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CHEMICAL ANALYSIS AND SAMPLING TECHNIQUES FOR GEOTHERMAL FLUIDS AND GASES AT THE FENTON HILL LABORATORY

by

P. E. Trujillo, D. Counce, C. O. Grigsby, F. Goff, and L. Shevenell

ABSTRACT

A general description of methods, techniques, and apparatus used for the sampling, chemical analysis, and data reporting of geothermal gases and fluids is given. Step-by-step descriptions of the procedures are included in the appendixes.

I. INTRODUCTION

The Fenton Hill laboratory is located at the Los Alamos National Laboratory Hot Dry Rock (HDR) site, west of the Valles caldera in the Jemez Mountains of northern New Mexico. Although the laboratory was originally established to support the HDR project and to study the geochemistry of fluids from the Fenton Hill area,¹ geochemical samples are now being analyzed from other geothermal areas in the United States,^{2,3} in the Caribbean, and in Central America. The HDR project⁴ is a research and development program designed to demonstrate the technical and commercial feasibility of energy derived from manmade reservoirs in hot, impermeable rock. Chemical analyses done at Fenton Hill play an important role in understanding the behavior of geothermal energy sources and other geothermal phenomena. The analyses are used for geothermal exploration (geothermometers, geologic interpretation) and for reservoir analysis and development (lifetime and volume estimates, scaling, flow rate, etc.).

This report describes the instrumentation and methods used to sample and analyze gases and fluids submitted to or collected by the Fenton Hill chemical laboratory. Section II addresses sampling and describes the techniques used

to collect the various sample fractions that make a total sample. Section III describes the instrumentation available for chemical analyses at the Fenton Hill laboratory and the methods used in the operation of that instrumentation. Section IV briefly summarizes the format and methods used for reporting the data generated in the laboratory. Detailed descriptions of the analysis techniques are presented in Appendixes A-M.

II. SAMPLING PROCEDURES

A. General

Chemical analyses performed at the Fenton Hill laboratory vary greatly depending on the information required from the individual samples and the diverse nature of the sample types. This sampling section discusses the nature and purpose of some of the samples and describes the apparatus and techniques used for their collection.

Three types of samples may be collected: pressurized samples from pipes or wellheads, samples collected by downhole instruments, and samples collected from hot springs and fumaroles. Regardless of the type of sample, collection of a single sample usually means the collection of several fractions of filtered and unfiltered fluid. Each fraction is specially labeled and treated in the manner best suited for the type of analysis required on that fraction. Filtered samples are passed through a Gelman 0.45- μm -membrane filter to remove sediment and colloidal particles. Certain samples (for example, samples of drilling mud) require prefiltration through a membrane having a larger pore size to reduce the loading of the 0.45- μm membrane. Fractions requiring acidification for preservation are acidified to 0.1% nitric acid unless additional acid is required to lower the pH below 2.

A complete sample consists of the following fractions. (Terms such as BOD bottle, gas bag, Giggenbach bottle, etc., are fully explained in the detailed procedures which follow.)

Liquids

1. 250 ml filtered, acidified fluid for cation analysis
2. 250 ml filtered fluid for anion analysis
3. 25 ml of a 1 to 5 dilution of filtered fluid for monomeric silica
4. 125 ml unfiltered fluid for water-stable isotopes
5. 250 ml unfiltered fluid for carbon isotopes
6. 500 ml unfiltered fluid for sulfur isotopes

7. 500 ml unfiltered fluid for tritium analysis
8. 250-1000 ml filtered fluid for chloride isotopes
9. 500 ml filtered fluid for monomeric aluminum extraction
10. 500 ml unfiltered fluid for total suspended solids
11. BOD bottle for dissolved oxygen analysis

Gases

12. Gas bag or gas flask for major gas analysis
13. Giggenbach bottle for gas isotope and trace gas analysis
14. Gas bag for radon analysis

Depending on the information to be retrieved from a given sample, some of the aliquots listed above may be deleted or the volumes may be increased or decreased. In particular, the sample volumes for the carbon, sulfur, or chloride isotope analyses can be adjusted when the concentrations of carbonate, sulfate, and chloride ions are known. This point will be discussed in the detailed procedure for collection of each of these aliquots.

B. Collecting Samples

The procedure for collecting a liquid sample depends upon the temperature, pressure, and location of the fluid to be sampled. One advantage of a wellhead sample over other types of samples is that the wellhead pressure can often be used to force the fluid through a filter. Samples collected at atmospheric pressure must be filtered by another means. Several types of filter apparatus used at the wellhead, in the laboratory, and in the field are shown in Figs. 1 and 2.

Wellhead fluids are often pressurized and may be at temperatures well above the normal boiling point. Cooling the fluid below the boiling point before the pressure is relieved prevents both flashing (steam separation) and loss of noncondensable gases. Loss of water from a sample due to boiling causes the residual fluid to be more concentrated and causes fractionation of isotopes. If sufficient steam is lost, solids may become supersaturated and may precipitate. Loss of noncondensable gases such as CO_2 can change the pH of the fluid and also cause the precipitation of minerals such as calcite (CaCO_3). Precipitation is particularly important at higher temperatures where the solubility of both CO_2 and calcite is low and where the rate of precipitation of calcite is high. At lower temperatures, calcite and CO_2 are more soluble in water, and the kinetics of precipitation are slower. Where

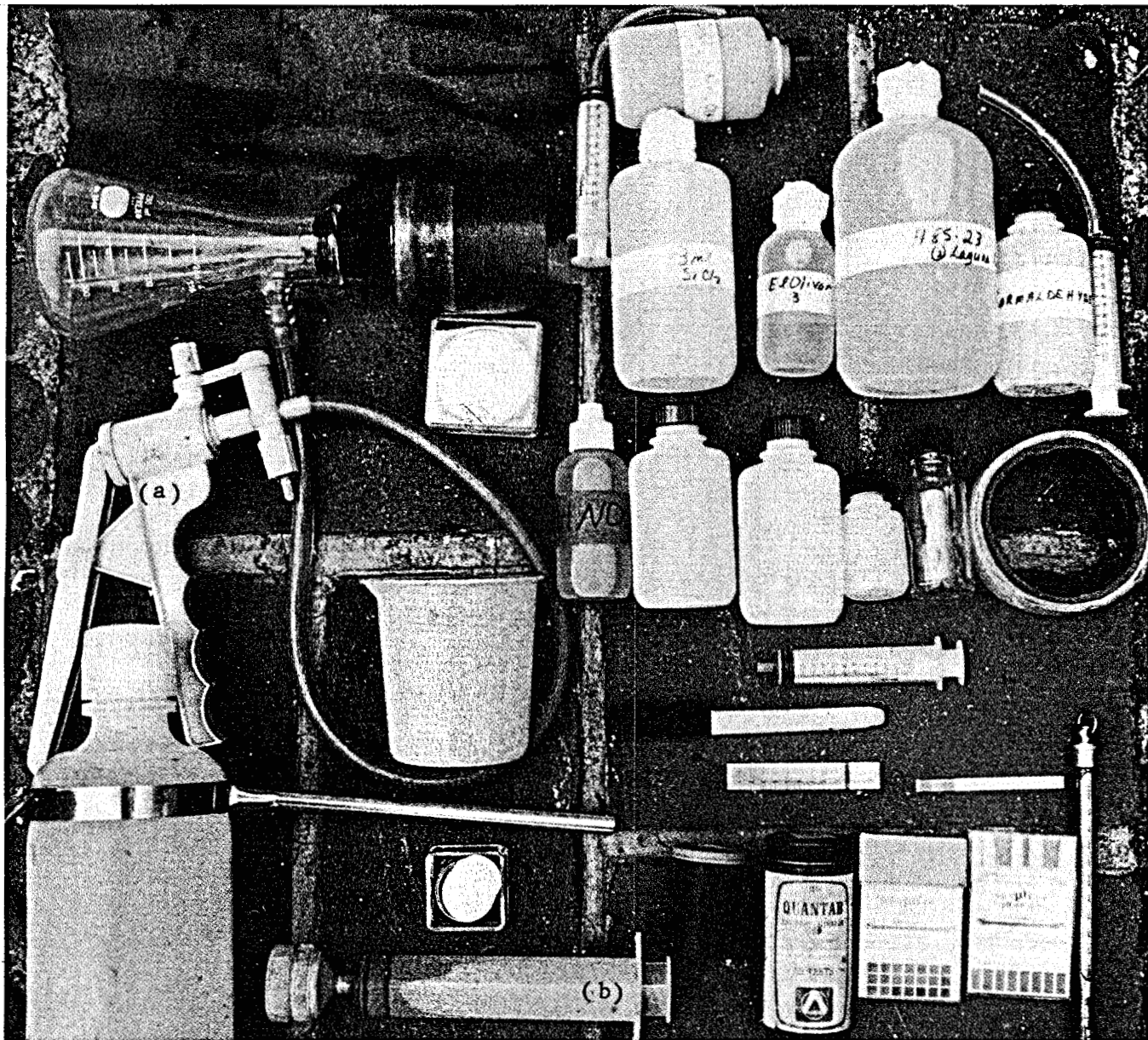


Fig. 1.

Field filter apparatus. (a) Field filter. The sample is filtered by evacuating the side-arm flask with the hand pump. For hot samples, care must be taken to avoid boiling the fluid by overevacuating the flask. (b) Syringe filter.

precooling of the sample is impossible, portable separators are used to separate the steam and gases from the liquid.

Two arrangements for sampling hot pressurized fluids are shown in Figs. 3 and 4. In the first, a heat exchanger is used to cool the fluid before it goes to a high-pressure filter holder. The second apparatus is a Webre-type

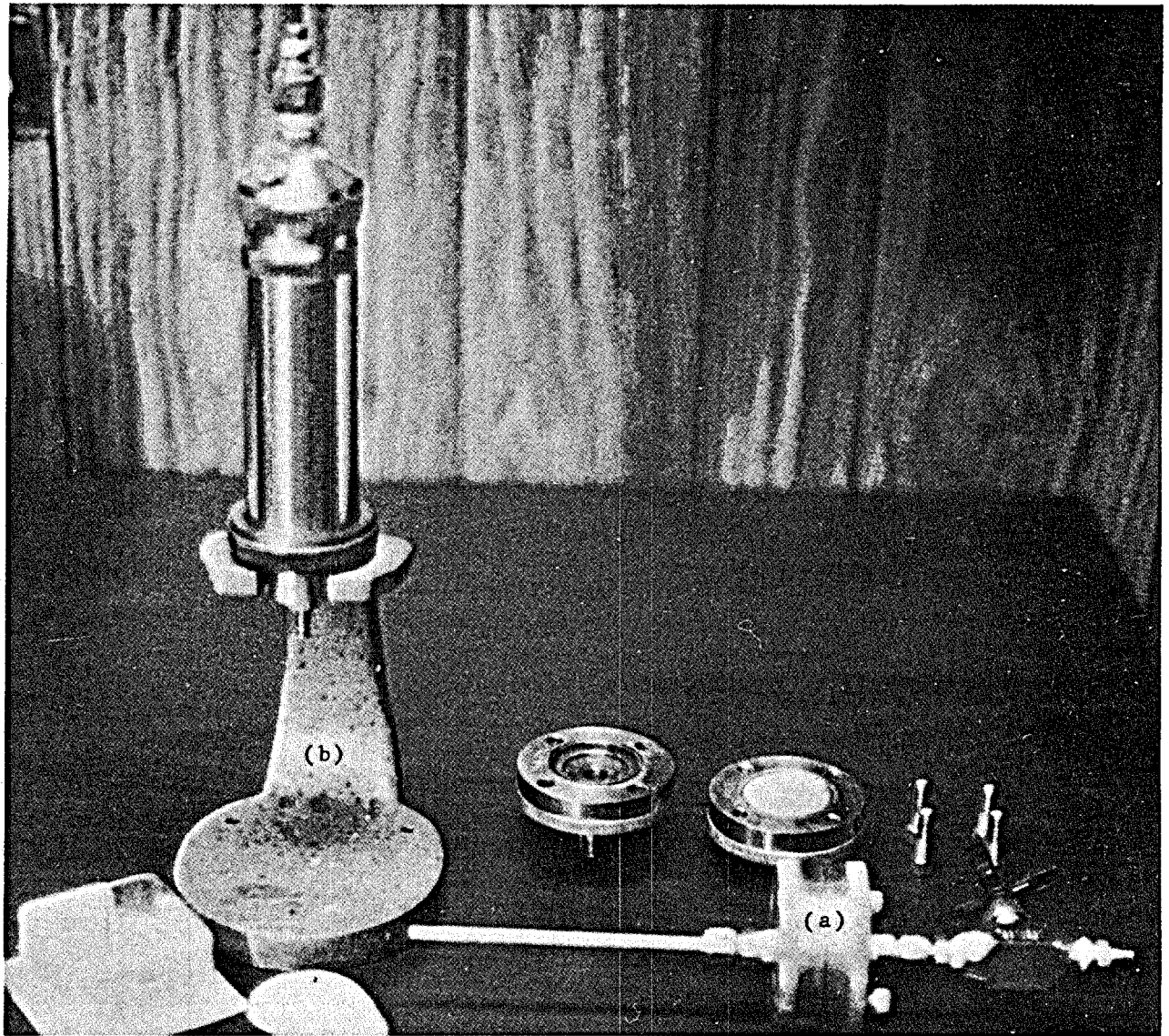


Fig. 2.

Wellhead and laboratory filter apparatus. (a) High-pressure filter holder used for wellhead samples. (b) Pressure filter used in the laboratory. The sample is forced through the filter using dry nitrogen.

gas separator that allows the noncondensable gases to be separated and collected.

The separation pressure is adjusted by opening or closing the liquid and vapor outlet valves. To collect a gas sample, the liquid outlet valve is adjusted so that gas exits from both the gas side and the liquid side of the separator. For a liquid sample, the valves are adjusted so that some liquid

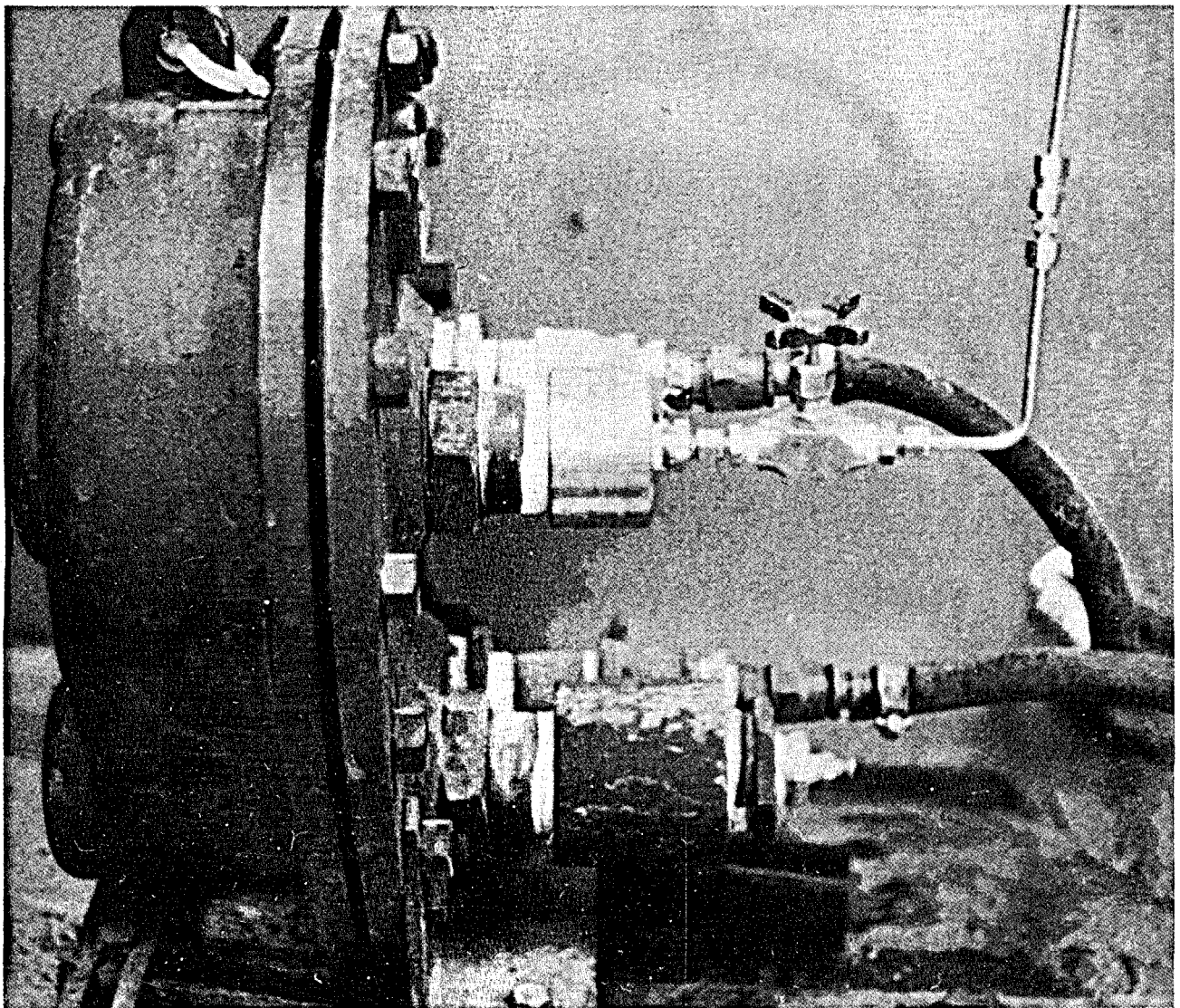


Fig. 3.

High-pressure heat exchanger for cooling and collecting hot fluids from wellheads.

is carried in the vapor stream. Both the temperature of the fluid before separation and the pressure of separation must be recorded in order to reconstruct the original fluid chemistry.

Hot springs are sampled at atmospheric pressure and at temperatures up to the normal boiling point of water. The usual method for collecting these samples is to dip fluid out of a pool near the mouth of the spring using a polyethylene beaker or bottle. For vigorously bubbling or boiling springs, a pole attached to the bottle or beaker is convenient (Fig. 5). In many cases a

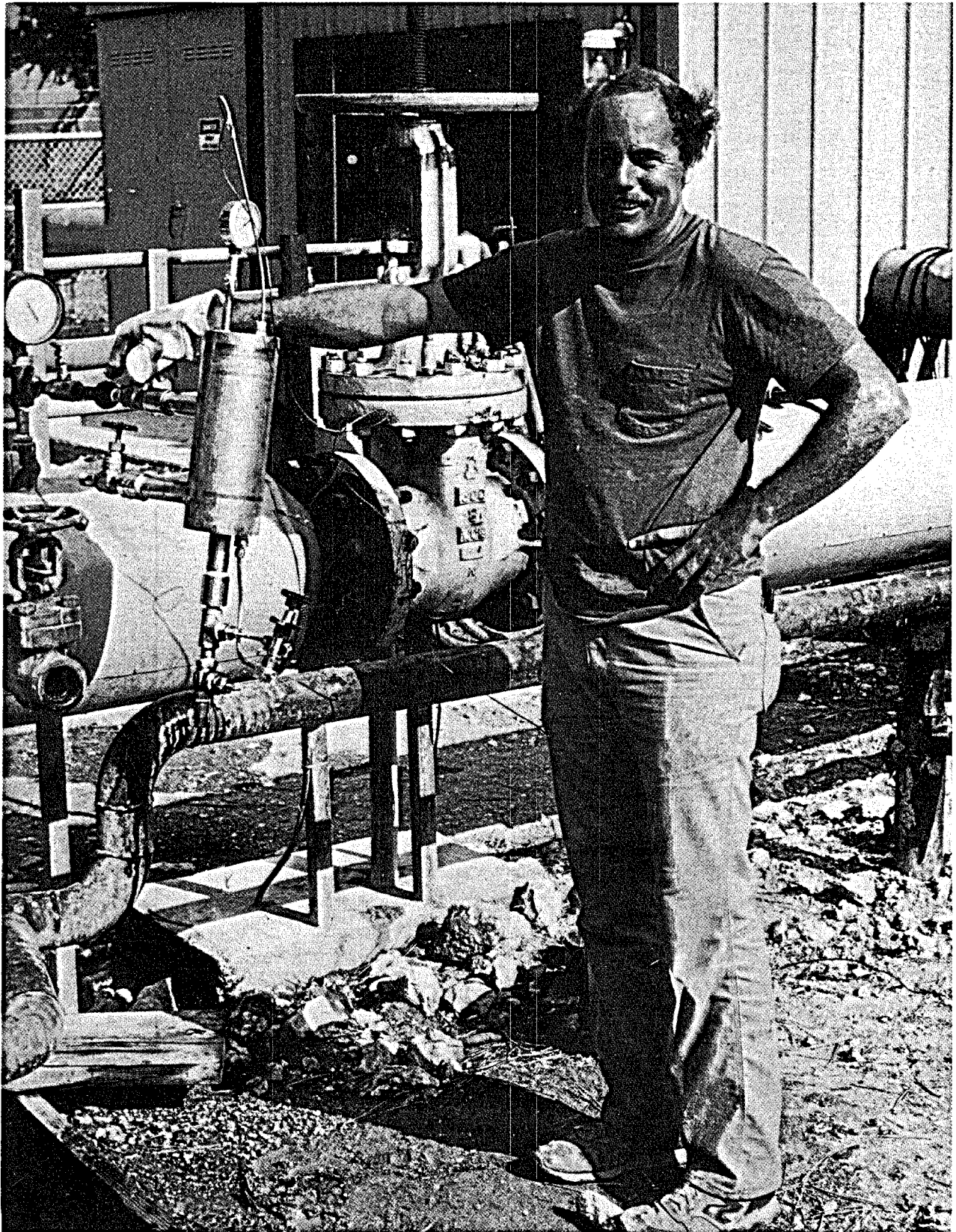


Fig. 4.
Webre gas and fluid separator.



Fig. 5.

Collecting a hot spring gas sample using a long pole.

pool is not deep enough for a beaker or a bottle, and then a plastic syringe is used to collect the fluid.

Filtering the spring samples is accomplished using either the hand vacuum pump or the syringe filter shown in Fig. 1. When filtering apparatus is not available or when a sample is particularly hard to filter, unfiltered samples may be collected and filtered in the laboratory using the laboratory filter shown in Fig. 2. Samples that cannot be filtered in the field should never be acidified, and to avoid confusion, these samples are labeled "raw."

Downhole samples are collected in special instruments designed for that purpose. A schematic of the Los Alamos downhole sampler is shown in Fig. 6. This instrument contains a 1- to 2-l sample chamber that is washed and

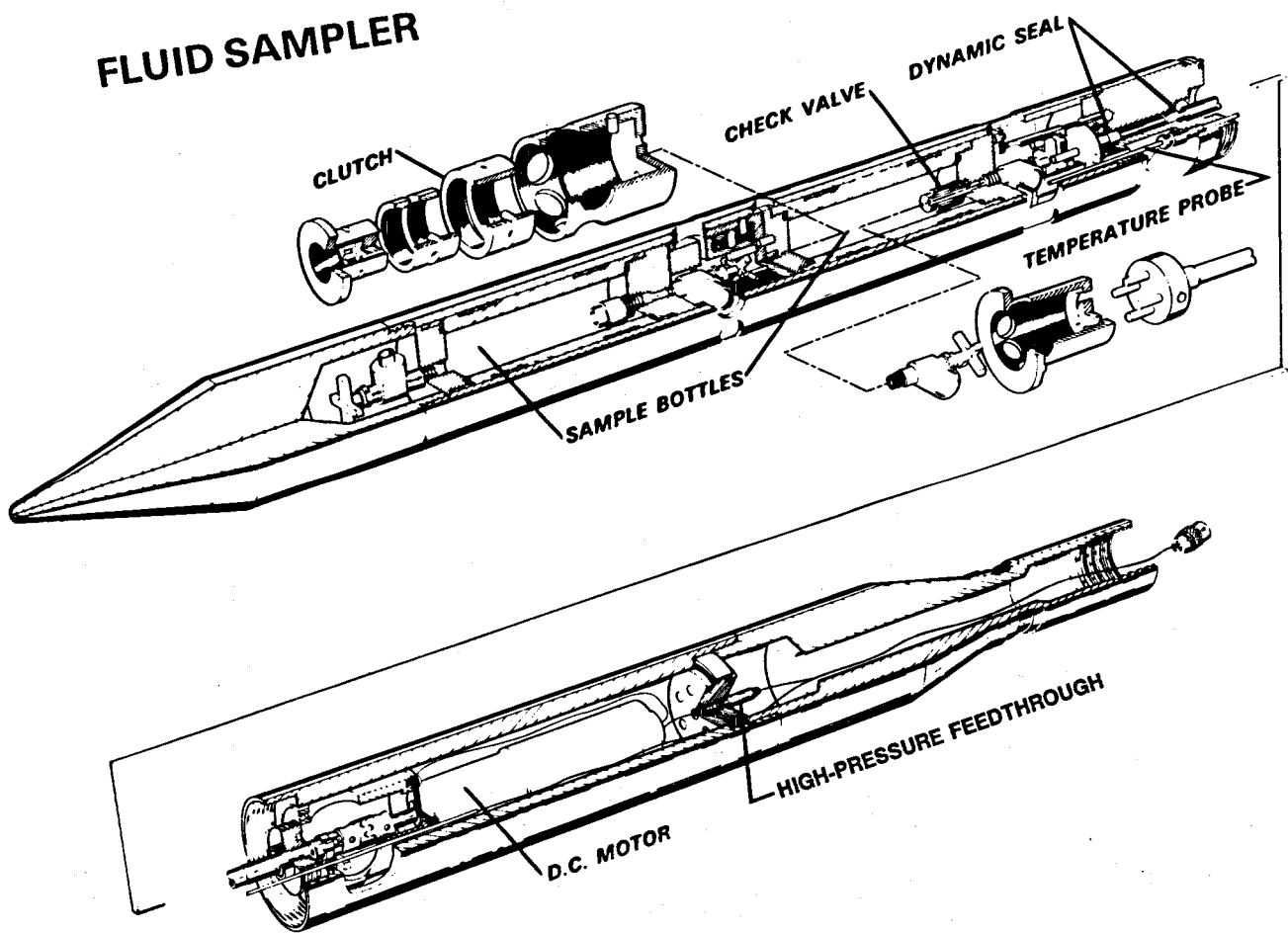


Fig. 6.
Schematic for Los Alamos downhole sampler.

evacuated and then lowered into a well on a cable. At the appropriate depth, the sample chamber is opened and closed by remote control from the surface. The sampler is then returned to the surface where the sample is removed from the sample chamber.

If the dissolved gases are not to be collected, the sample chamber is opened and the liquid is filtered and divided into the appropriate aliquots. If the gases are to be collected, the outlet of the sample chamber is connected to a gas sampling bottle by a gas extraction line. The transfer line is evacuated before the sample chamber is opened, and the gas sample is transferred to the gas sampling bottle (see Fig. 7). After the gas sample is isolated from the sample chamber, the chamber is returned to atmospheric pressure and is opened. The fluid phase is then filtered as described above.

C. Detailed Procedures for Collecting and Preserving Liquid Samples

Filtered acidified samples are collected in 250-ml polyethylene bottles that have been rinsed at least twice with filtered sample. Ten drops of

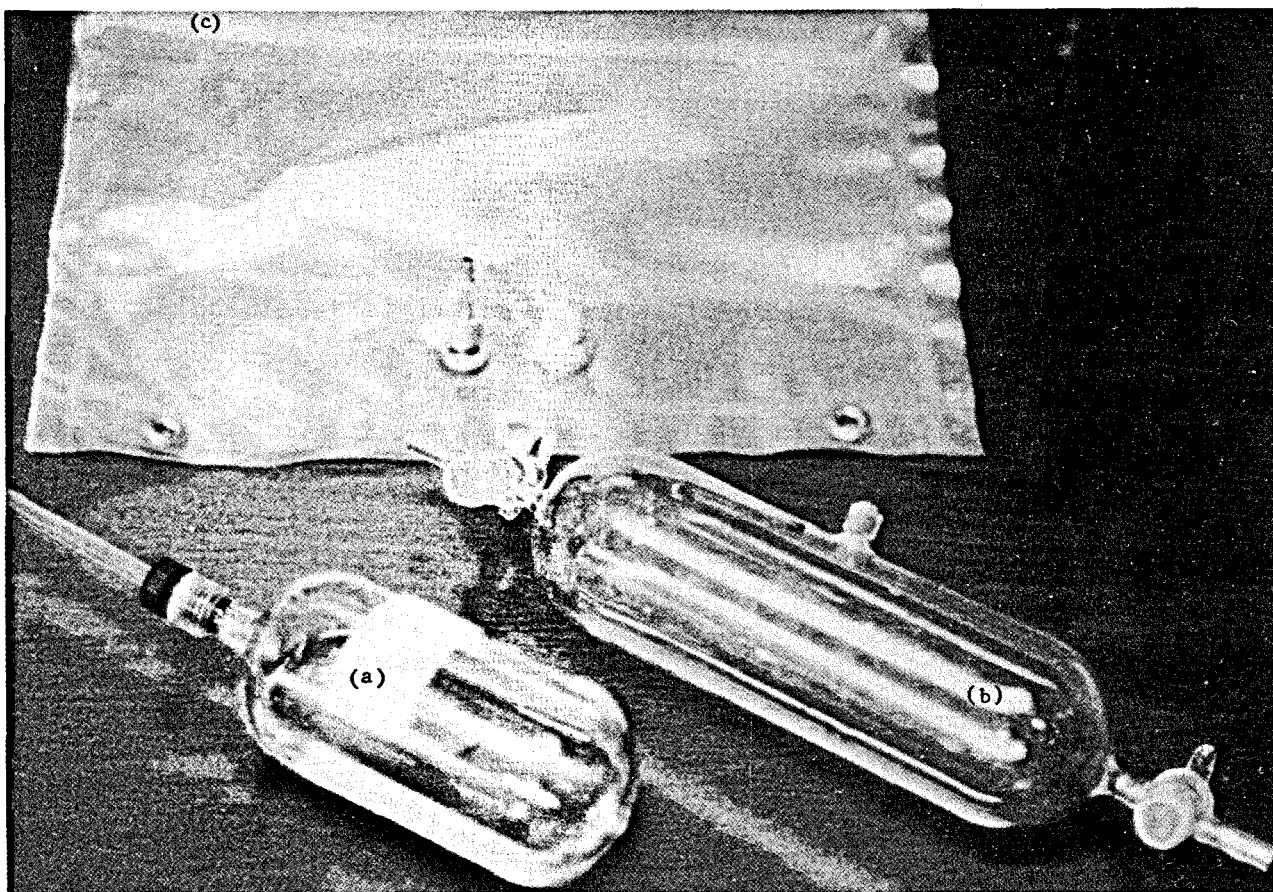


Fig. 7.
Gas sampling containers: (a) the modified Gigenbach bottle, (b) a flow-through gas flask, and (c) a Mylar gas bag.

concentrated HNO_3 are added to adjust the pH to a value ≤ 2 , and the bottle is sealed with a conical plastic cap. To prevent loosening of the cap, masking tape is wrapped around the cap and the neck of the bottle. Information recorded on the bottle includes a sample number, the date and time of collection, the sample location, and the letters "FA," which indicate that this bottle has been filtered and acidified. This information must be recorded with an indelible pen and should be recorded both on masking tape wrapped around the bottle and directly on the bottle.

Filtered unacidified samples are collected in 250-ml polyethylene bottles that are also rinsed twice with filtered sample. The bottle is capped, taped, and labeled as above except that this bottle is labeled "FU" to indicate that no acid has been added. If it is not possible to filter the sample in the field, the bottle is labeled "raw" to indicate that it has not been filtered.

Silica dilutions are made on samples that may be saturated or super-saturated with respect to amorphous silica. Five milliliters of filtered sample are added to a 30-ml polyethylene bottle that contains 20 ml of deionized water (previously added in the laboratory). The bottle is not rinsed in the field. The bottle is capped, taped, and labeled with the designation "1:5 dilution."

Water samples for stable isotopes are collected in a 125-ml flint glass bottle that is not rinsed. The bottle is filled to the brim with unfiltered sample and is capped with a plastic cap. The cap is taped and the bottle labeled "water isotopes."

Water samples for carbon isotopes are collected in a 250-ml or larger polyethylene bottle that is not rinsed in the field. Unfiltered sample is added to the bottle, and 5 ml (to 20 ml) of SrCl_2 solution (prepared by saturating a 10N solution of NH_4OH with $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) is injected into the bottle. The analysis requires 50 mg of SrCO_3 , so 1 l of sample is required for samples containing 20 ppm HCO_3^- . If the bicarbonate concentration is higher, sample volume can be reduced. The bottle is capped, taped, and labeled with the designation "C isotopes." The amount of SrCl_2 solution added should also be recorded.

Water samples for sulfur isotopes are collected in unrinsed 500-ml polyethylene bottles. Unfiltered sample is added to the bottle and is preserved with 5 ml of formaldehyde to kill bacteria that could convert sulfate to sulfide. The bottle is capped, taped, and labeled "S isotopes."

Water samples for tritium are collected in unrinsed 500-ml polyethylene bottles. The bottle is filled with unfiltered sample, capped, taped, and labeled "³H."

Water samples for chloride isotopes are collected in 250-1000-ml polyethylene bottles that are not rinsed in the field. The bottle is filled nearly to the top with filtered sample, and an excess of saturated AgNO₃ solution (in deionized water) is added to precipitate all of the chloride as AgCl. The bottle is capped, taped, and labeled "Cl isotopes."

A water sample for monomeric aluminum is prepared by complexing with 8-hydroxyquinoline and extracting the complex into MIBK (methyl isobutyl ketone). The details of this procedure are presented in Appendix H.

A water sample for total suspended solids is collected in an unrinsed 500-ml polyethylene bottle. The procedure is identical to that used to collect tritium samples. The bottle is designated "TSS."

A water sample for dissolved oxygen is collected in a 300-ml glass biological oxygen demand (BOD) bottle. The sample is not filtered. The bottle is filled brimful, capped, taped, and labeled "O₂."

Measurements made in the field at the time of sample collection include temperature, conductivity, pH, Eh, and chloride. Usually a portable instrument such as the Presto-Tek Model 550 is used with the appropriate probes or combination electrodes (Fig. 8). The pH, Eh, and conductivity electrodes are standardized in the field using commercially prepared buffers and standards. All measurements are temperature corrected, and the temperatures at which the measurements are made are recorded. When the spring is far from a road and too far to carry the portable meter, pH is measured using ColorpHast™ pH measuring sticks available from EM Laboratories, Inc. Chloride is measured in the field using Quantab™ chloride titrator sticks, which are available from the Ames Division of Miles Laboratories, Inc.

D. Gas Sampling Procedures

The apparatus used to collect gas samples from hot springs or fumaroles is easily constructed from several meters of silicone tubing, a tubing clamp, a small hand pump, several sizes of funnels (plastic is better for most applications, but glass doesn't melt in fumaroles), glass sample bottles, a long collapsible pole, masking tape and markers, and two bottle clamps (Fig. 9). Two types of sample bottles are used (see Fig. 7). The first is a modified Giggensbach bottle,^{5,6} which has been prepared according to the



Fig. 8.

Field measurement apparatus: Presto-Tek Model 550 meter with electrodes and sample bottles.

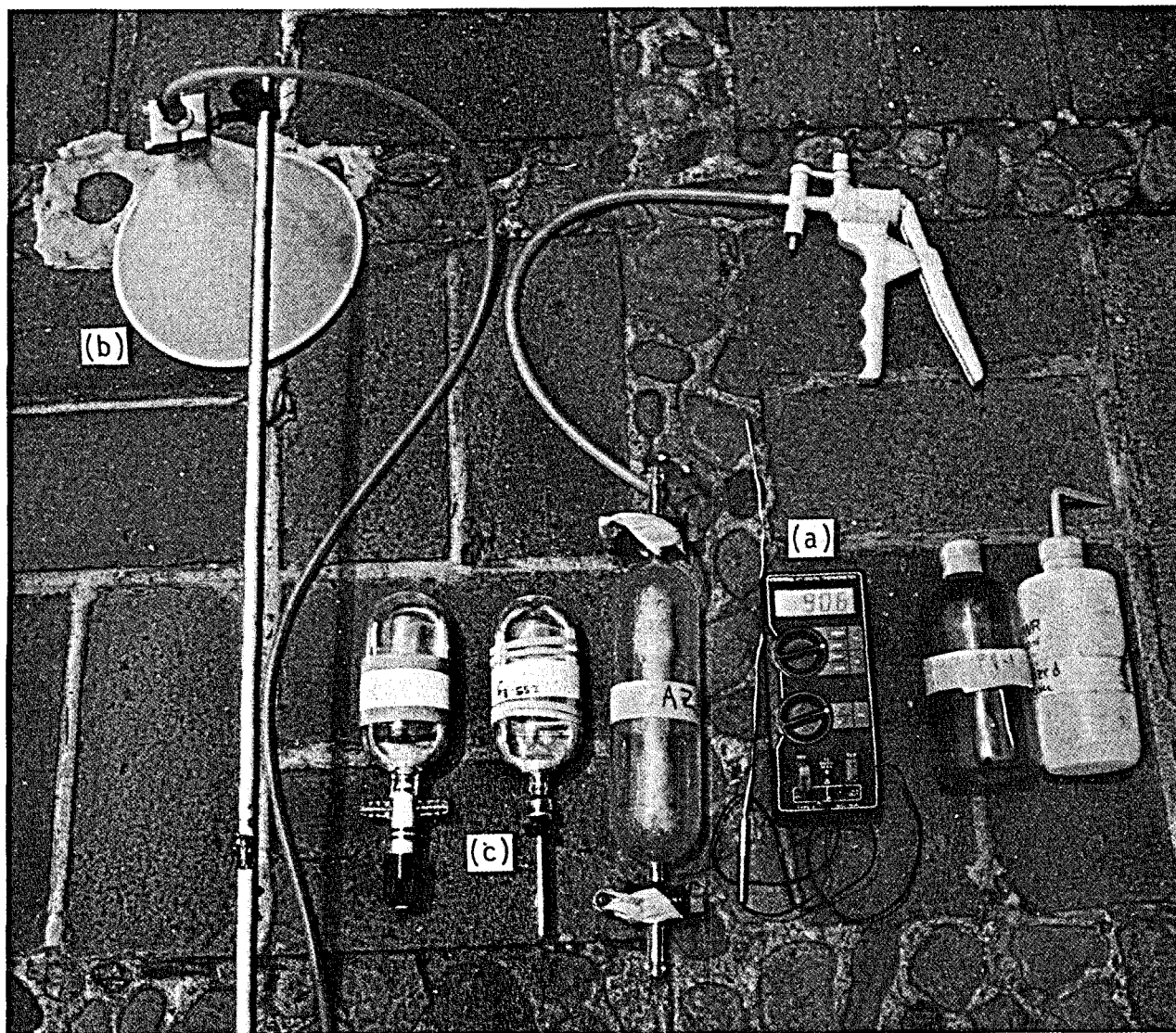


Fig. 9.
Field gas sampling apparatus: (a) temperature probe, (b) collection funnel with pump, and (c) various sampling bottles.

procedure described below, and the second is a gas flask with a stopcock at each end. One piece of tubing is attached to the suction stem of the hand pump and to the side of the sample bottle. The tubing clamp is placed between the hand pump and the sample bottle when a Giggenbach bottle is used. Another piece of tubing connects the other side of the sample bottle with the stem of the funnel. Hence, tubing is attached to both openings on the sample bottle with the pump at one end and the funnel at the other end. The clamps are attached to the end of the pole in such a way that the funnel can be clamped

to the pole (see Fig. 5). This arrangement allows the operator to place the funnel over the main area of gas discharge and to remain a safe distance away from boiling springs or superheated fumaroles.

To collect the sample, submerge the wide end of the funnel into the bubbling water directly over the gas source, or if sampling a fumarole, dig out the area of interest, set the funnel into the earth, and pack earth around the funnel. The rim of the funnel must be completely covered with water or earth so that air will not contaminate the gas sample.

Begin pumping with the hand pump, being careful not to suck water up through the tubing into the sample bottle. As gas is pumped from the funnel, the water level may rise in the funnel. When the water level approaches the apex of the funnel, cease pumping until gas fills the funnel. For the Giggensbach bottles, the pump is used to flush the line. When this is done, close the tubing clamp and open the Teflon valve slightly while inverting the bottle. Gas will bubble through the caustic. Take care to prevent loss of caustic by adjusting the valve. Shake the bottle occasionally to absorb the CO_2 and H_2S into the caustic. If the gas is largely CO_2 , the bottle will become hot. Have water available to cool the bottle and use rubber gloves to handle it. When the bottle no longer takes gas (no bubbles form), close the Teflon valve and tape it closed. Label the bottle.

For the flowthrough bottles, pump vigorously for about 2 min (125-ml bottles) to 5 min (500-ml bottles) until all air is out of the sample bottle and has been replaced with geothermal gas. Close both stopcocks on the sample bottle before the funnel is removed from the spring or fumarole. Wrap masking tape around the stopcocks to avoid accidental opening of the gas bottle and contamination of the sample. Wrap masking tape around the body of the bottle and label the bottle with a marking pen.

Gas samples are collected at wellheads using a gas separator. The sample bottle is connected to the gas outlet of the separator with plastic or silicone tubing, and the sample is collected as described above. In addition to the glass sample bottles, gas sampling bags may also be used. These bags are purchased commercially (Calibration Instruments, Inc.) and are usually made of tough Mylar plastic. They are equipped with valves and septums for gas introduction and removal. Gas bags are convenient for collecting samples that are to be analyzed quickly after collection. Although the bags are best suited for collecting samples from a pressurized source, gas may also be

introduced into the bags using a large gas syringe such as the Hamilton Super Syringe.

Gas samples may be collected from a downhole sampler as described in the section on collecting downhole samples.

Preparation of Giggenbach bottles. First, weigh the empty bottle (with the Teflon valve stem) and scribe the weight on the bottle. Then prepare a 4N solution of CO₂-free NaOH and fill approximately one-third of the bottle with this solution by removing the valve stem from the bottle. Replace the valve stem and evacuate the bottle with a vacuum pump. If possible hold the bottle in a hot water bath (~60°C) to drive any dissolved gases out of solution. Close the valve when the evacuation is complete and weigh the sealed bottle. Record the total weight of the bottle on the bottle with an indelible pen. It is convenient to wrap the bottle with masking tape and write the weight on the tape.

III. INSTRUMENTATION AND METHODS

A. General

At Fenton Hill most anion determinations are analyzed by ion chromatography; however, some are also done using selective ion electrodes, colorimetry, and titration. Since the addition of acid during sampling interferes with ion chromatography and alters the CO₃⁻², HCO₃⁻, and sulfide concentrations, unacidified sample aliquots are used for anion analysis. Cation analyses are usually measured by atomic absorption (AA) or by inductively coupled plasma (ICP) emission spectroscopy on the acidified aliquot. To avoid many of the analysis problems associated with long storage, all analyses are done as quickly as possible after collection.

Quality control of results is of major concern when collecting data. Multiple analyses on identical samples or on dilutions are used to check precision and accuracy. In some cases results from two different analytical methods are compared. Whenever possible, standard solutions from the Environmental Protection Agency (EPA) or the US Bureau of Standards are included with each sample run, and a record of the results for these standards is kept.

B. Anion Analysis

Ion Chromatography. Many anions associated with geothermal fluids can be determined using ion chromatography that simultaneously analyzes F⁻, Cl⁻, NO₂⁻, PO₄⁻³, Br⁻, NO₃⁻, and SO₄⁻². Nitrite, phosphate, and nitrate are usually present

only if introduced into the geothermal fluid or reservoir from external sources such as in a drilling operation. The sensitivity of ion chromatography is good, and the simultaneous and automated nature of the method saves operator time.

The instrument used for ion chromatography is the Dionex AutoIon System 12 shown in Fig. 10. Anions are separated with an HPIC Anion S4 Separator column followed by an Anion Fiber Suppressor. The acid forms of the anions from the suppressor are detected on a conductivity meter that is adjustable to different conductivity levels. Signals from the meter are integrated and processed by a Spectra-Physics 4100 Integrator. Some modifications of the System 12 were necessary to enable the use of the S4 columns and fiber suppressor. The sample injection system was also revalved so that the sample loop and injection valve could be flushed with deionized water between samples to prevent the cross-contamination problems encountered when high-concentration samples are analyzed. Programming and operation of the ion chromatography apparatus are done according to the instruction manuals.^{7,8}

With an autosampler, up to 99 samples and/or standards may be run without operator intervention. A multilevel linear calibration of five standards is usually done at the beginning of each analytical run and is repeated at designated intervals during the run. The average run time from injection to analysis report is usually 9 min; however, this may vary slightly because of flow rate adjustments (within pressure limitation of <1000 psi for the modified system) and varying eluent strengths, which are sometimes necessary to optimize component separation.

Since Cl^- or SO_4^{2-} concentrations in many samples are usually much higher than are other components, a series of dilutions are usually analyzed. This assures that all ions fall within the linear concentration range, at the maximum sensitivity, and that peak overlap is minimal. Filtered unacidified samples collected in the manner prescribed in the sampling section are used, and a sample of at least 4 ml is used per analysis.

The eluent solution used for anions is a 0.0028M NaHCO_3 and 0.00225M Na_2CO_3 solution. Because of bacterial growth in this solution and particulates in the injection fluid, a precolumn is always placed before the separator column to prevent it from plugging. Solids are caught in the less expensive precolumn or in the bed support at the top of the column. Plugging of either column results in high back pressure. A number of wash procedures

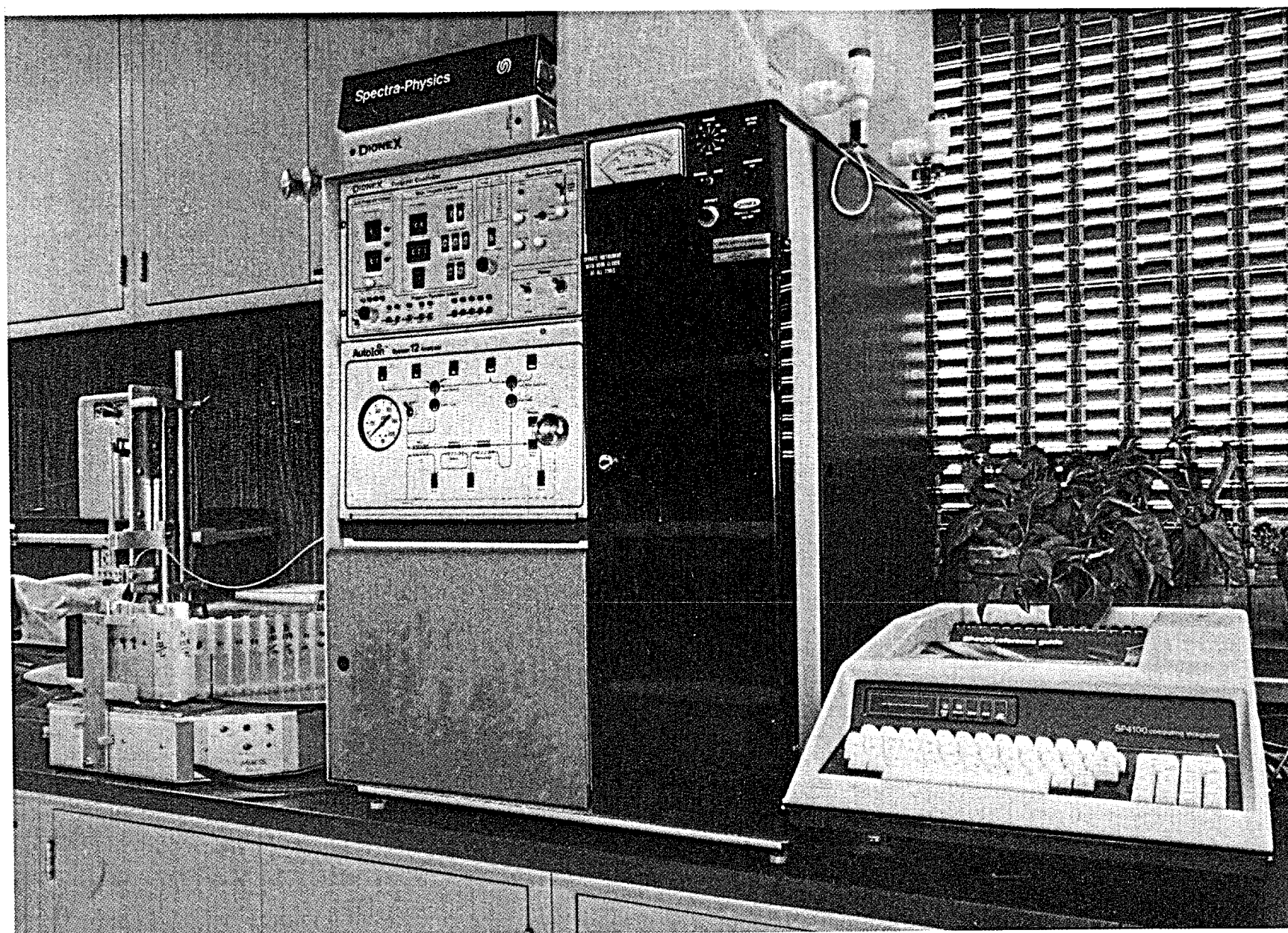


Fig. 10.
Dionex AutoIon System 12 used for anion analysis.

are given in the Dionex manual and in various application notes,⁹ but these have not been very successful for saving plugged columns at this laboratory. Prevention seems to be the best approach.

The only major interference found with some of the samples using ion chromatography is in the analysis of fluoride, which has a short retention time. High carbonate/bicarbonate concentrations in the samples as well as some organic acids cause a false fluoride peak, which can be distinguished from the usual fluoride peak by the broad shape. Because of these problems, fluoride analyses are checked using a selective ion electrode method if there is any question about validity of the fluoride result.

Titration. In the laboratory, titrations to determine carbonate and bicarbonate are done using a Fisher Titrimeter II Automatic FEP System (Fig. 11). Filtered unacidified samples are titrated with 0.1N H₂SO₄ to a pH of 8.3 for carbonate and 4.5 for bicarbonate.¹⁰ Most geothermal samples contain only HCO₃⁻, and levels are usually high enough to make it one of the major anionic species.

Titration procedures are occasionally used in the field for measuring dissolved oxygen or chloride. The dissolved oxygen method is a modification of an iodometric method (Winkler method) in which azide is used in a reaction that converts manganous ions to manganic ions in the presence of dissolved oxygen. Addition of acid causes the manganic ion to release free iodine from iodide. The free iodine is then titrated with thiosulfate. The chloride method is based on the titration of an acidified sample with dilute mercuric nitrate solution in the presence of a mixed diphenylcarbazone-bromophenyl blue indicator. The end point of the titration is the formation of a violet mercury complex with excess mercuric ions.

Colorimetry. Borate, silica, and sometimes sulfide are analyzed colorimetrically. Measurements are done on a Beckman Model 25 Spectrophotometer (Fig. 12) equipped with a sipper cell, set up and operated according to the instrument manual.¹¹

Boron concentrations ranging from 10 to 100 ppm are not unusual. Samples with high boron concentrations are usually analyzed by ICP, but lower concentrations are measured using the azomethine-H method.¹² In this method a disodium EDTA buffer is used to reduce ionic species that may interfere with absorption by the yellow color complex formed by boron with the azomethine-H. Absorption is measured at 420 nm after development of the color. For the

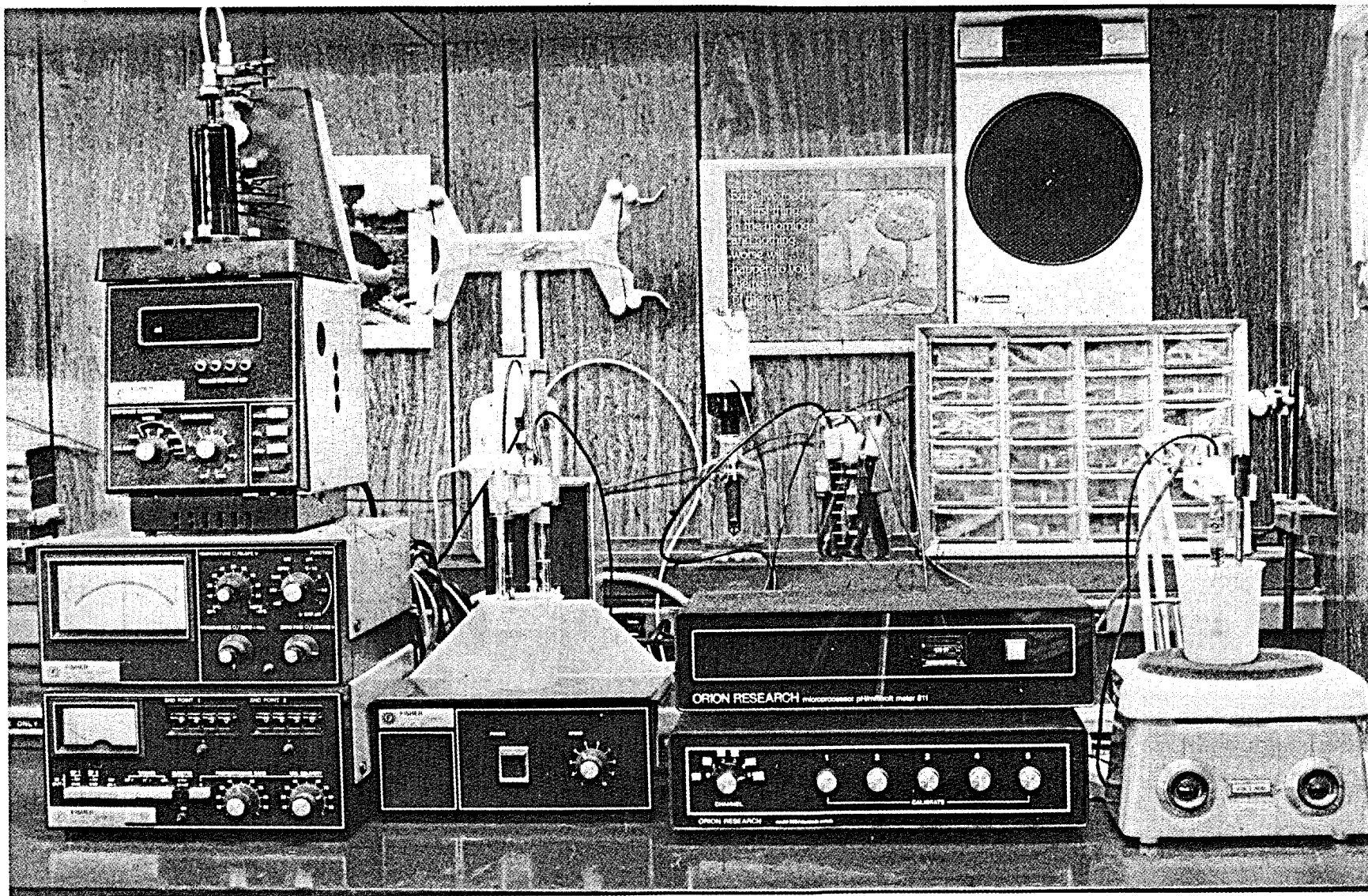


Fig. 11.
(Left) Fisher Titrimeter II automatic titration system. (Right) Orion model 811 pH/millivolt meter with switching unit for making electrode measurements.

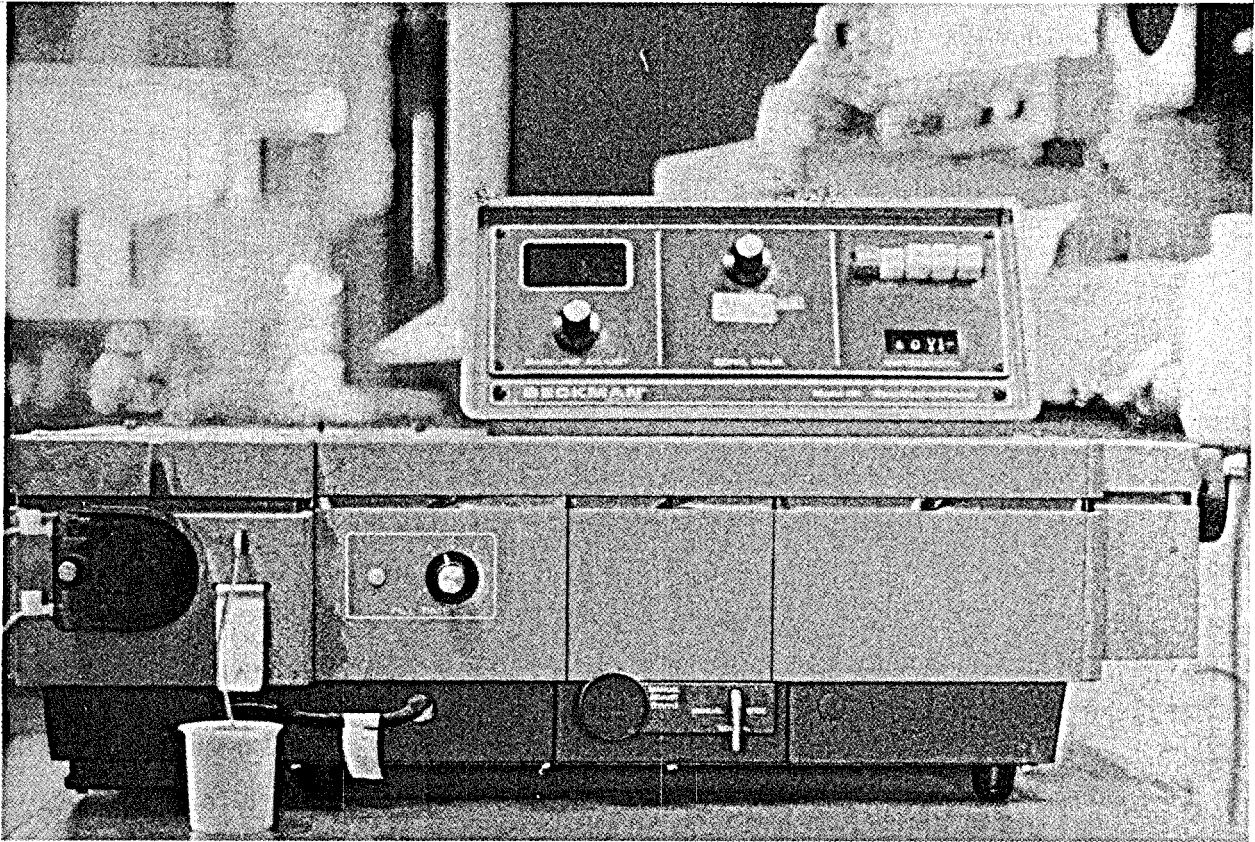


Fig. 12.
Beckman Model 25 UV-Vis Spectrophotometer.

sipper cell the upper standard used is 10 ppm, which is the upper limit of the linear range for that cell. Either filtered acidified or unacidified samples may be used, and blanks and standards are prepared by the same technique used on the samples. Occasionally a sample is colored after filtering, but then an extra blank must be prepared from the sample by adding fresh 1% ascorbic acid solution instead of the azomethine-H reagent. By doing this, a correction for the color in the sample can be made by subtracting the reading for this blank from the reading obtained for the sample, provided the readings fall in the linear range. Details for the procedure are given in Appendix C.

Soluble silica (monomeric SiO_2) is also analyzed colorimetrically. The method is based on the formation of the yellow molybdosilicate complex that forms when soluble silica reacts with molybdate ion. The absorbance of this complex is measured at 410 nm on the spectrophotometer. Since silica geothermometers are based on the amount of soluble silica in the sample, preventing polymerization of the silica before analysis is imperative. For

most hot geothermal samples or samples containing more than 100 ppm silica, polymerization is prevented by making 1:5 dilutions of the samples immediately at the time of collection. Samples that contain less than 100 ppm are usually not diluted. Standards are prepared to cover the range of the samples, usually 0 to 250 ppm when 250 ppm is used as the highest standard.

Few interferences have been found when using the molybdate method for geothermal samples, possibly because of sample dilution with the molybdate reagent (Ref. 13, pp. 487-490). This reagent is usually stable for one week. Reagent deterioration is indicated by loss of sensitivity and the formation of solid scales in the reagent container. Because of the possibility of contamination with silica from glassware, plastic flasks are used for mixing and storing reagents.

Sulfide levels from 0.01 to 1 ppm can easily be measured by the methylene blue colorimetric method that is based on the reaction of sulfide and dimethyl-p-phenylenediamine under conditions which form methylene blue dye (Ref. 13, pp. 503-505.) Because of the instability of sulfide ion toward reduction or oxidation, immediate analysis is advisable. Interferences occur in the presence of reducing agents (such as thiosulfate), heavy metals, and sulfite.

C. Cation Analysis

In this laboratory the two methods used for the majority of cations are atomic absorption (AA) spectroscopy, with either flame or graphite furnace, and inductively coupled plasma (ICP) emission spectroscopy.

Atomic Absorption. Flame AA is sometimes used for elements found in the parts per million (ppm) range that do not require high atomization temperatures or do not form stable refractory compounds. Although the flame AA method is very reliable, it is not used extensively because it lacks the speed of the ICP method. Graphite furnace AA is the method used for trace metals usually occurring in the parts per billion (ppb) range.

Both AA methods are very specific for the analyte being measured, but difficulties sometimes arise in both because of matrix interferences. Many of these matrix problems can be eliminated or reduced by proper sample preparation or control of operating parameters. The control of matrix problems for both AA methods is important for samples having high salinity because of the increased likelihood of interfering species. The steps taken to avoid matrix problems depend on the method used and the element being analyzed. Some of these steps are discussed in more detail in later sections of this report.

The instrument used at this laboratory for AA is a Perkin-Elmer Model 5500 Atomic Absorption Spectrophotometer equipped with an HGA 500 Graphite Furnace, AS-1 and AS-50 Autosampling Systems, and a 3600 Data Station with printer (Fig. 13). Hollow cathode lamps are used as spectral sources for both flame and graphite furnace methods. The Model 5500 has a nonlinear curve calibration capability, and a continuum background correction is used for all analyses.

Table I lists the elements occasionally analyzed by flame AA and the parameters used in their analysis. The general matrix referred to in the table contains an alkali salt, in this case cesium, to control ionization interferences, and lanthanum to suppress silica interference when using an air-acetylene flame. Nitric acid helps keep the sample in solution. The burner angles referred to in the table indicate the angle between the flame and the instrument light path (see Fig. 14).¹⁴ The greatest sensitivity is obtained when the lamp beam passes through the entire length of the flame, and the lowest sensitivity occurs when the flame length is set perpendicular to the beam. Changing the burner angle allows the analyst to control the sensitivity of the absorption signal allowing expansion or reduction of the linear range. The value for integration time indicates the length of time over which the signals are averaged during a reading.

Two different types of flame systems are available with the Perkin-Elmer 5500: the air-acetylene flame, which is used most often for convenience and maximum sensitivity, and the nitrous oxide-acetylene flame, which is used for silicon or when the lanthanum matrix modifier does not eliminate the SiO_2 interference with the air flame. The types of gas and the gas flows are controlled automatically by the Perkin-Elmer 5000 Burner Control, which is also available with the AA instrument. This instrument can calibrate with nonlinear curves, and this feature is frequently used when signals fall above the linear range if flattening of the absorption curve is not too pronounced.^{14,15}

If a complete set of analyses is to be done by flame AA, preparing a set of standards and sample dilutions and then adding the general additive described in Table I usually save time. All the necessary modifications needed in most geothermal fluid analyses for the elements listed in the table are then made, except Cs, which cannot be run in the CsCl matrix. The extent of dilution depends on the linear range of each element and its concentration

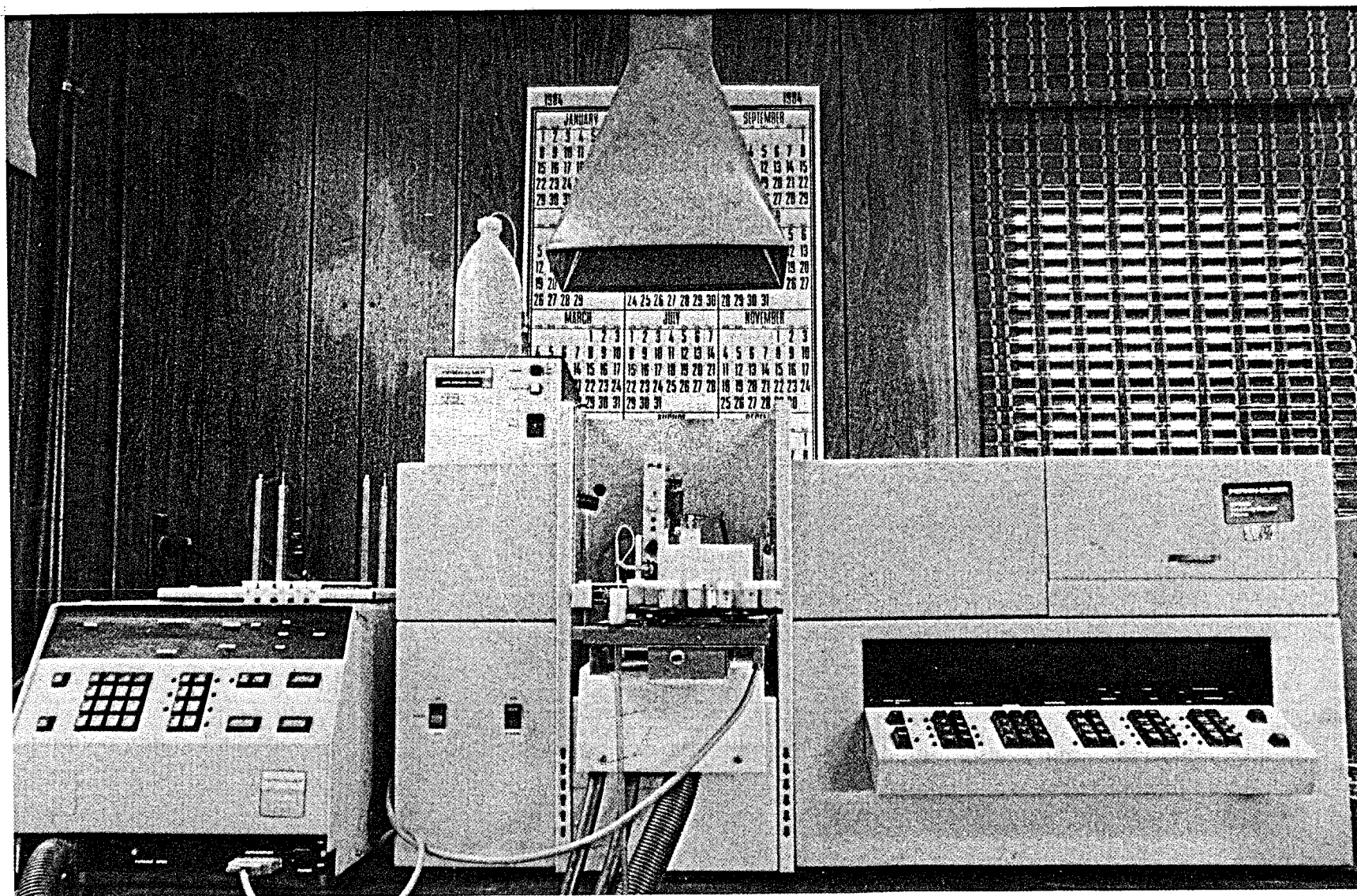


Fig. 13.
Perkin-Elmer Model 5500 Atomic Absorption Spectrophotometer with graphite furnace.

TABLE I
FLAME ATOMIC ABSORPTION STANDARD CONDITIONS

Matrix Element	Modifier	λ , nm	Slit nm	Std. ppm	Abs	Fuel Flow	Gas	Gas Flow	Comments
Ca	General ^(a,b)	422.7	0.7	5.0	0.225	32	Air	47	
Cs	0.7% KCl ^(b)	852.1	1.4	10.0	0.150	32	"	47	Red filter
Fe	General ^(a,b)	248.3	0.2	5.0	0.085	32	"	40	
K	General ^(a,b)	766.5	1.4	10.0	0.120	32	"	47	45° burner angle, red filter
Li	General ^(a,b)	670.8	1.4	10.0	0.100	32	"	47	"
Mg	General ^(a,b)	285.2	0.7	1.0	0.250	32	"	47	
Mn	General ^(a,b)	279.5	0.2	1.0	0.036	32	"	40	
Na	General ^(a,b)	589.0	0.4	20.0	0.265	32	"	47	90° burner angle
Rb	General ^(a,b)	780.0	4.0	5.0	0.200	32	"	47	Red filter
Si	None	251.6	0.2	50	0.080	32	N ₂ O	13	Si may drop out with time if gen. add. is used
Sr	General ^(a,b)	460.7	0.4	1.0	0.053	55	N ₂ O	36	Air-C ₂ H ₂ flame may also be used.

^a General additive for flame AA: 0.7% CsCl
5.0% La₂O₃
10% HNO₃

^b Reagent concentration may be varied depending on the percentage of salt in the samples. Usually add 1 ml modifier per 10 ml sample or standard.

Note: All integration times are 3 s. The fuel used for all analyses is acetylene, C₂H₂.

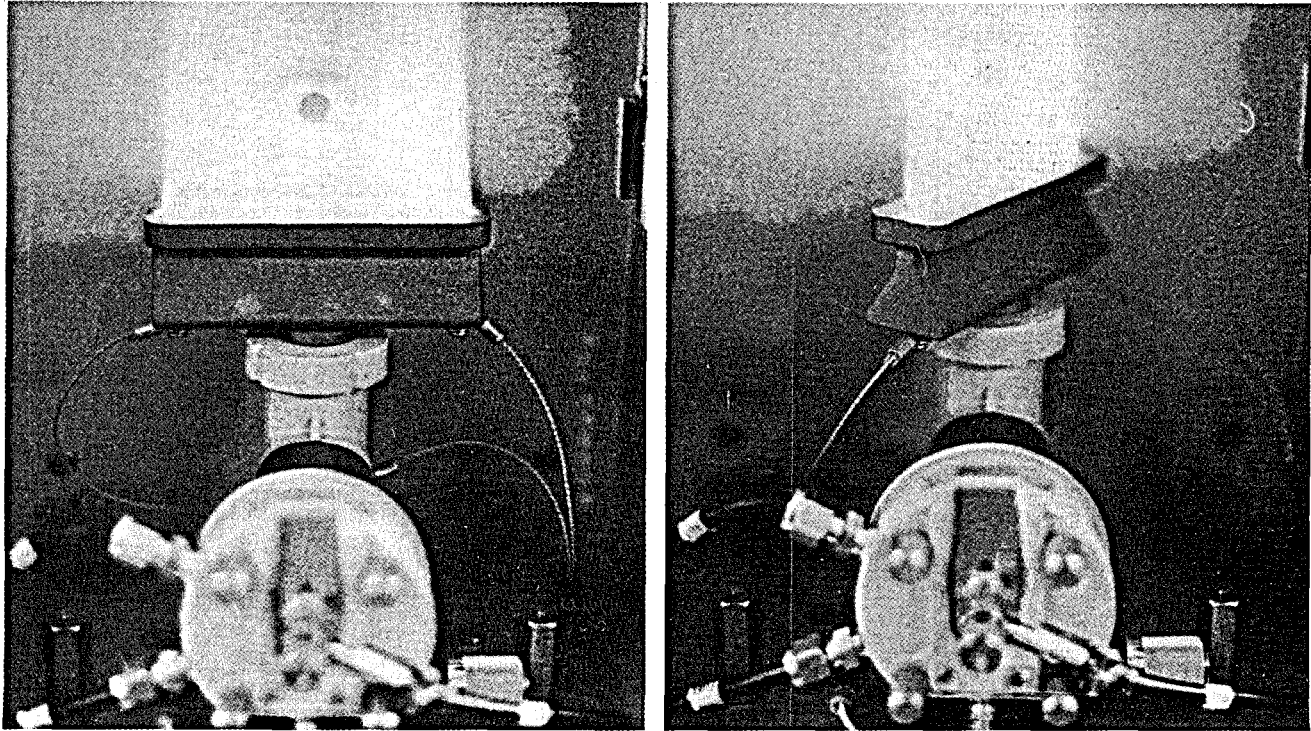


Fig. 14.

Adjustment of burner angle for flame atomic absorption. (Left) normal setting. (Right) 45° angle.

in the sample. Dilution also has the advantage of reducing matrix interferences; however, high dilution factors compound the error associated with the readings. To avoid excessively high dilutions, the signal may be reduced either by rotating the burner head or by using a less sensitive wavelength. Sometimes samples with high concentrations of the element of interest are more easily analyzed using ICP.

Table II lists elements that are commonly analyzed by the graphite furnace. For geothermal applications, only Ag, Al (monomeric), Cd, Co, Cr, Cs, Cu, Ni, Pb, and Rb are run routinely. Most elements are run in a 0.1% nitric acid solution, which is usually the concentration of the filtered acidified aliquot collected for cation analysis. Aqueous samples and standards are also diluted with 0.1% nitric acid. In cases where matrix modifiers are used, both samples and standards are treated identically when possible.

In general, the instrument settings and analysis techniques used for most aqueous samples are in the Perkin-Elmer procedure manual;¹⁶ however, due to the nature of certain samples, special techniques are sometimes used. For

TABLE II
HGA GRAPHITE FURNACE STANDARD CONDITIONS

Element	Matrix	λ , nm	Slit nm	Std. ppb	Abs	Char °C	Atomize T, °C	Argon ^a Gas Flow
Ag	0.1% HNO ₃	328.1	0.7	10	0.170	50	2300	300/150
Al	MIBK	309.3	0.7	20	0.400	See Table III		
Cd	5% HNO ₃	228.8	0.7	10	0.170	250	2300	300/300
Co	0.1% HNO ₃	240.7	0.2	25	0.140	1000	2700	300/50
Cr	0.1% HNO ₃	357.9	0.7	50	0.200	1200	2700	300/50
Cs	0.1% HNO ₃ or DI water	852.1	0.4	50	0.125	100	2700	300/300 ^b
Cu	0.1% HNO ₃	324.7	0.7	25	0.150	900	2700	300/50
Fe	0.1% HNO ₃	248.3	0.2	50	0.220	1100	2700	300/100
Li	0.1% HNO ₃ or DI water	670.7	1.4	50	0.326	700	2700	300/300 ^b
Mg	0.1% HNO ₃	285.2	0.7	10	0.157	1200	2700	300/300
Mn	0.1% HNO ₃	279.5	0.2	100	0.275	1100	2700	300/300
Ni	0.1% HNO ₃	232.0	0.2	50	0.180	1000	2700	300/50
Pb	10% NH ₄ NO ₃	283.3	0.7	25	0.150	500	2700	300/200
Rb	0.1% HNO ₃ or DI water	780.0	4.0	25	0.235	1000	2700	300/300 ^b
Sr	0.1% HNO ₃	460.7	0.4	25	0.125	800	2700	300/300
Zn	0.1% HNO ₃	213.9	0.7	25	0.280	500	2300	300/300

^a Argon gas flow readings represent normal flow/interrupted flow during atomization stage.

^b With red filter.

Note: All integration times are 3 s. Sample volume is 20 mL.

example, such special techniques are shown in the steps necessary to eliminate or minimize the chloride ion interferences in samples containing high Cl^- concentrations. A number of elements, particularly Cd and Pb, are lost as metal halides during the charring step (Ref. 16, p. 6-6). In some cases stable metal chloride molecules may form that cause problems during the atomization step either because they do not give an absorption signal or because they form smoke, which produces high backgrounds. For most geothermal samples with high Cl^- , it has been found that the addition of 10% NH_4NO_3 very nearly eliminates Cl^- interference for Pb analyses. The same is also true for Cd if 5% HNO_3 is added, albeit at the expense of the pyrolytic graphite tubes, which have shorter lives. Samples with high salt content sometimes cause splattering during the dry cycle that may be avoided by using lower temperatures or longer ramp times. A precautionary final step is sometimes used to clean the graphite tube to prevent sample carry-over or memory. Whenever smoke is present during the atomization cycle, gas flows through the graphite tubes are not interrupted because the instrument background correction is usually ineffective. Graphite furnace operating parameters for most of the elements analyzed by this method are shown in Table II.

Special graphite furnace AA procedures are also necessary for analyzing monomeric aluminum, which is extracted into an organic phase. The organic phase (MIBK) from the extraction of both samples and standards requires the rather elaborate temperature cycle shown in Table III.

Plasma Emission Spectroscopy. The major metallic elements in the samples at Fenton Hill are analyzed using an inductively coupled argon plasma source for emission spectroscopy. The technique is based on the excitation of the

TABLE III
ALUMINUM ANALYSIS IN MIBK--
PROGRAMMING SEQUENCE FOR HGA 500 GRAPHITE FURNACE

Step	#1	#2	#3	#4	#5
Temperature °C	30	130	1400	2800	2800
Ramp t (s)	1	20	20	1	0
Hold t (s)	50	10	15	4	5
Interrupted flow	--	--	--	200	--
Read	--	--	30	0	--

analyte elements in a highly energetic plasma sustained by a radio-frequency electromagnetic field to give the emission spectra of the elements. The high excitation temperatures in the plasma, up to 10,000 K, cause essentially all elements to be excited, including nonmetals and those elements that form high refractory compounds.

The system used at this laboratory is a Perkin-Elmer Model ICP/5500, which is a sequential instrument with a Czerny-Turner monochromator driven by a remote microcomputer (3600 Data Station) and equipped with a cross-flow nebulizer. A sample is introduced into the nebulizer by a peristaltic pump that draws liquid samples from a Perkin-Elmer Model AS-50 automatic sampler (Fig. 15). Argon gas for the torch is supplied by a dewar containing liquid argon. The techniques and parameters for operation of the instrument are outlined in the various instruction manuals supplied with the instruments.^{17,18} Calibration is done using standard solutions in conjunction with the programs available on the microcomputer software. Calculations, analytical results, and reports are also processed through the microcomputer.

In order to optimize analytical conditions and to avoid spectral interferences, ICP analyses are usually done in the four main groups listed in Table IV. Also included in the table with the groups are the internal standards used with each group. Some elements such as uranium, which is more conveniently run by itself, and trace metals that are found to be too concentrated to be easily analyzed by graphite furnace AA are not included in the main groups. These elements either are analyzed separately or are grouped according to elements of interest. In these cases samarium is usually the internal standard.

All samples are prepared by adding 0.5 ml of concentrated nitric acid and the appropriate amount of internal standard to 10 ml of sample. If a precipitate forms with the acid, the acid is omitted. In general, concentrations of standards for each group are selected to cover the expected concentration range of each element in the sample. In cases where the total salt content of the sample is high enough to cause nebulization problems or when the expected sample concentration range is outside the linear range, samples are diluted before the addition of internal standard.

Group 1 consists of boron, iron, barium, calcium, magnesium, strontium, and manganese. Samarium was selected as the internal standard because it gave

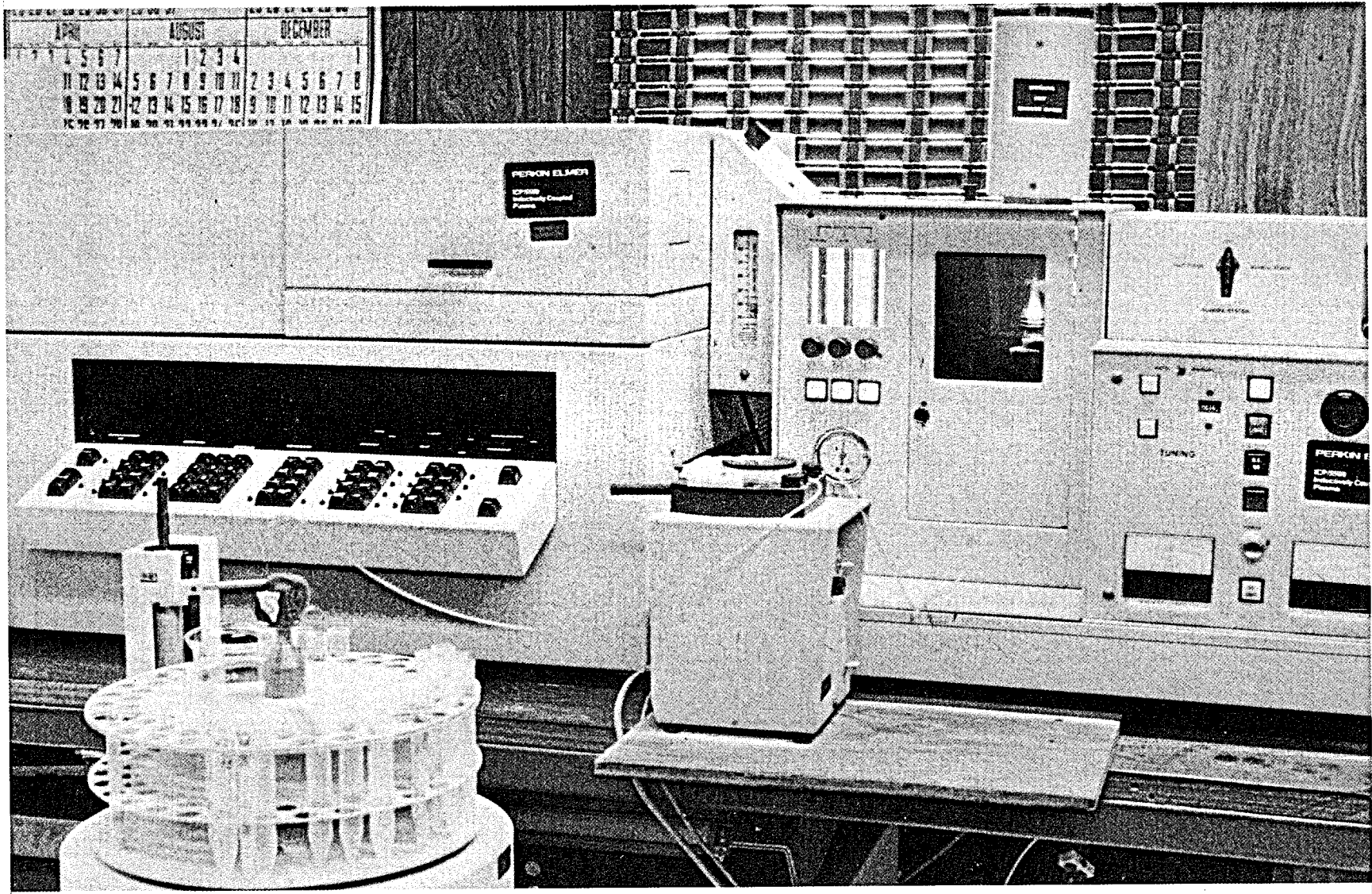


Fig. 15.
Perkin-Elmer Model ICP/5500 with inductively coupled plasma emission spectrometer.

TABLE IV
ICP ANALYSIS GROUPS

Element	λ (nm)	Usual Top of Range (ppm)
<u>Group One</u>		
Boron	249.77	100
Iron	259.94	3
Barium	455.40	3
Calcium	317.93 (>10 ppm) or 393.37 (<10 ppm)	100
Magnesium	279.08 (>10 ppm) or 279.55 (<10 ppm)	10
Strontium	407.77	10
Manganese	257.61	1
Samarium (internal standard)	359.26	20
<u>Group Two</u>		
Silicon	212.41	100
Molybdenum	202.03	1
Antimony	206.83	3
Zinc	213.86	1
Aluminum	226.92	3
Hafnium (internal standard)	196.38	50
<u>Group Three</u>		
Mercury	194.33	3
Selenium	196.03	3
Arsenic	193.70 and 197.20	10
Hafnium (internal standard)	196.38	50
<u>Group Four</u>		
Lanthanum (internal standard)	492.18	50
Sodium	589.00 (589.59)	low/300
Lithium	670.78	10
Potassium	679.90	100

no spectral interferences, was not present in the samples, and had a wavelength located between those of the other group elements. Samarium is added to each sample, standard, and blank to give a concentration equal to 20 ppm.

Group 2 consists of silicon, molybdenum, antimony, zinc, and aluminum with 50 ppm of hafnium as an internal standard. Total silicon is usually compared with the SiO_2 values obtained from the diluted SiO_2 sample aliquot, and therefore this diluted aliquot is used for total silicon. Using the diluted aliquot is especially important if the sample is collected at high temperatures since the silicon in the filtered acidified aliquot would polymerize and precipitate on cooling. Silicon is run using a special aluminum-oxide torch-tip accessory that gives a low background signal not possible with the usual quartz tip. Aluminum is run in the aqueous solution, and it represents total aluminum rather than the extracted monomeric form.

The elements in group 3, arsenic, mercury, and selenium, are analyzed together because the analytical wavelengths are all in the same spectral region. Although arsenic is the only element of this group normally found in the HDR geothermal water, mercury and selenium are also monitored. Arsenic is measured at two wavelengths as a check for possible spectral interferences since the signals for arsenic are relatively insensitive.

Although ICP emission spectroscopy is not usually recommended for the alkali metals because of low sensitivity, the concentrations of lithium, sodium, and potassium found in many geothermal samples are high enough to make the method useful. Difficulties encountered in analyzing these group 4 metals arise primarily because torch temperatures are too high for the easily ionized alkali metals. To avoid some of these difficulties and to increase sensitivity, group 4 is analyzed using reduced power to the torch. Since potassium is the most ionizable of the group, its sensitivity is the poorest, and occasionally samples with low potassium must be reanalyzed by atomic absorption. Sodium concentrations are usually high enough to require sample dilution.

D. Electrode Measurements

Five determinations are routinely made using electrode techniques. Direct measurements are made for dissolved oxygen, fluoride, and sulfide ions. Indirect methods using titration are used for carbonate/bicarbonate, or alkalinity determination. The analyses are done as soon as possible after collection. Because of sample instability, dissolved O_2 and $\text{S}^{=}$ are best

measured in the field. In field samples, electrode responses are routinely measured using portable instruments such as the Presto-Tek Model 550. In the laboratory an Orion Model 811 pH/millivolt meter with a Model 605 electrode switching unit (Fig. 11) is used. Combination electrodes are used when possible. The electrodes and meters are operated and maintained according to the instruction manuals and booklets furnished with the equipment.¹⁹⁻²¹

The dissolved oxygen (D.O.) content of water is measured on unfiltered samples using an Orion Model 97-08 oxygen electrode. Standardization is done on water-saturated air at barometric pressure, and the barometric pressure reading is used to calculate oxygen concentration levels. If the salt content of the sample is high, as it is in many geothermal fluids, a correction factor is applied as discussed in the electrode instruction manual and in the detailed procedure in Appendix E.²²

Sulfide ion, like dissolved O_2 , is also present in most geothermal fluids, especially at low pH where it combines to give H_2S . Relatively interference-free measurements of sulfide ion down to 0.1 ppm can be made using a sulfide electrode, Orion Model 94-16.²³ Before analysis, filtered unacidified samples and standards are stabilized with a high pH buffer containing a reducing agent to prevent oxidation of the S^{2-} to HS^- or H_2S as described in Appendix L. Most hot geothermal samples at Fenton Hill have a pH between 6 and 9 and therefore must be cooled, stabilized, and analyzed immediately after collection.

The determination of F^- is done using a special total ionic strength adjuster buffer (TISAB) to provide a constant background ionic strength, to decomplex fluoride, and to adjust solution pH. An Orion Model 94-09 electrode is used.²⁴

Ammonium cations are analyzed with an Orion Model 95-12 ammonia electrode²⁵ after the pH of the sample has been raised to above 10 to release ammonia gas. No interferences in the technique have been found with the geothermal samples; however, the analysis is done at room temperature to prevent water vapor from crossing the electrode membrane barriers and thus changing the concentration of the internal filling solution.

In addition to the measurement of fluoride, ammonium, sulfide, and dissolved oxygen by selective ion electrodes, certain other determinations are routinely done that require special electrodes or electrical probes. These

determinations are conductivity, oxidation-reduction potential (Eh), and pH. Because of sample instability, Eh and pH measurements (especially with dilute samples) are best done in the field using portable instruments; however, in the HDR loop systems, high temperatures and pressures prevent direct insertion of electrodes in production and injection lines. The best approximation to true in situ measurements in this case is measurements under reproducible conditions at reduced temperature and pressure. As with anion electrode methods, the instruments used are the Orion Model 811 pH/millivolt meter in the laboratory and the Presto-Tek Model 550 in the field.

Conductivity is measured on the Presto-Tek 550 using a 0 to 100,000 $\mu\text{mho/cm}$ range meter with a temperature compensation probe. The conductivity probe is calibrated by preparing standard solutions of known conductivity, measuring the specific conductivity, and setting the zero and gain on the instrument.

Oxidation-reduction potentials (Eh) are most valuable when readings are taken in the field or when electrodes are placed directly into the sample stream because the potentials are easily affected by pH, temperature, and oxidation by air. Determinations in the laboratory should be done immediately on unacidified samples before the sample changes. Standardization is done using quinhydrone-saturated pH buffers that are prepared daily.^{26,27} A direct reading of Eh in millivolts is obtained by setting the meter to the Eh value of the standard and comparing that reading with the millivolt reading obtained for the sample. In natural systems that are commonly dominated by multi-oxidation state species (e.g., O, C, N, S), which are not electroactive on the platinum electrode, Eh values measured may be far less than what is actually present in the system. In the HDR system, Eh is at best only an indication of general changes in the mixed potential, and therefore repeatability in the measuring techniques is vital.

Analyses for pH are done using standard methods (Ref. 13, pp. 460-465, and Ref. 28) either on the Orion Model 811 or on the Presto-Tek 550. Both instruments have probes for temperature correction, and standard buffer solutions are prepared and used for calibration.

E. Gas Analysis

At this laboratory most gases are analyzed by gas chromatography (GC); however, some gases, which may be present at levels not readily detected by GC, require special apparatus. For example, a special scintillation counter

measures radon and a special H₂S monitor detects H₂S at 10 ppm (H₂S is hazardous at concentrations down to 10 ppm). Although samples are collected for the analysis of carbon isotopes, the samples must be analyzed elsewhere because of the special equipment needed.

Two gas chromatographs are used for gas analysis (Fig. 16). The first is a Hewlett-Packard Model 5831A equipped with a thermal conductivity detector. In this GC sample introduction has been modified so that sampling bulbs containing gas samples collected at or below atmospheric pressure can be used. This instrument may also be used to separate and detect argon and helium. The second instrument (Fig. 17) is a Carle Model 111 H, Series S, which is a more portable instrument designed for natural gas analysis with hydrogen sulfide and hydrogen separation. This instrument routes the gas sample through different internal columns using a series of valves, thus making this GC much easier and quicker to use than the Hewlett-Packard system.

The Hewlett-Packard 5831A is controlled by a separate Hewlett-Packard Model 18850A terminal, which is capable of temperature programming and peak integration. This GC is used with two carrier gases, argon and helium, and two different stainless steel columns, a 15-ft x 1/8-in.-diam Molecular Sieve 5A (80 to 100 mesh) and a 15-ft x 1/8-in.-diam Poropak QS (80 to 100 mesh). The first set of analyses (Run 1) on a gas sample is done at low temperature (-40°C) using the Molecular Sieve 5A column with argon gas carrier to separate and detect H₂ and He. Temperature programming from 0°C to 295°C is used with the same column and helium carrier to separate and detect H₂, O₂, Ar, N₂, and CH₄ in the second analysis step (Run 2). For Run 3 the molecular sieve is replaced with the Poropak QS column, and it is used to analyze H₂, N₂, Ar+O₂, CH₄, CO₂, H₂S, and C₂H₆. This run is also done with temperature programming from 35°C to 100°C. A list of the parameter settings for each run is given in Table V. The settings are programmed into the GC terminal according to the instruction manual furnished with the instrument.²⁹

Besides the gases listed above, other gases such as CO, SO₂, and the oxides of nitrogen may also be separated and detected with slight modification and refinement of the parameters. Water may also be detected, but water vapor is usually removed before analysis with a cold trap, and results are reported on a dry gas basis.

The sample injection system for the Hewlett-Packard GC is a modification of a functioning system designed by A. H. Truesdell (US Geological Survey,

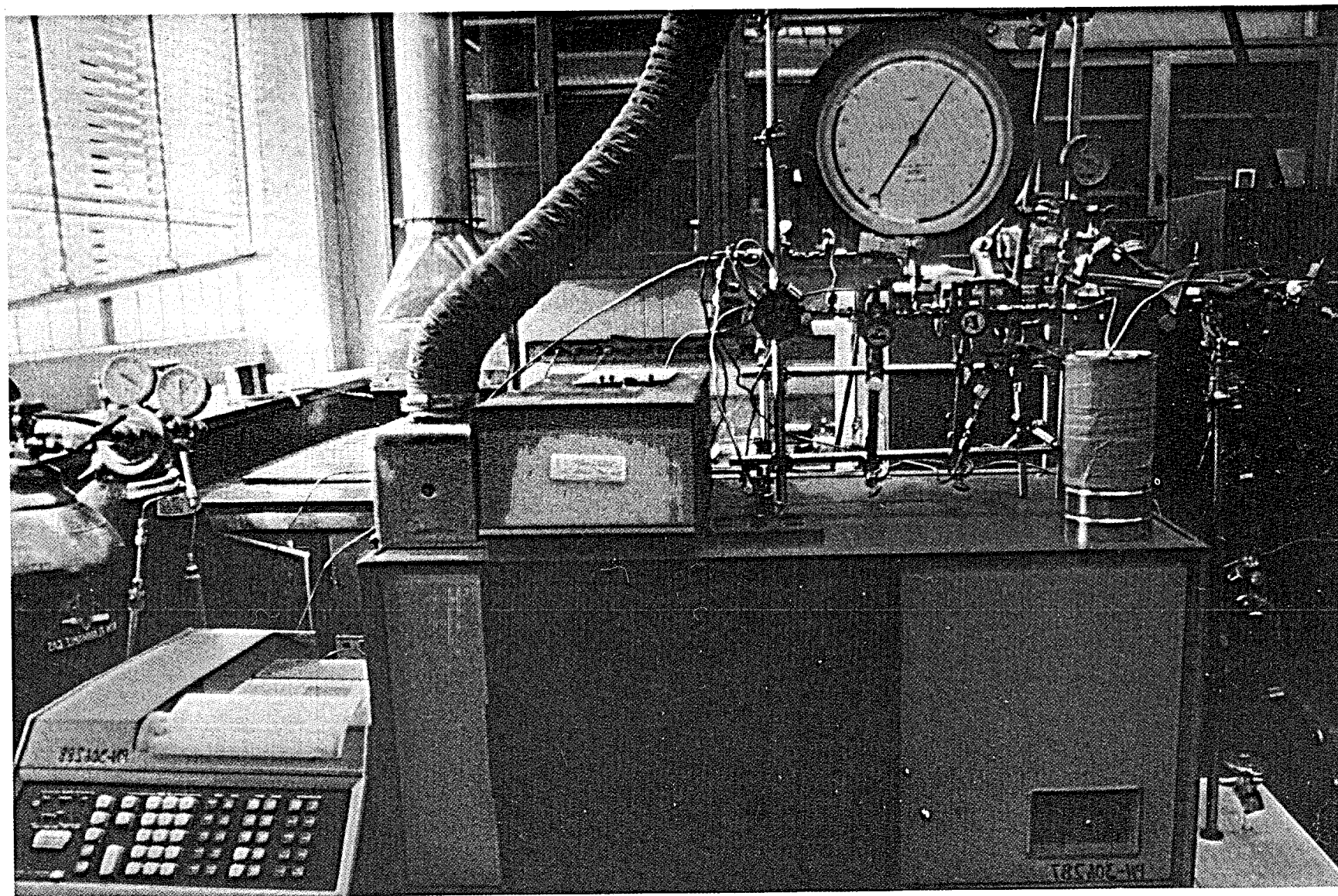


Fig. 16.

The Hewlett-Packard Model 5831A with the sample injection system (modified after the gas injection system used by A. H. Truesdell, USGS, Menlo Park).



Fig. 17.
Carle Model 111 H Gas Chromatograph.

TABLE V

PARAMETERS USED FOR THE THREE RUNS ON THE HP GAS CHROMATOGRAPH

Parameter	Run 1	Run 2	Run 3
TEMP 1	0	-40	35
TIME 1	5.0	3.5	7.0
RATE °C/m	30.0	0	20.0
TEMP 2	295	--	100
TIME 2	11.0	--	5.0
CHT SPD	0.50	0.50	0.50
ATTN 2	5	7	6
TCD SGNL	A	+B	A
SLP SENS	0.40	0.40	1.00
AREA REJ	200	200	250
OPTN	0	0	0
VLV/EXT	2 at time 0.1	2 at time 0.1	2 at time 0.1
VLV/EXT	-2 at time 0.2	-2 at time 0.2	-2 at time 0.2
SLP SENS	0.05 at time 12.0	(delete)	0.02 at time 3.0
INJ TEMP	100	50	100
TCD TEMP	250	200	200
OVEN MAX	300	300	225

Menlo Park, California). Basically, the system is composed of a vacuum system that uses a series of manual and automatic valves to inject small volumes of gas sample into the GC at reduced pressures. The injection pressures are adjusted using a piston cylinder with a manual crank that increases or decreases the pressure of the sample before injection. Details on the operation of the injection system and the Hewlett-Packard GC can be found in a report by Shevenell et al.⁵ The Hewlett-Packard system is calibrated using a tank of premixed standard simulating the composition of geothermal gas and a tank containing pure CO₂. The mixed standard is used for calibration with both columns and carrier gases, whereas the pure CO₂ is used only to calibrate the Poropak QS column, which is used primarily for CO₂. Room air is also routinely used as a standard to check peak retention time drift. Because of

the corrosive nature of the H₂S in the mixed standard, stainless steel tubing is used instead of copper in the system. Proper ventilation is also necessary.

Gas samples for the Carle Model 111 H are collected either automatically with gas sampling valves at a gas separator or manually at other locations in gas sampling bags or bottles. Samples are introduced into the GC by a series of computer-controlled valves that route the gas from a gas collection tank through a cold trap. Samples collected in bags or bottles are extracted through septums with a gas syringe and injected into the GC. In both cases an internal gas sampling valve in the Carle GC introduces a 1-ml gas sample into the carrier gas stream. If water vapor is present in the samples from the gas bags or bottles, a small cold trap with brine solution is used in front of the syringe. The Carle Model 111 H contains several columns and an internal valving system that routes the helium carrier stream through the columns to give maximum separation of sample components. The types of columns are listed in Table VI. These columns separate all the gases of interest except hydrogen, which is separated by a special hydrogen transfer system composed of a permeable metal tube. Hydrogen molecules flowing through the tube preferentially diffuse through the tube wall into a nitrogen stream that carries them to the detector. Since the gas chromatograph works at relatively low temperatures for the gases of interest (92°C), thermistor detectors are used rather than the optional thermal conductivity detectors.

Settings used for the GC are those recommended in the instrument manual.³⁰ The settings were determined in a factory calibration of the

TABLE VI

COLUMNS USED IN CARLE MODEL 111 H GAS CHROMATOGRAPH

Column 1A	7 ft - 15% SF96 on Porapak P 50/80
Column 1B	8 ft - 15% SF96 on (75% Porapak N + 25% Porapak QS) 50/80
Column 2	5 ft - Molecular Sieve 5A 42/60
Column 3A	4 ft - 20% Carbowax 1540 on Chromosorb T 40/60
Column 33B	8 ft - 15% SF96 on Porapak S 50/80
Column 4	6 ft - 8% OV-1001 on Chromosorb W AWMCS 80/100

instrument. Although the valve-switching sequence is the same, the mechanical switching motor supplied with the instrument has been replaced with programmable switching from the integrator used with the GC.

Analog chromatogram signals from the GC are integrated and processed to direct concentration readings using a Spectra-Physics Model SP4270 integrator. Calibration is done using either volume mixture standards or gas cylinders containing known gas mixtures. The volume standards are prepared by mixing known volumes of pure gases in a large gas sampling bag with a large "super" syringe. The mixtures in the cylinders are prepared either by mixing gases in the cylinder using partial pressures to estimate concentrations or by obtaining commercial standards. Mixtures prepared by partial pressures are standardized against volume mixture standards or against the commercial standards.

Since the Carle GC can only detect H_2S down to about 0.1% by volume, it is necessary to use a more sensitive method for H_2S measurements. This is done using an Ecolyzer Model 12 H_2S Analyzer with a 0- to 250-ppm range and a 0- to 50-ppm range. Gas samples are drawn into the analyzer by a pump in the Ecolyzer, and concentrations are read directly off the meter or on a recorder. The instrument is calibrated using standard gas cylinders that are purchased with the analyzer. H_2S is detected in the instrument by a catalytic cell, which detects down to 1 ppm by converting the H_2S into H_2SO_4 . Although the cell is subject to interferences by SO_2 and oxides of nitrogen, the SO_2 is eliminated by a filter supplied with the instrument, and nitrogen oxides are usually absent in geothermal samples. When NO and NO_2 are suspected, concentrations of the gases are determined by drawing known volumes of sample gas through $NO+NO_2$ detector tubes. Detector tubes designed to analyze H_2S are occasionally used when approximate H_2S determinations will suffice. Both types of detector tubes are manufactured by Draeger AG of West Germany and are purchased commercially.

Radon is measured in the gas from the Fenton Hill geothermal system to investigate any correlation between radon content in the gas and the surface area of the loop reservoir.³¹ Radon is counted automatically using a scintillation cell large enough and sensitive enough to count the gas directly without concentration steps. As with the GC analysis using the Carle 111 H, dry gas from the gas collection tank of the automatic sampler is fed

directly into the cell. To avoid contamination of the scintillation cell by particulate radium, a filter is placed on the intake of the cell.

In order to allow for buildup of radon daughter products in the cell and to establish detector equilibrium, the cell contents are counted 3 h after introduction of the radon. After the count, the cell is purged with the new gas, and another sample of this gas is collected for counting.

The counting system consists of an Eberline Model SAC-R5 scintillation cell with a 500-ml gas capacity attached to a Ludlum Model 2200 counter (Fig. 18). The system is calibrated using radon-222 generated from radium-226 contained in a radon generator manufactured by Pylon, Ltd., of Canada.^{32,33} The concentration of the radon entering the counting cell during calibration is controlled by the flow of carrier gas (nitrogen) through the radon generator.

F. Tracer Studies

Along with the usual complement of gas and water analyses, tracer studies involving dyes and radioactive isotopes have been used in the HDR project to determine residence times and reservoir volumes in the geothermal system. Although dyes are readily available and frequently used as tracers, the use of radioisotopes is limited to projects with access to short-lived isotopes.

Tracer experiments using soluble fluorescein dye have been very effective as a means of ascertaining flow paths and rates. However, this dye begins to decompose at 150°C, so its use at high temperatures is limited. Also, the dye must have a pH above 7 or the yellow-green fluorescence cannot be detected. Both sample and standards are buffered at the same pH, between 8 and 10 depending on the buffer system used. (If the pH goes too high, precipitation can occur in samples that contain minerals insoluble in alkaline solutions.) Acidifying samples eliminates the dye absorption and is used as a technique to differentiate between the dye and natural sample color. During dye tracer experiments the dye is injected into the system being tested, and samples from the system are analyzed spectrophotometrically or visually for the presence of the diluted dye. An absorption wavelength of 490 nm is used with a detection limit of 0.05 ppm.

The surface gamma-counting system at Fenton Hill (Fig. 19) is used primarily for bromine-82 tracer studies designed to obtain information during geothermal loop operation. For the HDR Phase I loop, a single-channel analyzer was used for gamma counting; however, a multichannel analyzer is now



Fig. 18.

The radon detection system consists of an Eberline Model SAC-R5 scintillation cell and a Ludlum Model 2200 counter/HV power supply.

available in the sampling trailer. The multichannel analyzer not only allows for the specific measurement of bromine-82 but also makes it possible to study other gamma emitters that may be present in the system simultaneously.

During operation, cooled circulation fluid from the production side flows at a controlled rate through a specially constructed counting vessel enclosed by lead shielding. This vessel is constructed of polyethylene and is in the shape of a Marinelli beaker with special taps to allow flow through the beaker. The counting vessel is designed to fit around the sodium iodide

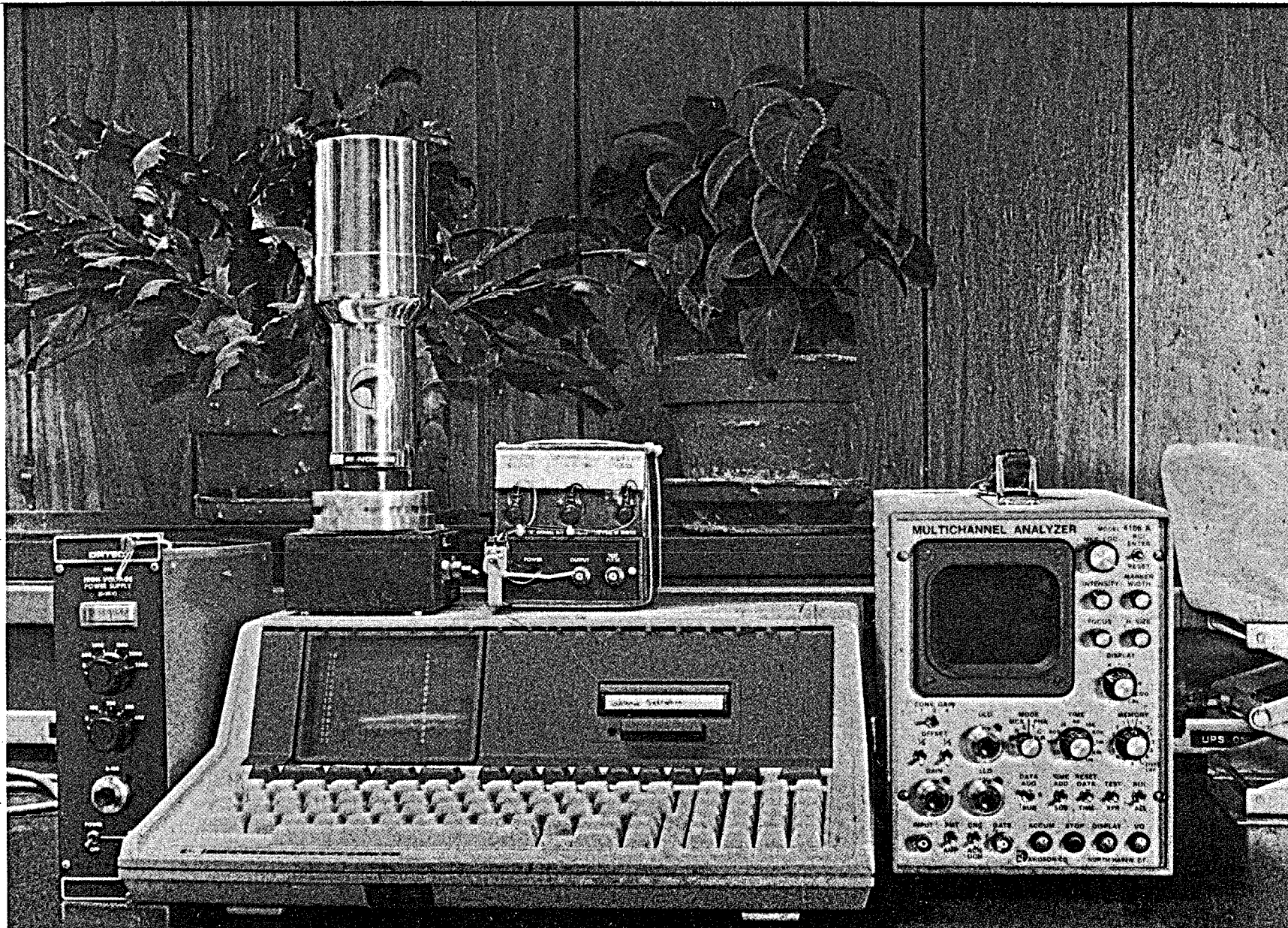


Fig. 19.
Gamma counter used for measuring bromine-82 tracer.

crystal of the gamma detector to optimize the efficiency of the counter by exposing a large liquid surface to the crystal. Another option is a cell enclosed inside the crystal that uses less volume but yields a much better counting efficiency. The flow of geothermal production fluid through the counting system is controlled by a series of by-pass valves and needle valves in the automatic sampling system.

Power to the crystals is supplied by an Ortec Model 456 High-Voltage Power Supply, and signals from the crystals are amplified before they enter the multichannel analyzer by an Ortec Model 113 Scintillation Preamplifier. The multichannel analyzer used is a Model 4106A Pulse Height Analyzer manufactured by the D. S. Davidson Company. It has 4096 channels and gives a visual display of the spectrum.³⁴

The entire system is calibrated by preparing a large volume of standard solution in a heated water bath at approximately 70°C and pumping the standard through the counting vessel. The solution is prepared by adding a known amount of gamma emitter (usually bromine-82) to a measured volume in the water bath to obtain the desired activity per unit volume. Once the system is calibrated with the flowing standard solution, the calibration may be checked more frequently by placing a gamma source containing cesium-147 on top of the crystals. If the counting efficiency remains the same for the solid cesium source, it is assumed that the electronics in the system are working properly. Any change in the cesium efficiency requires recalibration with the liquid standard. The spectral window of the multichannel analyzer is calibrated by placing an europium-152 source on the crystals and adjusting the gain setting to the known energy peaks.

IV. DATA MANAGEMENT AND REPORTING

Data from the instruments described above are entered into an IBM PC-AT using Lotus Symphony™ software and are stored on floppy disks. The Symphony™ software package has been programmed to automatically calculate charge balances as well as estimate reservoir temperatures from various geothermometers. Results of the analyses are printed from the disk.

ACKNOWLEDGMENTS

The authors would like to thank M. Jones and J. N. Gardner for their time and effort in processing and editing this report.

APPENDIXES A THROUGH M

DETAILED PROCEDURES

APPENDIX A

ALKALINITY

Principle of Method

This determination is based on the acid-base titration of carbonate and bicarbonate using standard sulfuric acid. In this procedure, the titration is done using an automatic titrimer that uses pH measurement to determine end points.

Sensitivity

The sensitivity of the method for the CO_3^{-2} and HCO_3^- end points is 1 ppm.

Interferences and Precautions

1. Samples to be tested should be covered and analyzed as quickly as possible.
2. Gentle stirring of the sample and standards is required.

Apparatus

1. Fisher Titrimeter II (Automatic FEP system)
2. Instruction Manual, Fisher Titrimeter II
3. Orion Ross Combination pH Electrode - Model 81-02
4. Magnetic Stirrer

Reagents

1. 0.1N H_2SO_4 solution - Standardized or obtained commercially
2. pH Buffers - pH 4 and pH 7

Standardization of Electrometer

1. Place a beaker containing pH 7 buffer on the stirrer, stir gently, and insert the pH electrode.
2. Move the function switch from STBY to the 0-14 position.
3. Adjust the meter to pH 7 with the standardization knob and return to STBY.
4. Repeat using the pH 4 buffer and adjust the slope control if necessary to give a pH of 4 on the meter.

Setting of Titrate Demand Module

1. Enter 8.3 for EP1 (end point 1) and 4.5 for EP2 (end point 2).
2. Ensure that all buttons at the bottom of the module are in the "out" position except the Burette button.
3. Set the Min. Delivery and the Proportioning Band controls to 50 and maximum scale, respectively. During a titration, the adjustment of these knobs is sample dependent since they control the titration rate. (See p. 77 in the instruction manual.¹⁰)

Sample Preparation

1. Place a 100-ml aliquot of filtered unacidified sample on the stirrer and insert the electrode and delivery tip into the solution. Turn the stirrer on.
2. Adjust the tip approximately 1/2 to 1/4 in. downstream from the electrode.

Sample Titration

1. Turn the Power switch to ON position on the Burette/Dispenser and set the mode switch to REM.
2. Press the Fill button and then turn the Electrometer Function switch to the pH 0-14 range.
3. Depress the desired EP button and release the Burette button on the Titrate Demand Module.
Note: If the initial pH reading is below 8.3, the light under the EP1 button will be on. If this happens, go to step 6.
4. Push the Start button on the Dispenser Module to begin titrating.
Note: The titration may be stopped at any time by depressing the Burette button or the Stop button on the Dispenser. Titration will resume when the button is released or the Start button on the Dispenser is pressed.
Note: The rate of titration can be increased by decreasing the Proportioning Band adjustment.
5. When the first end point is reached, the light under the EP1 button will turn On and the titration will stop. Record the number of milliliters required to reach the end point.
6. To titrate to the second end point (4.5), depress the EP2 button.

7. When the second end point is reached, the light under the EP2 button will turn on and the titration will stop. Record the total volume of acid used.
8. Depress the Burette button on the Titrate Demand Module and set the pH Function switch to STBY.
9. Press the Fill button and remove the electrodes from the sample. Wash them with deionized water and dry them carefully.
10. Insert the dry electrodes in a new sample and proceed as before.

Calculations

1. General formula:

$$\text{Alkalinity, ppm CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml of sample}}$$

Where A = total milliliters of acid used

N = normality of acid.

2. For most samples: N = 0.1 and ml of sample = 100. The formula can be simplified to ppm CaCO₃ = Ax50.
3. If the alkalinity is to be calculated in terms of OH⁻, CO₃⁻², and HCO₃⁻, Table A-I is used.

TABLE A-I
ALKALINITY RELATIONSHIPS

Result of Titration	OH ⁻ Alkalinity as CaCO ₃	CO ₃ ⁻² Alkalinity as CaCO ₃	HCO ₃ ⁻ Alkalinity as CaCO ₃
P = 0	0	0	T
P < 1/2T	0	2P	T - 2P
P = 1/2T	0	2P	0
P > 1/2T	2P - T	2(T - P)	0
P = T	T	0	0

$$P = (\text{EP1}) \times 50$$

$$T = (\text{EP2}) \times 50$$

Where (EP1) = milliliters needed to reach the EP1 value (8.3), the phenolphthalein end point.

(EP2) = total milliliters needed to reach the EP2 value (4.5), the methyl orange end point.

4. To convert from CaCO_3 alkalinity to CO_3^{-2} and HCO_3^- alkalinity, use the following formulas:

$$\begin{aligned} \text{mg/l } \text{CO}_3^{-2} &= \text{CO}_3^{-2} \text{ as } \text{CaCO}_3 \times 0.6 \\ \text{mg/l } \text{HCO}_3^- &= \text{HCO}_3^- \text{ as } \text{CaCO}_3 \times 1.22 \end{aligned}$$

Multiplication factors are derived using the following ratios:

$$\frac{\text{formula wt. } \text{CO}_3^{-2}}{\text{formula wt. } \text{CaCO}_3} = \frac{\text{mg/l } \text{CO}_3^{-2}}{\text{mg/l } \text{CaCO}_3}$$

$$\frac{\text{formula wt. } \text{HCO}_3^- \times 2}{\text{formula wt. } \text{CaCO}_3} = \frac{\text{mg/l } \text{HCO}_3^-}{\text{mg/l } \text{CaCO}_3}$$

For further information see Standard Methods, Ref. 13, p. 278.

APPENDIX B AMMONIUM ANALYSIS

Principle of Method

Ammonia gas produced by the addition of NaOH to a solution containing ammonium ion is detected by an electrode that uses a hydrophobic gas-permeable membrane to separate the sample solution from the electrode solution. Dissolved ammonia diffuses through the membrane until its partial pressure is the same on both sides of the membrane. In any given sample the partial pressure is proportional to the ammonium ion concentration. The ammonia inside the electrode causes an electrode potential that is then measured on a voltmeter.

Sensitivity and Accuracy

1. At the low range, <1 ppm, the detection limit is about 0.01 ppm.
2. At the high range using a 100-ppm top standard, the limit is about 0.1 ppm.

Interferences and Precautions

1. Heavy metals that form ammonium complexes will cause problems if the pH is <13 and the ammonium concentration is below 18 ppm; however, this problem is usually avoided with the addition of 10M NaOH.
2. Be sure samples, standards, and electrodes are at the same temperature to avoid dilution of the electrode internal solution by osmosis of water through the membrane.
3. Stir the samples and standards with a magnetic stirrer at the same rate during measurements and protect them from temperature change due to the stirrer by placing insulation material between the stirrer and beaker.
4. To minimize the loss of NH_3 , slightly acidified samples should be used, and they should be analyzed as soon as possible.
5. Narrow beakers should be used during measurement to avoid loss of NH_3 through the surface.
6. Keep all samples, standards, and reagents tightly covered to prevent contamination from NH_3 fumes in the air. Deionized water is especially susceptible, and it should be fresh.

Apparatus

1. Orion Model 95-12 Ammonia Electrode
2. Digital pH/mV Meter
3. Magnetic stirrer
4. 4-cycle semilogarithmic graph paper (if a computer program is not used)
5. Electrode instruction manual

REAGENTS

1. 10M NaOH - Dilute 40 g of reagent-grade NaOH to 100 ml in a volumetric flask or dilute 80 ml of commercial 50% NaOH solution to 100 ml with deionized water.
2. 1000-ppm NH_4 Standard - Dilute 0.2965-g reagent-grade NH_4Cl to 100 ml in a volumetric flask with deionized water or purchase commercially as 1000 ppm N (Orion #95-10-17).
3. pH 4 buffer solution - available commercially
4. Internal filling solution - Orion #951202

Procedure

1. Low-level measurement (<1 ppm)
 - 1.1 Dilute internal filling solution 1:10 with deionized water (see electrode manual for assembly instructions²⁵).
 - 1.2 Make a 10-ppm NH_4 standard from the 1000-ppm stock solution.
 - 1.3 Set up meter to read mV ABS using the NH_3 electrode. The electrode should rest at a 20° angle to prevent gas entrapment.
 - 1.4 Place electrode in pH 4 buffer for several minutes.
 - 1.5 Prepare standard curve as follows:
 - a. Place 100 ml deionized water in a narrow beaker. Stirring slowly add 1 ml 10M NaOH. Place electrode in solution and set meter to 0.000 mV when stabilized.
 - b. Add increments of the 10-ppm standard to the solution as outlined below. Record the electrode potential after each increment.

Volume Added (mℓ)	Resulting Conc. NH ₄ (ppm)
0.1	0.01
0.1	0.02
0.2	0.04
0.2	0.06
0.4	0.10
2.0	0.30
2.0	0.50

c. Plot on semilogarithmic paper the concentration (log axis) versus the potential (linear axis), or input the values into a semi-logarithmic-curve-fit computer program for calculation.

1.6 Run samples as follows:

- a. Place electrode in pH 4 buffer for several minutes.
- b. Place 100-mℓ sample in narrow beaker. Stirring at same rate as standards, add 1 mℓ 10M NaOH.
- c. Place electrode in solution at 20° angle. Wait for a stable reading and record the potential. Compare the potential to the calibration curve for ppm NH₄ in sample.
- d. Place electrode in pH 4 buffer between samples if there is any delay.

2. For samples containing 1- to 18,000-ppm NH₄

2.1 Use undiluted internal filling solution.

2.2 Make standard curve as follows:

- a. Prepare 100-mℓ standards containing 1 ppm, 10 ppm, and 100 ppm NH₄.
- b. Place electrode in 10-ppm standard. Add 1 mℓ 10M NaOH and set mV ABS reading to 0.000 when stable.
- c. Add 1 mℓ 10M NaOH to 1-ppm standard and record potential. Repeat with 100-ppm standard. (Reading for 100-ppm standard should be -57 ± 3 mV.)
- d. Plot concentration against mV reading as in low-level calibration.
- e. Recalibrate every 2 h.

2.3 Run samples by adding 1 mℓ 10M NaOH to 100 mℓ. Record potential and compare to standard curve.

2.4 Store electrode in 10-ppm NH₄ plus NaOH between readings.

Electrode Storage

1. For less than one week, immerse tip in 500-ppm NH_4 without NaOH.
2. For indefinite storage, disassemble and clean electrode - see pages 4 and 5 of electrode manual.²⁵

APPENDIX C
BORON ANALYSIS-AZOMETHINE METHOD

Principle of Method

This method is based on the light absorption by a yellow color complex formed when boron reacts with azomethine-H reagent in a special buffer solution.

Sensitivity and Accuracy

1. The range of the method depends on the type of cell used and the concentration range selected for the standards. For the cell usually used in this laboratory, the upper linear range is 10 ppm with a detection limit of 0.05 ppm.
2. Cells of 1-cm and 5-cm lengths are used to increase the sensitivity for trace boron levels.

Interferences and Precautions

1. In some cases the samples may exhibit color before or after the addition of buffer solution. To correct for this possible error source, blanks are prepared by adding 2.0 ml of fresh 1.0% ascorbic acid solution to a duplicate sample instead of the azomethine-H reagent. The absorbance reading from this blank is subtracted from the sample prepared with azomethine-H.
2. Ascorbic acid oxidizes readily resulting in a colored stock solution; therefore, the ascorbic acid should be prepared daily.
3. The azomethine-H reagent should also be prepared daily, but it may be used for up to a week if refrigerated or up to a month if frozen. Loss of sensitivity indicates a new solution must be prepared.

Apparatus

1. Spectrophotometer, Beckman Model 25 with sipper cell
2. Vials; polyethylene, 5-ml capacity with caps
3. Pipets: adjustable, with disposable tips, for preparing standards and transferring samples and reagents.

Reagents

1. Buffer solution; pH 5.0 to 5.5, prepared by mixing the following:
 - 1.1 500 g ammonium acetate
 - 1.2 30 g disodium EDTA
 - 1.3 800 ml deionized water
 - 1.4 250 ml glacial acetic acid
2. Azomethine-H solution:
 - 1.1 Dissolve 1.0 g ascorbic acid in 100 ml deionized water and add 0.45 g azomethine-H reagent (available from Pierce Chemical Co.).
 - 1.2 When azomethine is completely dissolved, the solution is ready for use or storage.
 - 1.3 Store the solution in a polyethylene container by refrigeration for one week or by freezing for one month.

Note: Upon thawing azomethine make certain that it has completely dissolved before use.

Preparation of Standards

1. Prepare a working standard by diluting a commercial stock solution (1000 ppm) to 10 ppm with deionized water and storing it in a plastic container.
2. Pipet 0, 0.20, 0.40, 0.60, 0.80, 1.00 ml of boron stock solution, respectively, into six plastic vials and pipet enough deionized water to bring the volume in each vial to 1.00 ml.
3. Add 2.0 ml of buffer immediately followed by 2.0 ml of azomethine-H solution.
4. Stopper the vials, shake the contents, and allow the color to develop for 30 minutes before reading on the spectrophotometer.

Note: The standards and samples should be prepared and read at the same time.

5. Set the Beckman spectrophotometer to the absorbance (ABS) mode and read the absorbance of the standards and samples at 420 nm.

Note: The zero setting for the spectrophotometer should be set using deionized water.

6. Prepare a calibration curve by plotting the absorbance readings of the standards, respectively, against the concentrations, 0, 2, 4, 6, 8, 10 ppm.

Note: A computer program to handle calibration curves may also be used.

Preparation of Samples

1. Pipet 1.00 ml of sample into a plastic vial and add 2.0 ml of buffer and 2.0 ml of azomethine-H solution.
2. At this point the sample preparation is identical to the method used for the standards.

Calculations

1. Boron concentrations are calculated graphically using the calibration plot or are done by computer using a linear regression program.

APPENDIX D CONDUCTIVITY

Principle of Method

A special probe is used to measure the conductivity of a sample solution between two standard electrical contact surfaces. The conductivity measured between the surfaces on the probe increases with the number of ionized species in the solution, thus giving an approximation of sample salinity.

Sensitivity and Accuracy

1. The resolution is 1 $\mu\text{mho/cm}$ (0-2,000 range), 10 $\mu\text{mho/cm}$ (0-20,000 range), and 100 $\mu\text{mho/cm}$ (0-200,000 range).
2. The accuracy (including temperature compensation) is $\pm 2\%$ of full scale.

Interference and Precaution

1. Inaccurate readings may result if the gold surfaces on the probe are coated with mineral deposits or organic materials.
2. If calibration of the probe indicates possible coating of the probe surfaces, clean the probe in a warm Alconox™ detergent solution and softly clean the probe with a cotton swab. Organics may be removed with alcohol and then detergent solutions.

Equipment

1. Conductivity meter, Presto-Tek Model 550
2. Probe with temperature compensator, Presto-Tek #85347

Reagents

All solutions must be made with A.C.S. reagent-grade chemicals using deionized or distilled water.

1. Calibration solution: 0.01M KCl (1410 $\mu\text{mho/cm}$), 0.1M KCl (12,900 $\mu\text{mho/cm}$), 1M KCl (111,900 $\mu\text{mho/cm}$).

Calibration

1. Connect the conductivity probe to connector #1 on the Presto-Tek Model 550. Rinse it in deionized water and dry it.
2. Turn the control switch to X1 μM .

3. Dip the clean probe in the 0.01M KCl solution and stir gently until all air bubbles are removed from the probe.
4. If the reading does not equal 1410, adjust pot R40 until the reading does give that value.
5. Again, rinse and dry the probe and dip it into the 0.1M KCl solution.
6. Turn the control switch to X10 μM and read the conductivity value.
7. If the reading is not 1290, adjust pot R39 to get that reading.
8. For the 0-200,000- $\mu\text{mho/cm}$ range, repeat the above steps with control switch at X100 using 1M KCl adjusted to 1120 on pot R38.

Conductivity Measurement

1. Connect the conductivity probe to the front panel of the Presto-Tek 550.
2. Rinse the probe with deionized water.
3. Insert the probe into the solution being tested, making sure that the probe is inserted to a depth of at least 4 cm. Gently move the probe up and down to remove air bubbles from the probe.
4. Turn the control switch to the X1 range and read the conductivity.
Note: If only the figure "1" is displayed on the left side of the display, a higher range must be selected. If necessary, increase the range of the control switch until a reading other than "1" is obtained.
5. Allow 10 s for the temperature compensation network to stabilize and multiply the reading by the setting on the control switch to calculate the conductivity of the solution in $\mu\text{mho/cm}$.

Manuals

1. Presto-Tek Corp., Instruction Manual for Presto-Tek Model 550, Presto-Tek Corp., 7321 N. Figueroa St., Los Angeles, CA 90041.
2. Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 14th Ed., 1975, pp. 71-75.

APPENDIX E
DISSOLVED OXYGEN IN WATER (ELECTRODE METHOD)

Principle of Method

The dissolved oxygen electrode consists of a pair of polarized silver electrodes and an electrolyte that is separated from the test solution by a gas-permeable membrane. Oxygen passing through the membrane reacts with the electrolyte causing a reaction at the anode. This reaction produces a signal proportional to the partial pressure of the oxygen outside the membrane. The temperature compensator and electronics in the electrode convert the partial pressure signal to readings in dissolved O_2 in ppm.

Sensitivity and Accuracy

With hourly calibration using an air standard within $10^\circ C$ of the samples, reproducibility is ± 0.05 ppm or 2% of the reading (whichever is larger) from 15° to $30^\circ C$.

Interferences and Precautions

1. Although the electrode has temperature compensation, extremes in temperature between the sample and standard will cause errors.
2. If samples have a high salinity, a correction must be made using the table in Appendix II of the Orion Model 97-08 oxygen electrode instruction manual (Ref. 22).

Equipment

1. Barometer
2. Dissolved Oxygen Electrode, Orion model 97-08
3. Digital pH/mV meter
4. Magnetic stirrer
5. BOD bottles - 300 ml (nominal) capacity

Reagents

1. Deionized H_2O : For air calibration of electrode and electrode storage.
2. Calibration solution, 5% Na_2SO_3 : Prepare by dissolving about 12.5 g of Na_2SO_3 in 250 ml of distilled water.

Procedure

1. Connect the electrode to the pH meter or turn the electrode selector switch on the Orion 605 Selector Switch (if available) to O_2 .
2. Turn the electrode mode switch to OFF and switch the pH meter to the pH mode.
3. Set the pH meter slope setting to 100% and calibrate the pH meter to give a reading of 7.00.
4. Turn the electrode mode switch to BT CK and read the pH meter. A reading of 13.00 or greater indicates that the electrode batteries are charged.
5. Turn the mode switch on the electrode to ZERO and use the zero calibration control knob on the electrode to give a pH reading of 0.00.
6. Insert the funnel that comes with the electrode into a BOD bottle that contains just enough deionized water to cover the bottom.

Note: Make sure that no water droplets are on the electrode membrane.

7. Turn the electrode mode switch to the AIR position and set the pH meter to read the prevailing barometric pressure (divided by 100) by adjusting the calibration control knob on the electrode.
8. Check the electrode by placing the funnel and electrode into a BOD bottle containing about 250 ml of 5% Na_2SO_3 solution and switching the mode selector knob on the electrode to H_2O . Stir the solution gently with the magnetic stirrer.

Note: If the electrode is working properly, the reading on the pH meter should be <0.1 ppm after 2-1/2 min. If not, see the instruction manual.

9. Turn the mode switch on the electrode to OFF and wash the funnel and electrode with deionized water.
10. Insert the cleaned funnel and electrode into the BOD bottle containing sample to be tested.

Note: The BOD bottle must be filled to the top when the sample is taken.

11. Stir the sample gently with the magnetic stirrer and turn the electrode mode switch to H_2O .
12. When the signal on the pH meter stabilizes, record the reading as ppm dissolved oxygen.

Note: For samples with high salinity (above 2 parts per thousand), a correction of the ppm value must be made according to the electrode instruction manual.

13. Turn the mode switch to OFF and slowly remove the electrode from the funnel. Wash the electrode with deionized H₂O.
14. To analyze another sample, repeat steps 9 through 14.

Note: After all the samples have been read, store the electrode in H₂O-saturated air by placing it and the funnel in a BOD bottle containing a small amount of deionized water at the bottom.

Manuals

1. Instruction Manual Orion Model 97-08 Oxygen Electrode
2. Instruction Manual Orion Model 811 Microprocessor pH/millivolt Meter
3. Instruction Manual Orion Model 605 Manual Electrode Switch

APPENDIX F

FIELD TEST KITS

Introduction

Occasionally, when geochemical analyses on water must be done quickly in locations where laboratory facilities are not available, portable field test kits are used. The kits used by this laboratory were purchased from the HACH Company, P.O. Box 389, Loveland, CO 80539. A listing of the kits and a brief description of the methods used with the kits are given. Detailed instructions on the procedures are included in the kits.

Method

1. Chloride Kit: Chloride is determined by a titration method that uses mercuric nitrate titrant to give a sharp yellow to pinkish-purple end point with diphenylcarbazone. The indicator and a pH buffer are added to the sample by emptying the contents of a small capsule into a measured volume of sample.
2. Dissolved Oxygen Kit: As an alternative to the electrode method for dissolved O_2 , this kit uses the Winkler titration method. In this titration method the sample is treated with manganous sulfate and alkaline-iodide-azide reagent to form an orange-brown precipitate. Sulfamic acid is added, which reacts with the iodide to release free iodine. The iodine is then titrated using a starch indicator with phenylarsine oxide (PAO). The PAO titrant is delivered with a special titrator supplied with the test kit, and the concentration of dissolved O_2 is directly proportional to the volume of titrant used.
3. Sulfate Kit: Sulfate is determined using a modification of the barium sulfate turbidimetric method. In this method a capsule of powder containing barium is added to the sample in a special reaction tube. The turbidity of the suspended precipitate formed if sulfate is present is estimated visually in a special reading tube furnished with the kit. The turbidity is correlated to the sulfate concentration in ppm.
4. Hydrogen Sulfide Test Kit: Where accuracy is not critical, this kit is used to determine H_2S in water. In this test an Alka-Seltzer tablet is used to bubble the dissolved H_2S from the sample onto a chemically

treated filter that changes color if H_2S is present. Concentrations are estimated by comparing the color to a color chart.

5. Sulfite Test Kit: In this method, the water sample is acidified, treated with a starch indicator, and titrated with a standard $KI-KIO_3$ solution. Sulfamic acid is added to remove nitrite interferences.

APPENDIX G
FLUORIDE-ELECTRODE MEASUREMENTS

Principle of Method

The fluoride electrode has a single-crystal lanthanum fluoride membrane and an internal reference. The membrane is an ionic conductor where only fluoride ions are mobile. Measurements are based on the development of a potential across this membrane when it is in contact with a solution containing free fluoride ions. This potential is compared to a constant external reference potential.

Sensitivity and Accuracy

1. Range - 0.02 ppm to saturated solutions
2. Reproducibility - 2%

Interferences and Precautions

1. No critical interferences are present if solutions are buffered with the HACH reagent listed before measurements are made.
2. Electrode response is usually 99% in 1 min with concentrations greater than 0.5 ppm. Response time is slower at lower concentrations.
3. Stir solutions constantly while reading.
4. Standards and solutions should be at room temperature.
5. Restandardize every hour.
6. Rinse electrode with deionized water and dry between solutions.

Equipment

1. Orion Model 811 pH/millivolt meter with electrode selector switch
2. Orion Fluoride Electrode Model 94-09
3. Reference electrode
4. Magnetic stirrer

Reagents

1. Fluoride standards - 1 and 10 ppm
2. HACH Fluoride Adjustment Buffer Pillow

Fluoride Measurement

1. Add contents of HACH Buffer Pillow to approximately 20 ml of 1-ppm standard and stir.
2. Place electrodes in solution, turn channel switch to channel activating the F^- electrode, turn mode switch to mV, and depress push button to set 1-ppm standard at 000.0. Return to STD BY.
3. Add HACH Buffer to approximately 20 ml of 10-ppm standard and stir. Place electrodes in solution, set mode switch to mV, and record mV reading of 10-ppm standard. Return mode switch to STD BY.
4. Add HACH Buffer to approximately 20 ml of a sample and stir. Follow directions in step above to obtain the mV reading for the sample.
5. Calculate F^- concentration as follows:

$$F^- \text{ ppm} = 10^{(mV \text{ sample}/mV \text{ 10 ppm})}$$

Example: The value for the 10-ppm fluoride standard was -56.3 mV. A sample gave a value of -40.3 mV.

$$F^- = 10^{(-40.3/-56.3)} = 5.2 \text{ ppm}$$

Manuals

1. Instruction Manual Orion Model 811 Microprocessor pH/millivolt Meter
2. Instruction Manual Orion Model 605 Manual Electrode Switch
3. Instruction Manual Orion Model 94-09 Fluoride Electrode

APPENDIX H
MONOMERIC ALUMINUM EXTRACTION PROCEDURES

Principle of Method

Soluble Al in a filtered water sample is complexed with 8-hydroxyquinoline, and the organic complex is extracted into methyl isobutyl ketone at an adjusted pH of 8.3. The extraction is performed at the sampling location, and an aliquot of the organic phase is stored for subsequent Al analysis.

Sensitivity

A 500-ml sample extracted into a 20-ml organic phase has a sensitivity of 0.2 µg/l. At a working range of 20 µg/l, the relative standard deviation is ±2.4%.

Interferences and Precautions

1. Incomplete recovery of Al⁺³ may be encountered if the Fe⁺³ concentration is greater than 1 ppm. This condition is indicated by the formation of a greenish-black precipitate that forms with 8-hydroxyquinoline as the pH is raised. Reduction of Fe⁺³ to Fe⁺² as noted in the procedure eliminates the interference.
2. To prevent recovery losses due to the formation of aluminum fluoride complexes and insoluble aluminum hydroxides, the extraction is carried out above pH 8.
3. A pH below 8.5 is used to prevent the formation of Mg and Ca hydroxyquinolates.
4. The 8-hydroxyquinoline reagent loses its extracting capacity with time. It should be refrigerated between uses and new reagent prepared weekly.
5. If only the fast reacting monomeric forms of Al are to be determined, the extracting step must be done quickly after adding the 8-hydroxyquinoline. Excessive contact with the less reactive Al forms will convert them to the monomeric form.

Apparatus

1. Filtering equipment with 0.45-µm filters
2. 500 ml graduate
3. pH meter or pH paper with 3-5 and 7-9 ranges

4. Organic phase extractor made by attaching a disposable pipet tip to a rubber bulb
5. Sample bottles: narrow mouth, flexible-wall Nalgene, 500 mL capacity
6. Glass vials: approximately 25 mL capacity with plastic caps
7. Pipets with delivering capacities of 2, 5, and 20 mL, with disposable tips.

Reagents

All reagents must be A.C.S. reagent-grade quality and all dilutions made with deionized water. Aqueous solutions should be stored in polyethylene bottles except the 8-hydroxyquinoline, which is stored in amber glass.

1. 8-hydroxyquinoline (8-quinolinol) solution, 5%. Dissolve 5 g of 8-hydroxyquinoline in 10 mL of glacial acetic acid and dilute to 100 mL.
2. Phenol red indicator solution. Dissolve 0.1 g phenol red (phenolsulfonephthalein) in 28 mL of 0.01N NaOH and dilute to 250 mL with water.
3. Metal-free ammonium hydroxide (approximately 10M). Place a 1-L polyethylene bottle containing about 756 mL of water into an ice bath. Bubble ammonia gas through the water until the volume increases to 1 L or until the specific gravity measured by a hydrometer is 0.929 g/cm^3 .
4. Buffer solution. Add 223 mL of 10M metal-free NH_4OH and 115 mL of glacial acetic acid to approximately 500 mL water. Adjust the pH to 8.3 with 10M NH_4OH or glacial acetic acid. Dilute to 1 L with water.
5. Methyl isobutyl ketone (4-methyl pentanone-2)--MIBK.
6. Hydroxylamine hydrochloride solution, 20%. Dissolve 20 g hydroxylamine hydrochloride in water and dilute to 100 mL.
7. Phenanthroline-1,10 solution, 1%. Dissolve 1 g phenanthroline-1,10 in water to which a few drops of concentrated hydrochloric acid have been added and dilute to 100 mL with water. Warming and stirring the solution will help dissolve the phenanthroline-1,10.
8. Hydrochloric acid. Concentrated solution.

Procedure

1. Transfer 500 mL of filtered sample into a Nalgene bottle that has been rinsed with the fluid being sampled. Add 10 drops phenol red and mix.
2. Add 2 mL of the 8-hydroxyquinoline solution and mix.

3. Add 10M NH_4OH drop by drop until the entire solution turns pink. (pH should be 8 to 8.5 and can be checked with pH paper.)

Note: If a greenish-black precipitate forms as the NH_4OH is added, the sample probably contains excessive Fe^{+3} and must be treated as follows: (1) collect a new 500-ml sample as in step 1; (2) add 5 ml of 20% hydroxylamine hydrochloride solution and mix; (3) add 5 ml of 2% phenanthroline-1,10 solution and mix; (4) adjust pH to 4 with HCl or NH_4OH and let stand for 30 min; (5) add 2 ml of 8-hydroxyquinoline solution as in step 2; (6) adjust the pH from 8 to 8.5 with NH_4OH using pH paper or a meter to make measurements (A red color usually develops during the 30-min wait preventing use of the phenol red indicator); and (7) proceed to step 4.

4. Add 5 ml of buffer solution and mix.
5. Add 20 ml of MIBK and shake vigorously for exactly 20 s. Allow phases to separate.
6. Gently squeeze the sample bottle forcing the organic phase into the bottle neck. Extract as much of this phase as possible using a clean pipet tip and a rubber bulb.
7. Store organic phase in a tightly sealed 25-ml glass vial and refrigerate to preserve until analysis.

APPENDIX I
OXIDATION REDUCTION POTENTIAL OR Eh

Principle of Method

The oxidation-reduction potential (ORP) is the emf difference developed between the ORP metallic-indicating electrode and a constant voltage reference electrode.³⁵ When this millivolt difference is between the ORP electrode and a normal hydrogen electrode, it is called the Eh. Direct Eh measurements as discussed here can be used to determine the oxidizing or reducing capability of a solution.

Sensitivity and Accuracy

1. The sensitivity is dependent on the millivolt range of the pH meter.
2. Unless the chemical systems in a solution are in equilibrium, the ORP is time dependent. Immediate or in-line readings will not be the same as later off-line readings.

Interferences and Precautions

1. Though the ORP of a solution is usually not subject to other chemical interferences, it is affected by pH and temperature. Handle samples so neither of these factors is changed.
2. Sample readings will drift. Therefore, set a cutoff time equal to the time needed for the standard solution reading to stabilize.
3. If electrode poisoning is suspected, the tip may be cleaned with a mild abrasive powder (Ajax), or it may be soaked 1 min in warm (70°C) aqua regia (1 part concentrated HNO₃ to 3 parts concentrated HCl).
4. Wash electrode in deionized water and dry between solutions.

Equipment

1. Model 811 pH/millivolt meter with electrode switch
2. Orion combination platinum redox electrode
3. Magnetic stirrer
4. ATC probe

Reagents

1. Standardizing solution. Add a few crystals of quinhydrone to either pH 4 or pH 7 buffer. Prepare daily.

Eh Measurement

1. Place electrode and ATC probe in approximately 20 ml of standard solution. Set channel dial on electrode switch to position designated for Eh readings. Turn on calibration potential switch at rear of switching device.
2. Turn mode switch on meter to TEMP and record solution temperature. Turn mode switch to mV and set to appropriate millivolt reading using calibration dial for the Eh electrode on the switching device. Refer to chart below for the setting. Return to STD BY.

Buffer pH	4			7		
Temperature, °C	20	25	30	20	25	30
Eh, mV	467	462	457	291	287	278

3. Place electrode in the sample. Turn mode switch to mV and record Eh value from display. Report reading as Eh, mV.

Manuals

1. Instruction Manual Orion Model 811 Microprocessor pH/millivolt Meter
2. Instruction Manual Orion Model 605 Manual Electrode Switch
3. Instruction Manual Orion Platinum Redox Electrode Model 97-78
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APPENDIX J
pH MEASUREMENTS

Principle of Method

The pH of a solution is determined by measuring the potential created by the movement of hydronium ions across a glass membrane.

Sensitivity and Accuracy

1. Range - 1 to 14 pH units
2. Accuracy - 0.05 pH units between 0° and 100°C using automatic temperature compensation.

Interferences and Precautions

1. Measurements should be made as soon as possible before dissolved gases are lost.
2. Sodium will be an interference with some glass electrodes when samples have a pH greater than 12.
3. Stir samples and standards at same rate with minimum surface disturbance.
4. Keep samples closed before reading.
5. Take reading as soon as the sample is stabilized (approximately 1 min).
6. Wash electrodes with deionized water and dry carefully between samples.

Equipment

1. Orion Model 811 pH/millivolt Meter
2. Orion Ross combination pH electrode²⁸
3. Automatic temperature compensation probe
4. Magnetic stirrer

Reagents

1. Standard pH buffers

pH Measurement

1. If problems occur while installing the meter or during its operation, refer to the equipment or electrode manuals.

2. With mode switch in STD BY, immerse electrode and ATC probe into pH 7 buffer. Turn switch to pH/7.00 setting and set pH by depressing push button to the right of the mode switch. Return to STD BY.
3. Place probes in pH 4 buffer (pH 10 for alkaline samples). Turn switch to pH/4.01 (pH/10.01 if pH 10 buffer is used) and depress push button. Return to STD BY.
4. Place probes in a fresh sample. Reading may be taken in either of the modes used for standardization.

Manuals

1. Instruction Manual Orion Model 811 Microprocessor pH/millivolt Meter
2. Instruction Manual Ross™ Combination pH Electrode Model 81-02

APPENDIX K SILICA ANALYSIS

Principle of Method

The addition of ammonium molybdate to silica forms a molybdenum silicate compound that absorbs light at 400 nm.

Sensitivity and Accuracy

For most water samples a sensitivity of ± 1 ppm is adequate. If greater sensitivity is needed, up to 10 ml may be mixed with the color reagent, and a larger cell may be used.

Interferences and Precautions

1. Samples and standards should always be prepared in the same manner and at the same time.
2. Duplicate or preferably triplicate standards should be used to set the calibration curve.
3. If a SiO_2 dilution was not made during sample collection, the filtered acidified aliquot should be used. For low-level SiO_2 (75 ppm), this aliquot is preferable to the SiO_2 dilution.
4. Glassware must not be used for sample or reagent storage.

Apparatus

1. Spectrophotometer, Beckman Model 25 with sipper microcell.

Reagents

1. Ammonium molybdate reagent. Dissolve 100 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in deionized water and dilute to 1000 ml with deionized water while gently stirring. Adjust to pH 7 to 8 with NaOH or NH_4OH and store in a polyethylene container.
2. Sulfuric acid solution (1N). Dilute 27 ml of concentrated H_2SO_4 to 1000 ml.
3. Color reagent. Mix 20 ml of ammonium molybdate reagent with 50 ml of the prepared 1N H_2SO_4 solution and dilute to 500 ml in a polyethylene volumetric flask. The color reagent is unstable and must be remade every three days.

4. Silica standard, SiO_2 . 1000 ppm, purchased commercially.

Procedure

1. Turn on the spectrophotometer, set it on the CONC mode, adjust the wavelength dial to 400 nm, and set the sipper cell setting to 7. Allow 20 min for the lamp to warm up.
2. Prepare a set of standards with a top concentration slightly higher than that of the expected samples by making the appropriate dilution of the 1000 ppm SiO_2 standard.
3. With the expected sample range and the table below to determine the aliquot sizes to be tested, pipet equal amounts of standards and samples into mixing tubes.

<u>Range of Top Std. (ppm)</u>	<u>Amount of Std. or Sample Used (ml)</u>
250	200
100	500
50	1000

4. Add 10 ml of color reagent to each tube and mix thoroughly. Wait 10 min.
5. The color reagent will serve as the blank for this procedure. Flush and fill the sipper cell with blank for two cycles and adjust the base line to read 0000.
6. Similarly, fill the sipper cell with standard and set the CONC CALIB knob to the chosen concentration of the standard.
7. When the spectrophotometer is calibrated, fill the sipper cell with the samples using the above procedure. Readings will be given directly in ppm for each sample.
8. If any samples give readings above or far below the top standard setting, reanalyze the sample using another standard.
9. When the analysis is complete, flush the sipper cell with deionized water and turn off the spectrophotometer.

APPENDIX L
SULFIDE ANALYSIS (COLORIMETRIC)

Principle of Method

This method is based on the reaction of sulfide, ferric chloride, and dimethyl-p-phenylenediamine under conditions that produce methylene blue dye. Ammonium phosphate is added to remove the color of the ferric ion, and the absorption of the dye is measured on a spectrophotometer at 625 nm. The calibration curve for the spectrophotometer is constructed from methylene blue standards whose color intensities have been standardized against the color produced by a known sulfide standard.

Sensitivity and Accuracy

1. The sensitivity of the method with a sipper cell is about 0.02 ppm, but sensitivity can be improved by using larger cells.

Apparatus

1. Sample bottles: Nalgene or glass - 100 ml and 60 ml capacity
2. Spectrophotometer: Beckman Model 125 with sipper cell
3. Test tubes: 15 ml capacity
4. Volumetric flasks: 10 ml capacity
5. Pipets: Adjustable, with disposable tips for preparation of standards and for transferring samples and reagents.

Reagents

All chemicals must be A.C.S. reagent-grade quality, and all dilutions must be made with demineralized water.

1. Aluminum chloride, 6N. Dissolve 100 g of $AlCl_3 \cdot 6H_2O$ in 144 ml of deionized water.
2. Amine-sulfuric acid stock solution. Dissolve 6.75 g of fresh N, N-dimethyl-p-phenylenediamine oxalate in a cold mixture of 5 ml of deionized water and 12.5 ml of concentrated sulfuric acid in a 25-ml volumetric flask. Cool and dilute to 25 ml with deionized water. Store in a dark glass bottle.

3. Amine-sulfuric acid reagent: Dilute 2.5 ml of amine-sulfuric stock solution to 100 ml with 1:H₂SO₄ in a volumetric flask. Store in a dark glass bottle.
4. Diammonium hydrogen phosphate solution. Dissolve 40 g of (NH₄)₂HPO₄ in 80 ml of deionized water.
5. Ferric chloride solution. Dissolve 50 g of FeCl₃ · 6H₂O in 20 ml of deionized water.
6. Methylene blue stock solution. Dissolve 0.2500 g of certified (83%) methylene blue dye in 250 ml of deionized water. Store the dye solution in a glass container.
7. Sodium hydroxide, 6N. Dissolve 24 g of NaOH to 100 ml with deionized water. Store in a plastic bottle.
8. Standard sulfide solution, 100 ppm.
 - 8.1 Wash several grams of Na₂S · 9H₂O in a beaker with deionized water and wipe the excess water off the crystals with a clean paper towel.
 - 8.2 Make a 100-ppm sulfide solution by dissolving 0.7492 g of the Na₂S · 9H₂O salt in 1000 ml of deionized water.

Note: This solution is very close to 100 ppm sulfide, but the exact concentration can be determined using an iodine titrimetric method (1). This solution is unstable and should be prepared immediately before use.
9. Sulfuric acid solution, 1:1. Carefully add 20 ml of concentrated H₂SO₄ to 20 ml of deionized water and store in a plastic bottle.
10. Zinc acetate, 2N. Dissolve 22 g of Zn(C₂H₃O₂) · 2H₂O in 87 ml of water and store in a plastic bottle.

Preparation and Standards

1. Methylene blue standard.
 - 1.1 Pipet 0.000, 0.100, 0.250, and 0.500 ml of freshly prepared sulfide stock solution into four clean 10-ml volumetric flasks and dilute to the mark with deionized water.
 - 1.2 Transfer the contents of each flask into test tubes labeled 0, 1, 2.5, and 5 ppm, respectively.
 - 1.3 Add 0.5 ml of amine-sulfuric acid reagent to each test tube followed by 0.1 ml of FeCl₃ solution.
 - 1.4 Cap each test tube and invert each one to mix the contents.

- 1.5 After 3 min remove the caps and add 0.5 ml diammonium phosphate solution.
- 1.6 Replace the caps, again invert the tubes to mix the contents, and after 5 min read the absorbance of the solutions at 625 nm on the spectrophotometer.
- 1.7 Fill three 10-ml volumetric flasks with approximately 9.5 ml of deionized water and add methylene blue stock solution in 0.050-ml increments to each until the blue color intensities match the color obtained for 5-ppm sulfide.
- 1.8 Calculate the sulfide equivalent in the three dye solutions from a calibration curve constructed from the absorbance readings of the sulfide standards and find the average.

Note: For the dye solution used at Fenton Hill, 0.300 ml of dye solution in 10 ml water is equivalent to the color intensity obtained for 4.31 ppm sulfide.

Preparation of Calibration Curve

1. Pipet 0.000, 0.100, 0.200, and 0.300 ml of methylene blue stock solution into four test tubes labeled 0.00, 1.44, 2.87, and 4.31 ppm, respectively.
2. Add enough deionized water to bring the total solution to 10 ml and repeat steps 1.3 to 1.6 except use 1:1 sulfuric acid solution instead of the amine-sulfuric acid reagent.
3. Use the absorbance readings for the above dye standards to construct a calibration curve of absorbance versus concentration.

Note: Absorption readings for the dye standards should be taken at the same time the samples are read.

Separation of Soluble and Insoluble Sulfides

Note: This procedure is to be used on an unfiltered sample that contains suspended solids.

Note: H_2S is considered an insoluble sulfide.

1. Add 0.20 ml of 6N NaOH solution to a 100-ml glass sampling bottle and fill the bottle with sample (pH 6 to 9).
2. Add 0.20 ml of 6N $AlCl_3$ solution and stopper the bottle so that no air bubbles are under the stopper.

3. Rotate the bottle back and forth about its transverse axis vigorously for at least 1 min to flocculate the contents.
4. Let the precipitate settle and decant the pure supernatant into a 60-ml sampling bottle that contains 0.100 ml of 2N zinc acetate.

Note: Do not wait longer than necessary before removing the supernatant.

Sample Pretreatment

1. Put 0.100 ml of 2N zinc acetate solution into a 60-ml glass bottle and fill the bottle with fresh sample or with supernatant from the above procedure.
2. Add 0.100 ml of 6N NaOH (or enough to bring pH above 9) and stopper the bottle with no air bubbles.
3. Let the resulting precipitate stand for at least 30 min before separating the precipitate for analysis.

Note: This pretreatment may be necessary if the samples cannot be analyzed immediately. The treated sample is relatively stable and can be stored for several hours unless iron is present. Iron causes fairly rapid oxidation of the sulfide.

Sample Analysis (Methylene Blue Method)

1. If pretreatment has been done on the sample, pour off as much supernatant as possible and replace with an equal volume of deionized water. Shake the bottle to resuspend the precipitate and transfer 10 cm³ of the suspension into a test tube.
2. If no pretreatment is done, transfer 10 cm³ of sample directly into a test tube.
3. Treat the samples as outlined in Preparation and Standards steps 1.3 to 1.6.
4. Determine the concentration in the samples from the calibration curve obtained from the methylene blue dye standards as outlined in section on Preparation of Calibration Curve.

Manuals

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APPENDIX M

SULFIDE ANALYSIS (ELECTRODE)

Principle of Method

This method is based on the measurement of the electrode potential between a solution containing sulfide ion and a silver sulfide membrane. Before measurement the sulfide in solution is stabilized with a high pH buffer containing a reducing agent to prevent oxidation of S^{2-} to HS^- or H_2S .

Sensitivity and Accuracy

1. The sensitivity of the method under normal operating conditions is 0.1 ppm.
2. Although the method is not as sensitive as the methylene blue colorimetric method, the electrode method is better suited for turbid solutions.

Interferences and Precautions

1. Extremes in pH will cause erroneous readings; however, no problems are encountered from pH 2 to pH 12.
2. Samples and standards should be at room temperature before reading.

Equipment

1. Sulfide electrode, Orion model 94-16
2. Digital pH/mV meter, with electrode selector switch
3. Reference electrode, Orion model 90-02 double junction
4. Magnetic stirrer
5. Graph paper, 4-cycle semilog (computer program may also be used)
6. Burette or HACH titrator

Reagents

1. SAOB II solution. Place about 600 ml of deionized, deaerated water, 200 ml of 10M NaOH, 35 g ascorbic acid, and 67 g disodium EDTA in a 1-l flask and dilute to volume. Store in a tightly stoppered bottle to prevent oxidation. If the solution becomes dark brown, discard.
2. Lead perchlorate solution, 0.1M: Use either a gravimetric standard prepared by dissolving lead perchlorate in water or a commercially available standard (Orion Cat. No. 948206).

3. Sulfide Standards. Prepare a stock solution of saturated Na_2S (approximately 133,000 ppm S^{-2}) by dissolving approximately 100 g $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 100 ml of deionized, deaerated water. Store in a tightly stoppered bottle. Prepare a sulfide standard by pipetting 5 ml of the stock solution into a 500-ml volumetric flask, adding 250 ml of SAOB II solution, and diluting to the mark with deionized, deaerated water. Calibrate the standard weekly (approximately 1330 ppm S^{-2}) by titrating with 0.1M lead perchlorate standard as follows:

3.1 Pipet exactly 10 ml of S^{-2} standard into a 50-ml beaker and add about 20 ml of deionized water.

3.2 Insert the sulfide and reference electrodes into the beaker and stir the solution slowly with the magnetic stirrer.

3.3 Set the selector switch on the pH/mV meter to the S^{-2} channel and activate the calibrate adjustments by turning on the battery power switch. (For Orion Model 605, this switch is in back.)

3.4 Set the pH/mV meter to read millivolts and adjust the calibration dial to read -10.0 mV.

3.5 Titrate the sulfide solution with 0.1M lead perchlorate solution using the electrode reading inflection point as the end point (9.2 mV).

3.6 Calculate the concentration of the sulfide standard (C) from the volume (V) of lead standard used to reach the inflection point.

$$C = 320.6 V$$

$$C = \text{ppm sulfide (approximately 1330 ppm)}$$

Sulfide Measurement

1. Prepare three calibration standards by adding appropriate (depending on range of samples) amounts of sulfide standard to 50-ml volumetric flasks containing 25 ml of deionized water and adding SAOB II solution to the mark.

Note: Each standard will represent a concentration that is equal to twice the actual dilution. Example: a standard diluted to 10 ppm will represent 20 ppm in the calibration.

2. Set the pH/mv meter to STD BY and turn off the battery power to the calibrate dials.

3. Place the electrodes in the most dilute standard, set the meter function switch to MV and stir this sample gently. Wait for a stable reading and

set this reading to 0.00. (Press the white button on the Orion Model 811 pH/mV meter.)

4. Set the meter in the standby mode, rinse and blot dry the electrodes, and then measure the potential for the mid-range standard. Record the reading.
5. Repeat the measurement for the high standard and record the reading.
6. Prepare a calibration curve by plotting the millivolt readings (linear axis) against the concentration (log axis) on standard semilog paper or enter the values into a computer programmed to handle semilog plots.
7. Analyze the samples by transferring 25 ml of sample and 25 ml of SAOB II into a beaker and measuring the millivolt potential in the same way the standards were measured.
8. Calculate the sulfide in the samples either by using the calibration plot or by entering the reading in the computer.
9. Check the calibration every 2 h.

Manuals

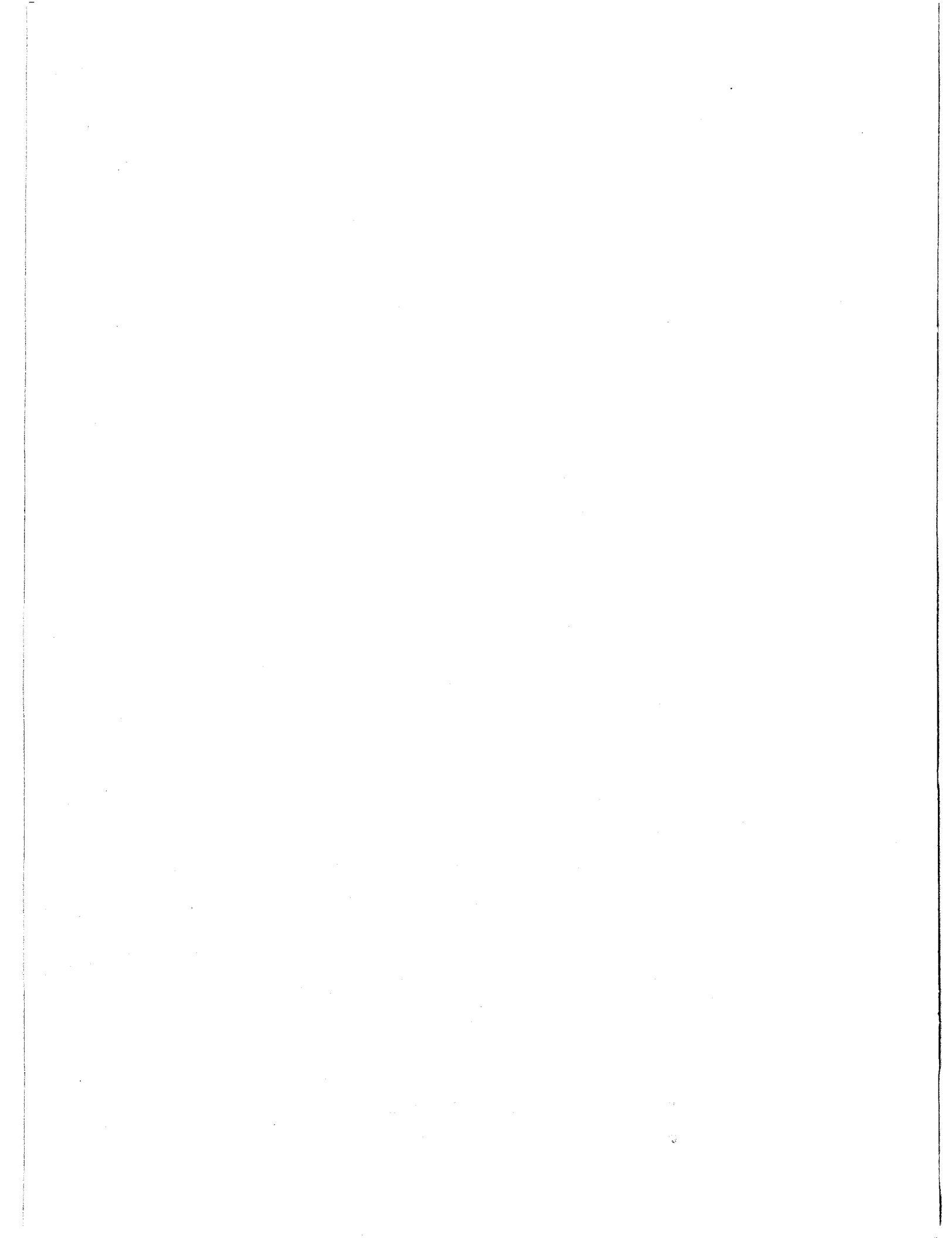
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