate (also called p-amino-dimethylamiline oxalate)
Sulfuric acid
Ferric chloride
Diammonium hydrogen phosphate
Sodium sulfide
Iodine
Potassium Iodide
Sodium Thiosulfate
Hydrochloric acid
Sodium Hydroxide
Starch

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.)

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S

Sulfide

Analysis: Specific Ion Electrode	**No.** 205-A

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 determined the potential-concentration relationship.

Sample Handling: Use filtered unacidified or raw unacidified brine.

Range:	**Precision:**	**Accuracy:**

Cross Reference:	**Literature Reference:**
Appendix 2 Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S	Analytical Letters, 1 (13), 825 (1968). Anal. Chem., 44 (5), 270 (1972). Orion Res. Inc., Cambridge, MA Literature
Reagents:	**Equipment:**
Sodium sulfide or other sulfide standard EDTA Sodium hydroxide Ascorbic acid	Sulfide specific ion electrode

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:
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Sulfide

Analysis: X-Ray Fluorescence

No. 206-A

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.

Range: **Precision:** **Accuracy:**

Cross Reference:
Appendix 2
Sampling Methods: 4-S, 11-S, 12-S, 29-S, 34-S

Literature Reference:
Nuc. Inst. and Methods, Vol. 106, pp. 525-538 (1973).

Reagents:
Sodium sulfide or other sulfide standard

Equipment:
X-ray fluorescence spectrophotometer

Remarks:

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Sulfide

Analysis: Spark Source Mass Spectrometry **No.** 207-A

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

Literature Reference:
Trace Analysis by Mass Spectrometry, A. J. Aheard, ed., Academic Press, NY (1977).
D. L. Donohue, J. A. Carter and J. C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:
Sodium sulfide or other sulfide standard

Equipment:
Spark source mass spectrometer

Remarks:

Edition:
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Sulfide

Analysis: Neutron Activation

No. 208-A

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:
Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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SUSPENDED SOLIDS

Suspended Solids

Analysis: Gravimetric **No.** 209-A

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)
USGS Book 5, Chapter A1 (1974)
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.

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4. Precipitation of iron, manganese, and silica in highly concentrated brines causes higher results than would be obtained on site.

TOTAL DISSOLVED SOLIDS (TDS)

Total Dissolved Solids

Analysis: Gravimetric	**No.** 210-A

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

Literature Reference:
APHA 208 B, C (1975)
ASTM D1888-67A (1977)
EPA 70300 (1976)
USGS Book 5, Chapter A1 (1974)

Reagents:
Drierite^R 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.

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4. Under certain conditions SiO_2 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

Turbidity

Analysis: Absorptometric	**No.** 211-A

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.

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TURBIDITY

Turbidity

Analysis: Visual Matching

No. 212-A

Method: Turbidity of sample is visually measured against turbidity standards made of Kaolin, formazin, or similar material.

Sample Handling: Use RU 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:

Kaolin

Equipment:

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.

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TURBIDITY

Analysis: Nephelometric (Turbidimetric) **No.** 213-A

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

Literature Reference:
APHA 214 (75)
ASTM D1889-71 (77)
EPA 00076 (76)
USGS Book 5, Chapter A1 (1974)

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.

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Zn

Zinc

Analysis: Atomic Absorption **No.** 214-A

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 HNO_3 per liter.

Range: (linear) 0.05-1 mg/l **Precision:** ±5% **Accuracy:** ±10%

Cross Reference:

Appendix 2
Sampling Methods: 11-S, 29-S
Analysis Methods: 215-A

Literature Reference:

EPA 01092 (1976) ASTM D2576-70,
APHA 301 A (1975) D1691-77C (1977)
USGS Book 5, Chapter A1 (1974)
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.

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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 D_2 background compensation.

7. Use of standard additions recommended.

Zn

Zinc

Analysis: Atomic Absorption Using APDC and MIBK Extraction

No. 215-A

Method: Zinc is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with mthyl 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

Literature Reference:
APHA 301 A (1975)

Reagents:
Zinc atomic absorption standard solution or zinc metal
Hydrochloric acid if zinc metal is used
Methyl isobutyl ketone
Ammonium pyrrolidine dithiocarbamate

Equipment:
Atomic absorption spectrophotometer
Separatory funnels

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.

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5. Alternatively, chloroform may be used as the extraction solvent (ASTM D1691-77D (1977).

Zn

Zinc

Analysis: Inductively Coupled Plasma-Atomic Emission Spectroscopy

No. 216-A

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 213.86 nm or alternate wavelength.

Sample Handling: Use filtered acidified or raw 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

Literature Reference:
Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System, EPA-600/4-77-032, June 1977.

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.
2. Additional reference: R. H. Scott and M. L. Kokot, "Application of Inductively Coupled Plasmas to the Analysis of Geochemical Samples", Anal. Chim. Acta 75, 257-270 (1975).

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3. Background correction and standard additions method recommended.
4. Upper limit of concentration range may be extended by using alternate spectral lines.

Zn

Zinc

Analysis: Spark Source Mass Spectrometry **No.** 217-A

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.) ±25%	**Accuracy:** ±5% (isotope dil.) ±25%

Cross Reference:

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

Literature Reference:

Trace Analysis by Mass Spectrometry, A. J. Aheard, ed., Academic Press, NY (1977).
D. L. Donohue, J. A. Carter and J. C. Franklin, Anal. Letters, 10(5) 371-379 (1977).

Reagents:

Zinc metal or other zinc standard
Hydrochloric acid (to dissolve zinc)

Equipment:

Spark source mass spectrometer

Remarks: 1. Additional references: J. A. Carter, D. L. Donohue, and J. C. Franklin, Trace Substances in Environmental Health-IX. U. of Missouri, 303 (1975). J. C. Franklin, J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23d Donf. on Mass Spectrometry and Allied Topics, Houston, TX 354 (1975). R. Alvarez, B. J. Paulsen, and D. E. Kelleher, Anal. Chem. 41 955 (1969).

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Zn

Zinc

Analysis: Neutron Activation **No.** 218-A

Method: Sample is exposed to neutron source (reactor) and radioactive zinc isotopes are formed. The isotopes and their associated beta and gamma spectra are iedntified 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:
Appendix 2
Sampling Methods: 11-S, 29-S

Literature Reference:
Robertson and Carpenter, "Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples", NAS-NS-3114, Jan. 1974.

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.

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Zn

Zinc

Analysis:	Emission Spectrometry	**No.**	219-A

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:**

Cross Reference:

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

Literature Reference:

Instrument Manufacturer's Literature

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).

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Analytical Methods

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8. *Standard Methods for the Examination of Water and Wastewater,* 14th ed. American Public Health Association, Washington, D.C., 1975.

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1. "Analytical Methods for Atomic Absorption Spectroscopy Using the HGA Graphite Furnace", Perkin Elmer Corp., Norwalk, CT, April, 1974.

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C. Inductively Coupled Plasma-Atomic Emission Spectroscopy:

1. "Evaluation of an Inductively Coupled Plasma, Multichannel Spectrometric Analysis System", EPA-600/4-77-032, Environmental Protection Agency, Environmental Research Laboratory, Athens, GA, 1977.

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3. Mulik, J., R. Puckett, D. Williams, E. Sawicki, "Ion Chromatographic Analysis of Sulfate and Nitrate in Ambient Aerosols, *Analytical Letters, 9* (7) (1976) 653.

4. Small, Hamish, T.S. Stevens, W.C. Bauman, "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection", *Anal. Chem. 47* (11) (1975) 1801.

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1. Aheard, J.A., ed., Trace Analysis by Mass Spectrometry, Academic Press, NY, 1977.

2. Alvarez, R., B.J. Paulsen, and D.E. Kelleher, Anal. Chem. *41* 955 (1969).

3. Carter, J. A., D. L. Donohue, and J. C. Franklin, "Trace Substances in Environmental Health, IX," U. of Missouri, 303 (1975).

4. Donohue, D. L., J. A. Carter, and J. C. Franklin, Analytical Letters, 10(5) (1977) 371.

5. Franklin, J. C., J. A. Carter, D. L. Donohue, and R. W. Stelzner, 23rd Conference on Mass Spectometry and Allied Topics, Houston, TX (1975).

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:

$$A = B\left(1 - \frac{Cp\Delta T}{\Delta H}\right)$$

where A is the concentration before flashing, B is the concentration after flashing and steam loss, ΔT is the temperature change during the flash in degrees centigrade, Cp is the heat capacity of the liquid, and ΔH is the heat of vaporization at the temperature of the flashed brine. ΔH and Cp 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. Cp and ΔH values at various weight percentages of NaCl are given in Tables 1 and 2 respectively.

Examples of this type of calculation are given below:

Example 1: Data is taken from "Geothermal Loop Experimental Facility," San Diego Gas & Electric Bi-Monthly Report, SAN/1137-6, May 1977, by H. K. Bishop, J. R. Bricarello, F. L. Enos, N. C. Hodgson, W. O. Jacobson, K. K. Li, and C. R. Swanson.

From Table 2-1 of this report, the conditions of the GLEF using Woolsey #1 well are:

	Temperature (°F)
Inlet	399.6
1st Stage flash unit	322
2nd Stage flash unit	305.4
3rd Stage flash unit	284.4
4th Stage flash unit	194.5

TABLE 1

Heat Capacities (cal deg^{-1}g^{-1}) for solutions containing various weight percentages of NaCl

		Cp							
Temp.	% NaCl	0	5	10	15	20	25	30	35
°C	°F								
80	176	0.996	0.936	0.874	0.809	0.740	0.664		
85	185	0.997	0.937	0.876	0.812	0.745	0.671		
90	194	0.997	0.938	0.878	0.815	0.749	0.678		
95	203	0.998	0.939	0.880	0.818	0.754	0.684		
100	212	0.998	0.940	0.882	0.821	0.758	0.690		
105	221	0.999	0.941	0.883	0.824	0.762	0.696		
110	230	0.999	0.942	0.884	0.826	0.765	0.701		
115	239	0.999	0.943	0.892	0.839	0.786	0.729		
120	248	1.000	0.945	0.892	0.839	0.786	0.730		
125	257	1.001	0.945	0.892	0.840	0.786	0.730		
130	266	1.001	0.946	0.893	0.840	0.786	0.731		
135	275	1.002	0.946	0.893	0.840	0.786	0.731		
140	284	1.003	0.946	0.893	0.840	0.786	0.731		
145	293	1.003	0.947	0.893	0.840	0.786	0.731		
150	302	1.004	0.947	0.893	0.840	0.786	0.730		
155	311	1.005	0.948	0.893	0.839	0.786	0.730		
160	320	1.006	0.948	0.893	0.839	0.785	0.730	0.669	
165	329	1.007	0.949	0.893	0.839	0.785	0.729	0.668	
170	338	1.008	0.949	0.894	0.839	0.784	0.728	0.668	
175	347	1.009	0.950	0.894	0.839	0.784	0.728	0.667	
180	356	1.011	0.951	0.894	0.839	0.784	0.727	0.666	

TABLE 1 (cont.)

Temp.		% NaCl			Cp				
		0	5	10	15	20	25	30	35
°C	°F								
185	365	1.012	0.951	0.894	0.839	0.783	0.726	0.665	
190	374	1.014	0.952	0.895	0.839	0.783	0.726	0.664	
195	383	1.015	0.953	0.895	0.838	0.782	0.725	0.663	
200	392	1.017	0.954	0.895	0.839	0.782	0.725	0.663	
205	401	1.018	0.955	0.896	0.839	0.782	0.724	0.662	
210	410	1.020	0.956	0.897	0.839	0.782	0.724	0.661	
215	419	1.022	0.957	0.897	0.839	0.782	0.724	0.661	
220	428	1.024	0.959	0.898	0.840	0.782	0.724	0.661	
225	437	1.026	0.960	0.899	0.840	0.783	0.724	0.661	
230	446	1.028	0.962	0.900	0.841	0.783	0.725	0.661	
235	455	1.031	0.963	0.901	0.842	0.784	0.726	0.662	
240	464	1.033	0.965	0.903	0.843	0.785	0.727	0.664	
245	473	1.036	0.967	0.904	0.845	0.787	0.728	0.665	
250	482	1.038	0.969	0.906	0.846	0.789	0.731	0.668	
255	491	1.041	0.971	0.908	0.848	0.791	0.733	0.671	
260	500	1.044	0.974	0.910	0.851	0.794	0.737	0.675	0.599
265	509	1.047	0.976	0.913	0.854	0.797	0.741	0.680	0.605
270	518	1.050	0.979	0.916	0.857	0.801	0.746	0.687	0.613
275	527	1.054	0.982	0.919	0.861	0.806	0.752	0.682	0.622
280	536	1.057	0.985	0.923	0.866	0.812	0.759	0.704	0.633
285	545	1.061	0.989	0.927	0.871	0.819	0.768	0.715	0.646
290	554	1.065	0.993	0.932	0.877	0.827	0.779	0.728	0.663
295	563	1.069	0.997	0.937	0.884	0.837	0.791	0.744	0.682
300	572	1.073	1.002	0.944	0.893	0.848	0.806	0.763	0.706

TABLE 1 (cont.)

			Cp							
Temp.		% NaCl	0	5	10	15	20	25	30	35
°C	°F									
305	581		1.077	1.007	0.951	0.903	0.861	0.824	0.786	0.734
310	590		1.082	1.013	0.959	0.915	0.877	0.845	0.813	0.768
315	599		1.087	1.019	0.969	0.929	0.896	0.870	0.845	0.808
320	608		1.092	1.027	0.980	0.945	0.919	0.901	0.884	0.857
325	617		1.098	1.035	0.993	0.964	0.946	0.937	0.931	0.916

Reference

Haas, J. L., Jr. Preliminary "Steam Tables" For NaCl Solutions, U.S. Geological Survey, Reston, VA 1975 Document No. USGS-OFR-75-675. Values in Table above were calculated from USGS values.

TABLE 2

Heats of vaporization (cal g^{-1}) for solutions containing various weight percentages of NaCl

Temp.		Wt. % NaCl			ΔH				
°C	°F	0	5	10	15	20	25	30	35
80	176	551.2	556.1	561.1	566.4	572.0	578.2		
85	185	548.2	553.3	558.6	564.1	569.9	576.3		
90	194	545.1	550.5	556.0	561.7	567.8	574.4		
95	203	542.0	547.7	553.4	559.4	565.6	572.4		
100	212	538.9	544.8	550.7	556.9	563.4	570.4		
105	221	535.7	541.9	548.1	554.5	561.1	568.3		
110	230	532.5	538.9	545.4	552.0	558.9	566.2		
115	239	529.2	535.7	541.9	548.1	554.5	561.3		
120	248	525.9	532.7	539.2	545.7	552.4	559.4		
125	257	522.5	529.6	536.5	543.3	550.3	557.6		
130	266	519.1	526.5	533.7	540.8	548.1	555.7		
135	275	515.6	523.4	530.9	538.3	545.9	553.8		
140	284	512.0	520.2	528.0	535.8	543.7	551.9		
145	293	508.5	517.0	525.1	533.2	541.4	549.9		
150	302	504.8	513.7	522.2	530.6	539.1	548.0		
155	311	501.1	510.3	519.2	527.9	536.8	546.0		
160	320	497.2	506.9	516.1	525.2	534.5	544.0	554.4	
165	329	493.3	503.4	513.0	522.5	532.1	542.0	552.8	
170	338	489.3	499.8	509.8	519.7	529.6	539.9	551.1	
175	347	485.2	496.1	506.5	516.8	527.2	537.8	549.4	
180	356	481.0	492.4	503.2	513.4	524.6	535.7	547.7	

TABLE 2 (cont.)

Temp.		Wt. % NaCl	ΔH							
°C	°F		0	5	10	15	20	25	30	35
185	365		476.7	488.5	499.8	510.9	522.1	533.5	546.0	
190	374		472.3	484.6	496.3	507.9	519.4	531.3	544.2	
195	383		467.8	480.6	492.8	504.7	516.7	529.0	542.3	
200	392		463.2	476.5	489.1	501.5	513.9	526.7	540.4	
205	401		458.4	472.3	485.4	498.2	511.1	524.2	538.4	
210	410		453.5	467.9	481.5	494.9	508.2	521.7	536.4	
215	419		448.5	463.5	477.6	491.4	505.1	519.1	534.3	
220	428		443.4	458.9	473.5	487.8	502.0	516.4	532.0	
225	437		438.1	454.2	469.3	484.1	498.7	513.6	529.6	
230	446		432.6	449.3	465.0	480.2	495.3	510.6	527.1	
235	455		427.0	444.3	460.5	476.2	491.8	507.5	523.8	
240	464		421.2	439.1	455.8	472.1	488.1	504.3	521.6	
245	473		415.2	433.8	451.0	467.8	484.2	500.8	518.5	
250	482		409.1	428.3	446.1	463.3	480.1	497.1	515.2	
255	491		402.7	422.6	440.9	458.6	475.8	493.1	511.6	
260	500		396.2	416.7	435.5	453.7	471.3	488.9	507.6	530.2
265	509		389.4	410.5	429.9	448.5	466.5	484.3	502.9	526.2
270	518		382.4	404.2	424.1	443.0	461.3	479.4	498.5	521.6
275	527		375.1	397.6	417.9	437.2	455.8	474.0	493.2	516.4
280	536		367.6	390.7	411.5	431.1	449.8	468.1	487.2	510.5
285	545		359.8	383.5	404.7	424.6	443.4	461.7	480.6	503.6
290	554		351.7	376.1	397.6	417.6	436.5	454.5	473.1	495.8
295	563		343.3	368.3	390.0	410.1	428.8	446.6	464.6	486.7

TABLE 2 (cont.)

Temp.		Wt. % NaCl			ΔH				
°C	°F	0	5	10	15	20	25	30	35
300	572	334.6	360.1	382.0	402.0	420.4	437.6	455.0	476.2
305	581	325.5	351.4	373.4	393.3	411.2	427.6	443.9	463.9
310	590	316.1	342.4	364.3	383.7	400.8	416.2	431.1	449.5
315	599	306.2	332.8	354.4	373.1	389.3	403.2	416.2	432.5
320	608	296.0	322.7	343.7	361.4	376.2	388.2	398.8	412.3
325	617	285.2	311.9	332.0	348.4	361.2	370.7	378.3	388.2

Reference

Haas, J. L., Jr. Preliminary "Steam Tables" For NaCl Solutions U.S. Geological Survey, Reston, VA 1975 Document No. USGS-OFR-75-675. Values in Table above were calculated from USGS values.

From Table 3-3 of the same report:

	mg/ℓ Potassium	Weight % NaCl
Wellhead	9800	16
1st Brine	10,500	17
3rd Brine	11,200	18
4th Brine	12,000	19

The potassium concentration in the third stage brine can be calculated from the potassium concentration in the fourth stage:

$$A = 12{,}000 \text{ mg}/\ell \left(1 - \frac{C_p \Delta T}{\Delta H}\right)$$

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 ΔH at 90°C for 19% NaCl (using the closest values for Cp and ΔH at 20% NaCl) are 0.749 cal $\text{deg}^{-1}\text{g}^{-1}$ and 567.8 cal g^{-1}:

$$A = 12{,}000 \text{ mg}/\ell \left(1 - \frac{0.749 \text{ cal deg}^{-1}\text{g}^{-1}\ (140 - 90)\text{ deg}}{567.8 \text{ cal g}^{-1}}\right)$$

$$= 11{,}209 \text{ mg}/\ell$$

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 ΔH values at 16% NaCl (using the closest values at 15% NaCl and 160°C) are 0.839 cal $\text{deg}^{-1}\text{g}^{-1}$ and 525.2 cal g^{-1}, respectively:

$$A = 10{,}500\ \text{mg}/\ell \left(1 - \frac{0.839\ \text{cal deg}^{-1}\text{g}^{-1}\ (205 - 160)\ \text{deg}}{525.2\ \text{cal g}^{-1}}\right)$$

$$= 9745\ \text{mg}/\ell$$

This compares favorably with the experimentally determined potassium wellhead concentration of 9800 mg/ℓ.

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