U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

PROCEDURES FOR COLLECTING AND ANALYZING

GAS SAMPLES FROM GEOTHERMAL SYSTEMS

by

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CONTENTS

ILLUSTRATIONS

APPENDICES

INTRODUCTION

This report describes methods used by the Stable Isotope and Gas Geochemistry Laboratory of the U.S. Geological Survey for routine preparation, collection and analysis of geothermal gas samples. Analyses of gases produced in geothermal systems provide information on mineral-fluid and fluid-fluid interactions that occur below the earth's surface. Because certain gases are ubiquitous in geothermal systems, routine analyses of these gases can be used to help characterize geothermal systems and to determine temporal and spatial changes in these systems. Geothermal gases that are routinely analyzed include: water vapor (H_2O), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), hydrogen (H_2), helium (He), argon (Ar), oxygen (O_2), nitrogen (N_2), and methane (CH_4). H_2O, CO_2 and H_2S generally comprise ninety-eight percent or more of these gases. Geothermal systems may also yield carbon monoxide (CO), hydrocarbon gases other than CH_4, and inert gases other than He and Ar. C_2-C_7 hydrocarbons (hydrocarbon molecules containing from two to seven carbon atoms) may be present, but are not routinely determined. CO and inert gases, other than He and Ar, are measured elsewhere on selected samples; they will not be discussed here.

Methods for collection and analysis of geothermal (and volcanic) gases have been reported by Finlayson (1970), Truesdell and Pering, (1974), Giggenbach (1975), Ellis and Mahon (1977), Nehring and Truesdell (1978a), Sheppard and Giggenbach (1985), Shevenell et al. (1985), Trujillo et al. (1987), and Giggenbach and Goguel (1989). Collecting geothermal steam and gas into evacuated glass bottles containing sodium hydroxide (NaOH) is the procedure used by this laboratory for obtaining samples from natural discharges and geothermal wells. NaOH absorbs H_2O, CO_2, H_2S, and NH_3 from the gas phase; and noncondensible gases (He, H_2, Ar, O_2, N_2, and hydrocarbons) are concentrated in the headspace of the bottle. This permits quantification of gases which may otherwise be present in trace amounts. Concentrations of gases in the headspace are determined by gas chromatography (GC) and concentrations of water vapor and dissolved gases are determined by other methods discussed in Sample Analysis (Section 3).

1. SAMPLE PREPARATION

Types of bottles

Two types of gas sampling flasks, bottles modified from those developed by Giggenbach (Nehring and Truesdell, 1978a) and doubleport bottles, are used in this laboratory (Figure 1). The modified Giggenbach bottle (Figure 1a) consists of a glass bulb with an Ace-thred adapter (#5027) attached to one end of the bulb. Closure consists of a nylon bushing (#5029-10 for Ace-thred adapter) with a bored hole (0.3-in. diameter) that is tightened upon a lightly greased #008 Viton rubber O-ring. A glass tube (0.28-in. O.D., 0.20-in. I.D., 4.5-in. length) closed on one end is inserted through the O-ring and bushing. A small hole (0.03-in. diameter) is pierced into the side of the glass insertion tube (stem) about 1.25 in. from the closed end, so that the glass stem can be positioned in a way to admit a sample to the bottle (Figures 1a and 2a). The volumes of Modified Giggenbach bottles used in this laboratory vary from 200 to 500 mL. Modified Giggenbach bottles are best used for sampling geothermal wells, where the fluids collected are at greater than atmospheric pressure. Precautions should be taken when handling this type of bottle during collections from wells. Bottles can become overpressurized such that the stem is forced out and the sample is lost. A vacuum/pressure gauge used during collection can help prevent this occurrence. This type of bottle is more likely to leak around the O-ring closure than the doubleport bottle, so care must be taken during opening and closing. With practice, one can become quite adept at handling these bottles.

0.28x3.94-in. glass stem with closed end and 0.03-in. hole

nylon bushing #5029-10

#008 Viton O-ring

Ace-thred adapter #5027

teflon stopcock

O-rings

sample ports

1a. Modified Giggenbach bottle

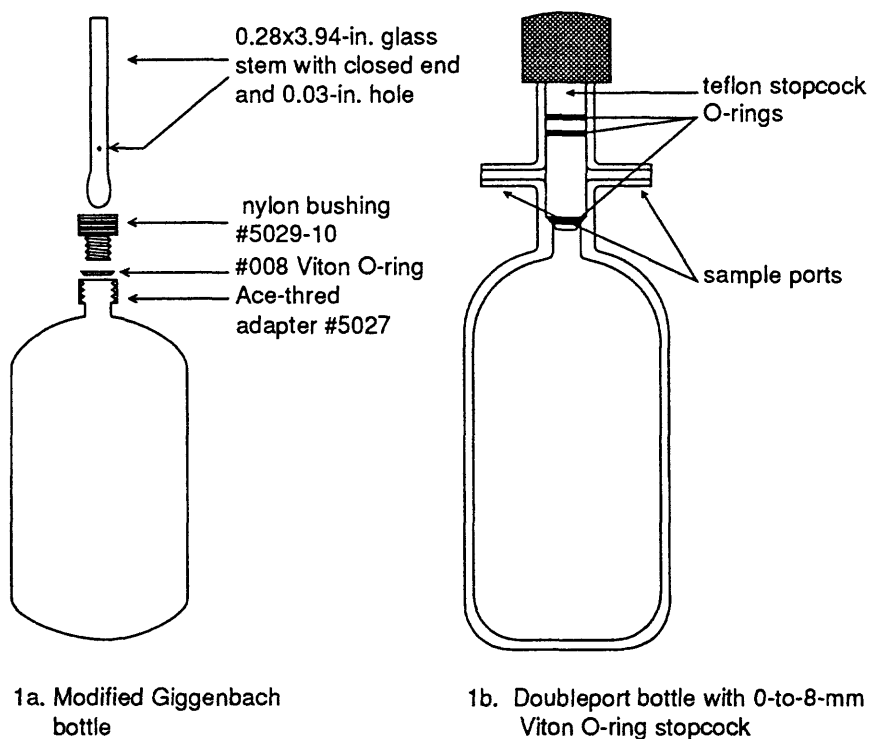1b. Doubleport bottle with 0-to-8-mm Viton O-ring stopcock

Figure 1. Two types of gas sample bottles used by this laboratory. 1a. Gas sample bottle modified from Giggenbach (Nehring and Truesdell, 1978a). 1b. Doubleport sample bottle with 0-to-8-mm Viton O-ring stopcock.

A doubleport bottle consists of a glass bulb with a 0-to-8-mm Viton O-ring stopcock on one end as illustrated in Figure 1b. Two 0.31-in.-O.D. sidearm ports protrude from either side of the stopcock-bottle junction. Doubleport bottles used are 300 mL in volume, but could be made to other sizes. Doubleport bottles are most useful for sampling spring and fumarole gases. They are easy to open and close, sturdy, and less likely to leak. If this type of bottle is used at wells, care should be taken to prevent overpressurizing the bottle because it may break.

Preparation of bottles

The first step in gas bottle preparation is to determine weight and volume of bottle. Each bottle is weighed empty with its closure. The Modified Giggenbach bottle requires a bushing, O-ring and glass stem for closure and the doubleport bottle requires a matching stopcock. Weight, to the nearest 0.1 g, is inscribed on the bottle. Volume is determined by filling the bottle with purified water at a known temperature and weighing. The gas bottle volume is determined to nearest mL using density and weight of water and is inscribed on the bottle. Along with weight and volume, a bottle number may be inscribed on each bottle. Numbers are inscribed on both stopcock and doubleport bottle so that these items can be properly matched to each other. Stopcocks are not uniform in weight and size; therefore, they are not interchangeable.

Sample bottles are prepared for collection the following way. Make 4 N NaOH solution by mixing 50% w/w NaOH with purified water. Keep this diluted solution closed to the atmosphere as it will rapidly absorb atmospheric CO_2 which contaminates the solution. Using a funnel or pipet, add caustic solution to fill one-third of volume of bottle and quickly close the bottle. If approximate composition of gases to be collected is known, then vary caustic solution volume accordingly. A geothermal fluid that is rich in acid gases may require more caustic solution and a fluid that contains abundant steam condensate collected as condensed water vapor may require less caustic solution. Remove any caustic solution that may get into neck or ports of bottle. After caustic solution is added, the bottle is placed in a simmering water bath (approximately 60°C) while attached to a water aspirator or small vacuum pump. Open bottle to vacuum and let solution boil gently. After four minutes, remove bottle from water bath, close, and detach bottle from vacuum. Check to make sure the bottle has been evacuated properly by listening for a clicking sound when it is sharply shaken. This indicates that the headspace in the bottle is at the vapor pressure of the caustic solution and that no air remains to cushion the solution as it hits the sides of the bottle. Let bottle cool to room temperature and again check for vacuum by shaking. Weigh bottle to nearest 0.1 g, then add label tape to bottle and weigh again. Record both weights on the label tape. Place two wide rubber bands around girth of the bottle for protection when handled and packed.

Operation of bottles

The stem of the Modified Giggenbach bottle is attached to silicone elastomer tubing (3/16-in. I.D., 3/32-in. wall or 3/32-in. I.D., 1/16-in. wall, about 4 to 6-ft. length) through which the sample fluid flows (Figure 2a). Be careful not to insert stem into bottle while attaching tubing to stem. While holding bottle in horizontal position, allow fluid to flow through stem and tubing to purge air from the sampling line. Once air is purged, invert bottle and carefully insert stem so that hole in stem is inside bottle and fluid is admitted. If stem does not slide along the O-ring, then the bushing may need to be loosened one-fourth turn before insertion. Keep bottle inverted so that gas flows through caustic solution, and shake bottle occasionally to help dissolve acid gases. Sampling is complete when NaOH is consumed by reaction with acid gases to form salts, the bottle is 75% full of liquid, or vacuum is replaced by noncondensible gases. Do not allow caustic solution to flow out of bottle. If caustic solution is lost, estimate how much and record this amount on bottle label. Carefully reposition stem in closed position. Tighten bushing, but do not overtighten because bushing or threaded glass adapter may break. Remove

silicone tubing from stem. After sample has cooled, check to make sure bushing is tightened sufficiently against the O-ring.

Doubleport bottles are handled differently (Figure 2b). A short length (about 5 in.) of silicone tubing with two tubing clamps is attached to one port. Tubing through which sample fluid flows is attached to the other port. Allow sample tubing and ports to be purged of air. Invert bottle and close the two tubing clamps, outermost first. Open stopcock slowly and collect sample as described for Modified Giggenbach bottle. When finished, close stopcock, open tubing clamps and remove tubing from both ports. Check tightness of stopcock seal when sample has cooled.
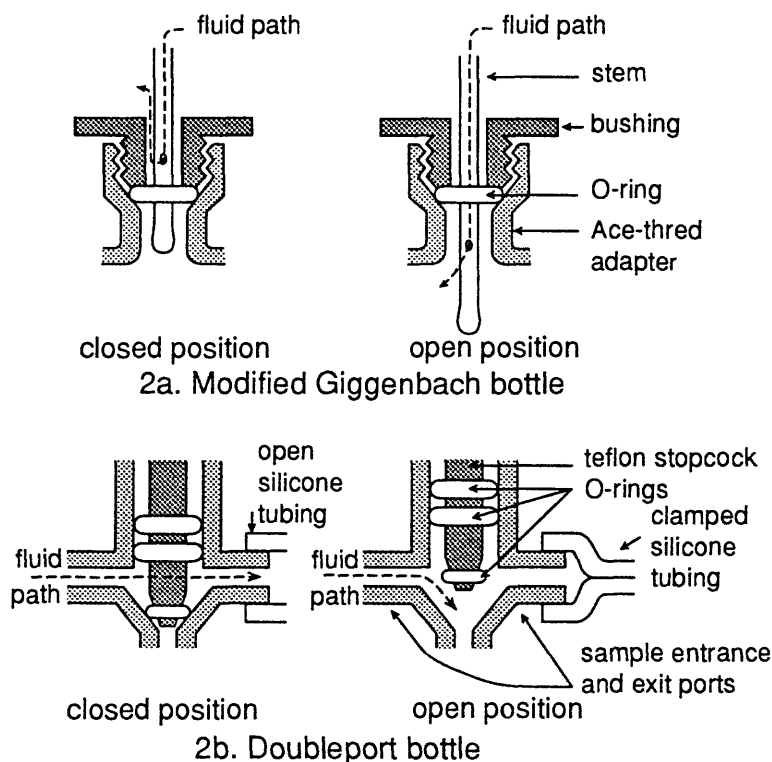

Figure 2. Illustration of fluid path through closed and open positions of both types of bottles. Note that when collecting a sample, hold bottle in inverted position. 2a. Closed and open position of Modified Giggenbach bottle. 2b. Closed and open position of doubleport bottle.

4

2. SAMPLE COLLECTION

Warm and hot springs

An 8-in. diameter translucent polypropylene (or polyethylene) funnel is used to trap gas. Approximately 4.7-in. length of (1/4-in. I.D., 3/16-in. wall) tygon vacuum tubing is cemented with silicone rubber adhesive into the neck of funnel. A larger piece of vacuum tubing is cemented onto the outside of the neck to add strength and to protect inner tubing. This larger tubing also provides a surface for a universal clamp to grab. The funnel is attached to a 6-ft., 0.5-in. diameter aluminum collection pole, as shown in Figure 3, using a universal clamp that is attached to the pole with an extension clamp. Nylon cord may be used to secure funnel to collection pole in case of failure of universal clamp. A 2-ft. aluminum crosspiece, connected with a right-angle clamp, may be added to pole for stability in positioning (funnel tends to rotate). An approximate 6-ft. length of silicone tubing is inserted into vacuum tubing in the neck of the funnel. Sometimes, a light application of vacuum grease is required to nest tubing. A package of miscellaneous accessories used for configuring the collection device includes spare clamps (universal, extension, and right-angle), tubing clamps, radiator hose clamps (for added stability at connections), nail (for wedge in extension clamp), grease (Apiezon N or H), and various lengths of silicone tubing.
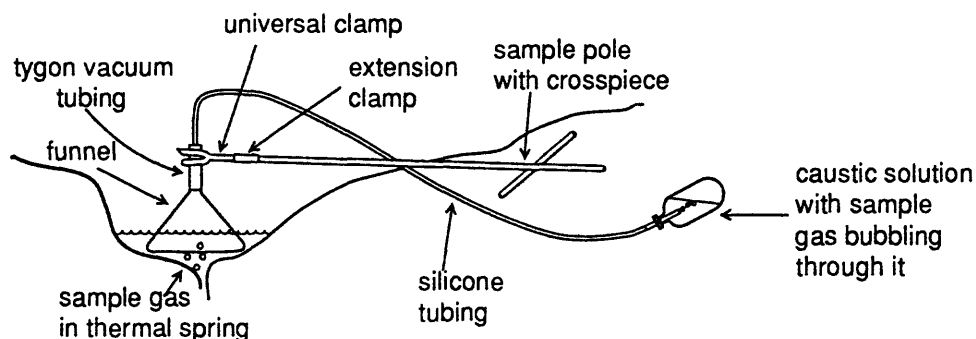
Figure 3. Equipment used for sampling springs.

Using either a digital thermocouple meter and probe or a maximum registering thermometer, locate hottest spring in area of interest that has gas flow sufficient for collection. If spring temperature is near boiling, do not confuse water vapor with other gases. The difference between water vapor and other gases can be determined by observing shrinkage of water vapor bubbles or expansion of gas bubbles as they rise to surface of spring. Avoid vigorously boiling springs because splashes may contaminate the sample.

Before starting a sample collection, shake the bottle to verify that it has remained properly evacuated. Place funnel over chosen sampling vent, making sure rim of funnel is submerged and as close to gas entry as possible. Accumulation of gas tends to force the funnel up, so some weight may be required on pole, crosspiece, or edges of funnel to hold it down. Purge funnel of atmospheric contamination by sucking on end of tubing until funnel fills with spring water and a small amount of this water enters tubing. Getting a small slug of spring water into the sampling line may also be accomplished by using a hand-operated vacuum pump attached to end of tubing. Crimp tubing so that water does not flow back into funnel. Allow gas to fill funnel again by displacing spring water and forcing the slug of spring water down the tubing. Just before slug is forced out, attach gas bottle to end of tubing. As slug passes through stem of Modified Giggenbach bottle, invert bottle and carefully insert stem into it. Watching water level in funnel, regulate gas flow by constricting tubing as necessary so that funnel remains

5

approximately half full of gas. For doubleports, invert bottle when slug passes through tubing on exit port, close tubing clamps and open stopcock slowly. Use stopcock to regulate flow if necessary. Occasionally shake bottle to dissolve gases into NaOH. A stream of cool water poured over the bottle may be required to condense steam. Insulating gloves or a handkerchief may be useful for holding bottle during sample collection. Collect sample until flow of bubbles into bottle almost stops (when atmospheric pressure is attained in the bottle) or when the amount of liquid is 75% of bottle volume. Close bottle, remove tubing, and check tightness of seal after bottle has cooled.

Fumaroles

Equipment required for fumarole sampling is similar to that for spring sampling, except that metal tubing is used instead of a funnel. A funnel may be used to collect a gas sample from low velocity fumaroles if necessary. High velocity fumaroles are more desirable because they generally have less or no air entrained in the gases. Locate hottest part of vent with temperature probe. Insert a stainless steel or titanium tube, with silicone tubing attached to other end, as far into vent as possible, taking care not to clog metal tube with debris (Figure 4). Various sizes and shapes of metal tubes can be used for sampling depending on geometry of vent. This lab uses 1-in. O.D., 0.063-in. wall titanium tubes, 3/8-in. O.D., 0.035-in. wall or 0.5-in. O.D., 0.063-in. wall stainless steel tubes of various lengths with right angle bends at about one-third the length of tubes. It may be desirable to clamp metal tube onto collection pole to position tube properly in vent. If necessary, attach an air-cooled condenser to silicone tubing as illustrated in Figure 4. Place sampling device in such a way that condensed steam may flow gravity-assisted through tubing. Cool water poured onto condenser or bottle may be required to condense sample further. Flush tubing with fumarole gas and condensate for a few minutes. If there is not enough force to push condensate through tubing, a hand-operated vacuum pump may be used to purge sampling line (or to pull sample into bottle if using doubleports). Collect sample as described for springs.
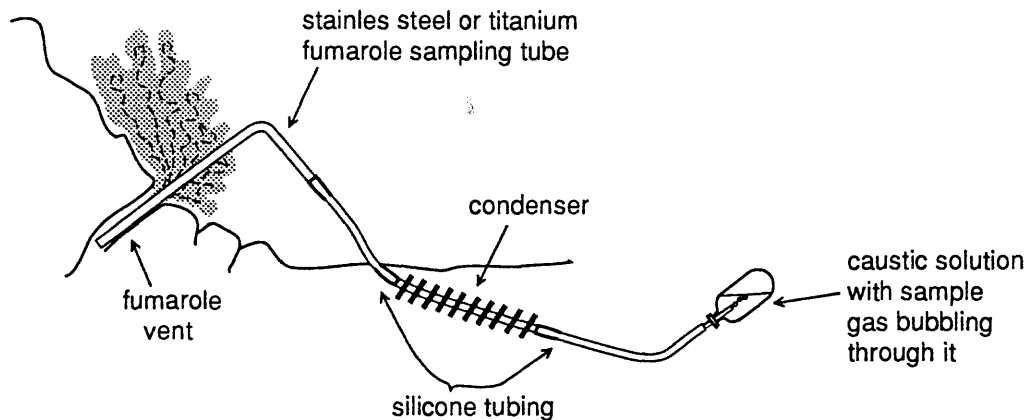
Figure 4. Equipment used for sampling fumaroles.

Two-phase thermal wells

In liquid-dominated geothermal systems, phase separation between water and steam often begins before the liquid reaches the surface such that a two-phase fluid is produced at the wellhead. Gases move preferentially into the steam phase. Production wells discharging two-phase flow are generally fitted with centrifugal Webre or cyclone separators, but in the initial stages of exploration and development, gas samples are collected from a rapidly flowing, two-

phase fluid using a portable stainless steel cyclone separator attached to the discharge line (Figure 5). Understanding operation and limitations of separators is necessary before reliable samples can be collected (Ellis et al., 1968; Ellis and Mahon, 1977; Nehring and Truesdell, 1978a; Giggenbach and Goguel, 1989). Water and steam flows are adjusted to allow some steam to issue from water outlet while collecting from steam outlet (adjustment similar to that of production separators). When miniseparator is adjusted properly for gas sampling, dry steam exiting the T-piece will have a blue-gray color. The miniseparator must be insulated and the valve at the junction between flow line and separator must be fully open to maintain pressure in the separator during sampling nearly equal to that in the flow line. These measures are necessary to ensure that a pressure decrease does not occur between the flow line and the separator and that gas collected from separator is representative of that in the total well discharge. Condensing coils are connected to the steam outlet of the separator and gas collection then proceeds as described under steam wells.
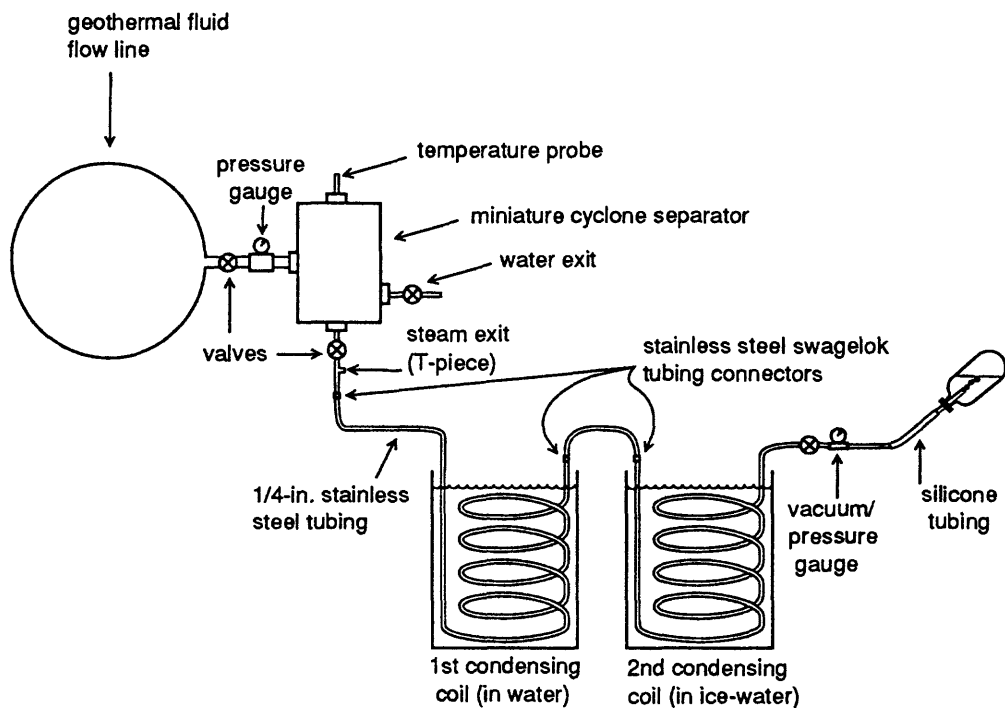
Figure 5. Equipment used for sampling wells.

Steam (single-phase) wells

It is usually sufficient to collect a gas sample directly from a sampling port on an insulated steam line near the wellhead of steam wells, taking precautions to avoid condensation at the inlet to the sampling apparatus. An isokinetic sampling probe inserted into the center of a large diameter steam line also provides representative samples and ensures that condensate forming on the inner surface of the pipe is not entrained in samples. Fluid exits from a well at temperatures considerably above boiling (100°C) and must be cooled to handle safely and to avoid loss of volatile compounds. Cooling is accomplished with a double coil condenser of 1/4-in. O.D. stainless steel tubing connected to steam line or separator by a regulating valve (Figure 5). The first coil is immersed in water which is allowed to boil, effectively reducing temperature of fluid to about 100°C. The second coil is placed in an ice-water bath, further cooling fluid to about 30°C. In some cases, only one condensing coil may be needed. Flow rate during collection can be regulated by a valve connected to the end of the second coil. A

7

vacuum/pressure gauge is also connected to end of coils and is used to determine pressure in sample bottle during collection. Silicone tubing connects vacuum/pressure gauge outlet to gas bottle. Steam condensate and gas issue from the outlet as discrete, uniformly sized slugs in the tubing. When collecting from wells, do not allow sample pressure to exceed that of atmosphere, as indicated by gauge.

Gas-to-steam Ratio

The slug flow of gas and steam condensate produced by the condenser tubing is uniform over the period of collection; therefore sample obtained is representative of the average composition of gas relative to steam in the issuing fluid. Samples collected from warm springs do not yield quantitative gas-to-steam ratios because some steam may condense in the sampling line and flow backward into the spring instead of into the bottle. Superheated fumaroles, where the sampling apparatus can be configured to allow gravity-assisted flow of condensate into bottle, will yield reliable gas-to-steam ratios upon analysis.

Record of Collection

Details of sample collection must be recorded in a field notebook and each sample must be properly labeled with a permanent marking pen at time of sampling. Required information on natural geothermal features includes field sample number, date, location (geographic area), map reference, name of feature, temperature, description (type of feature, physical appearance, rock type, alteration mineralogy, flow rate, velocity of steam discharge, etc.). For well samples, notes include field sample number, name of geothermal field or operator, date, well number, wellhead pressure (specify gauge or absolute), separation pressure, and water/steam flow rates (for two-phase wells). Well discharge enthalpy should be provided by the operator.

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3. SAMPLE ANALYSIS

Analytical procedures are reported in the order in which they are performed. Gas chromatographic analyses are performed first, followed by wet chemical analyses. Residual gases are defined as gas species that have very low solubilities in NaOH, i.e., gases that remain in headspace of sample bottle. Residual gases in geothermal systems include H_2, He, Ar, O_2, N_2, and hydrocarbon gases, and are analyzed by gas chromatography (GC). The gases, H_2, He, Ar, O_2, N_2, and CH_4, are analyzed by thermal conductivity detection gas chromatography (TCD-GC). (It is possible to analyze for ethane (C_2H_6) via TCD-GC, but this analysis is not routinely performed in this laboratory.) Hydrocarbons, including CH_4, are analyzed by flame ionization detection gas chromatography (FID-GC). The remaining gas species, NH_3, CO_2, H_2S, and steam condensate (H_2O), are absorbed in NaOH solution; therefore, wet chemical or gravimetric analytical techniques are used to quantify their concentrations.

Gas Chromatography - Residual Major Gases

Exterior of sample bottle is cleaned and rubber bands removed prior to analysis. If the stem contains carbonate or hydroxide deposits, it should be cleaned with a cotton swab wetted with 1 M HCl. Bottle is weighed to nearest 0.1 g and this weight is recorded on a Gas Analysis Worksheet (Appendix A). Information previously recorded on gas bottle or in field notebook is transferred to worksheet at this time.

Two Carle AGC 111 gas chromatographs with thermal conductivity detectors (TCD-GC) are connected to a common sampling inlet system that allows samples to be injected at known pressures less than atmospheric pressure (Figure 6; from Sheppard and Truesdell, 1985). One chromatograph uses He as the carrier gas, and the other uses Ar. A standard gas, with known composition similar to geothermal gases, is analyzed first for calibration of GCs. Air is used as a N_2 standard when the N_2 concentration is greater than 60% of the headspace gases.
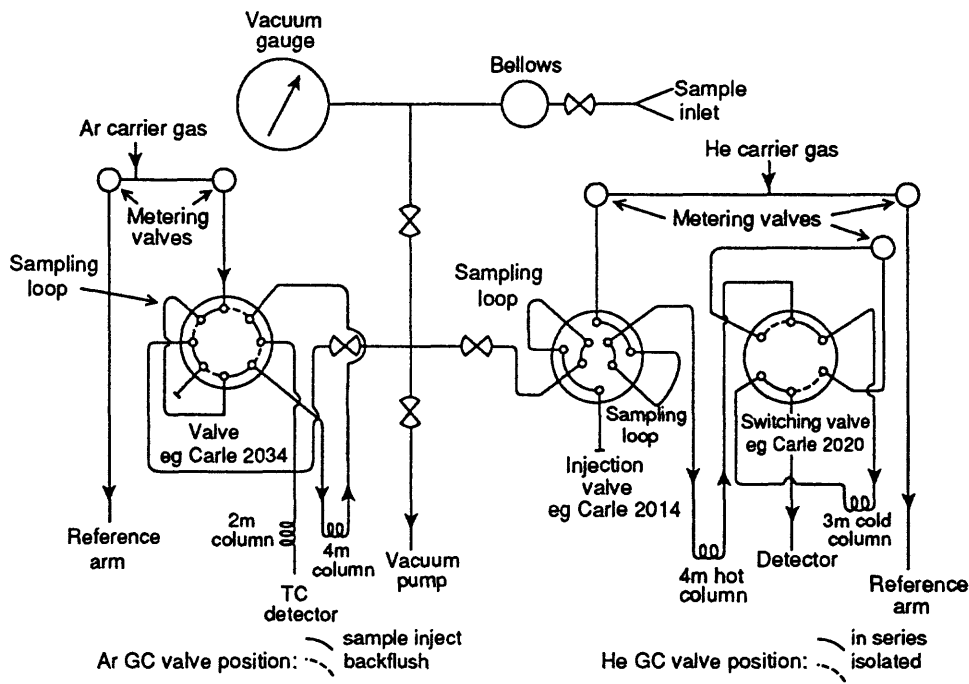

Figure 6. Diagram of double gas chromatograph system (Sheppard and Truesdell, 1985).

9

Modified Giggenbach bottles are attached to GC inlet system using a modified bushing (threaded part removed), greased O-ring, and pinch clamp to isolate inside of stem from atmosphere when attached to GC (Figure 7a). Open end of stem is attached to GC inlet using Cajon adapters. Doubleports are attached using silicone tubing, a glass tube, and Cajon adapter on one port and clamped silicone tubing on other port (Figure 7b). After stem or port of bottle is evacuated, a known-volume section of the GC inlet system which is connected to a pressure transducer, is isolated from vacuum and the bottle is opened to admit gas. Pressure and temperature of residual gas is recorded on worksheet. Sample is admitted to sampling loops, injection pressure is adjusted using a variable volume bellows, and GC analysis proceeds as described in detail in Sheppard and Truesdell (1985). After GC analysis, GC data (peak areas in counts) are recorded on worksheet. An approximate determination of residual gas composition should be made at this time to evaluate GC analysis. For each gas species i,

$$\text{vol\% i in sample} = (\text{counts sample/counts standard}) \times \text{vol\% i in standard.} \quad (1)$$

Replicate analyses should be performed if total residual gas composition is more than 3% in error, i.e. $\Sigma \text{vol\%} \neq 100 \pm 3\%$.

7a. Modified Giggenbach bottle   7b. Doubleport bottle
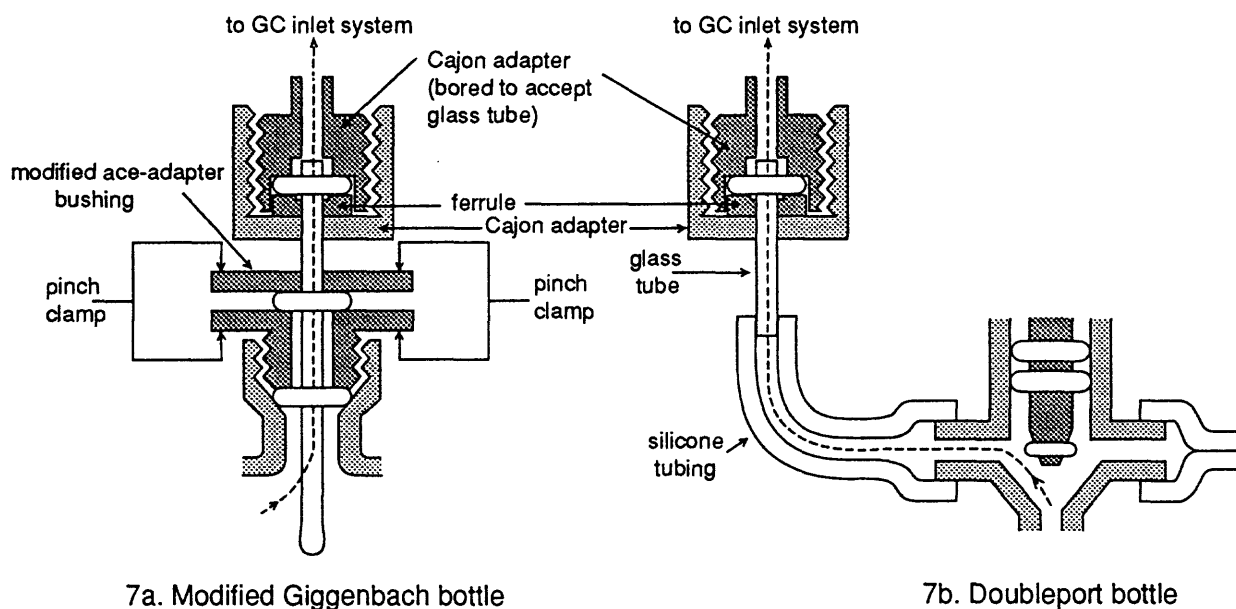
Figure 7. Method used for connecting bottles to GC inlet system for headspace gas analysis. Bottles are shown in the open position with flow path of gas to GC inlet system. 7a. Modified Giggenbach bottle. 7b. Doubleport bottle.

Gas Chromatography - Residual Hydrocarbon Gases

Selected samples are analyzed for C1–C7 hydrocarbons using a Hewlett-Packard 5700A gas chromatograph equipped with a flame ionization detector (FID-GC) and temperature programmable oven. A Spectraphysics Minigrator and chart recorder are used to record and integrate peaks. Dual columns, 6-ft by 1/8-in. diameter, are packed with Porapak Q, 60-100 mesh, and He carrier gas is used at 60 psig inlet pressure. Each analysis is temperature programmed starting at -30°C for 2 minutes, temperature ramped at 8°C/min. to 150°C, and then held at 150°C for 32 minutes. Identification of gases has been confirmed by GC-MS (gas chromatography-mass spectrometry) on representative samples (Nehring and Truesdell, 1978b). Initial oven temperature of -30°C is achieved by placing crushed dry ice directly in oven.

An aliquot of standard gas is withdrawn from a gas cylinder pressurized to greater than 1 atm into a graduated gas-tight syringe through a septum. The valve on the syringe is briefly opened so that upon contact with atmosphere, excess gas escapes. Then valve is closed when pressure within syringe is 1 atm. Standard is introduced to FID-GC with syringe through a slow-bleed septum at injection port. Better than 90% reproducibility for standard gas is routinely obtained using this technique.

A portion of gas sample to be analyzed is transferred from sample bottle or from GC inlet system via a septum port to a gas-tight syringe. If sample is to be removed directly from bottle, then stem of gas bottle is sealed with O-ring, modified bushing, and pinch clamp as described previously, and a septum is fitted upon end of stem. A 60-cc plastic syringe is connected to one end of a luer stopcock and a septum is placed on the opposite end. A hypodermic needle is inserted through septa on luer stopcock and stem as illustrated in Figure 8. Air from stem is removed by using large syringe as a vacuum pump and exhausting air through open arm of luer stopcock. After evacuation, a 10-cc gas-tight syringe is attached to open arm of stopcock. Gas bottle is opened to sample and the 60-cc syringe is used to remove gas from bottle. Then the 60-cc syringe is used to compress gas into 10-cc syringe. Valve on gas-tight syringe is closed and then sample bottle is closed. Gas-tight syringe should be preconditioned with sample for approximately twenty minutes in order to saturate hydrocarbon adsorption sites in syringe. After preconditioning, a fresh aliquot of sample is extracted for analysis. Syringe pressure is adjusted by compressing gas and opening syringe valve to release gas until pressure inside equilibrates at 1 atm. Slight air contamination that may result during this extraction process is not a problem during analysis. Approximate sample size averages 0.5 cc to 1 cc at atmospheric pressure; however some samples require adjustment to prevent overloading FID-GC column with methane. Samples are injected in the same way as standards.
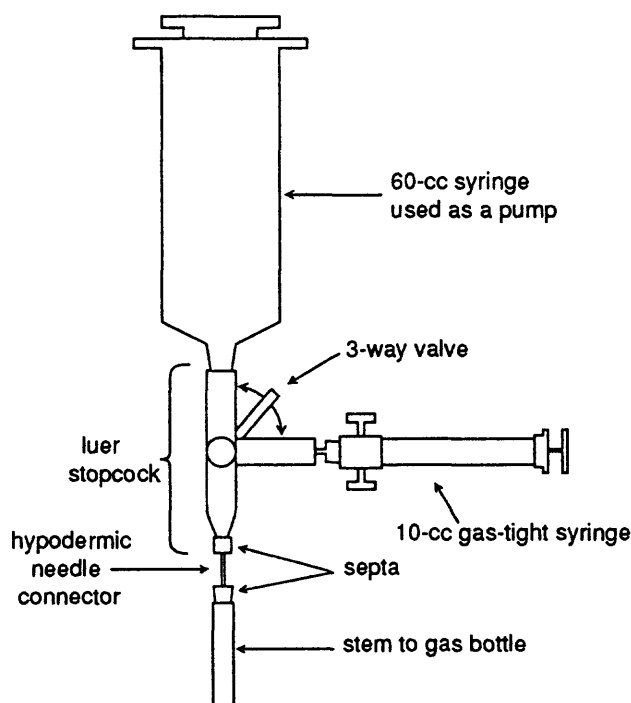

Figure 8. Gas transfer technique from sample bottle to gas-tight syringe.

After FID-GC analysis, peak areas in counts, and volume of sample are recorded on Hydrocarbon Gas Analysis Worksheet (Appendix B). Since samples are injected at an approximate known pressure, concentration of methane as determined from TCD-GC is used to normalize FID-GC analysis using the following formula:

$$N = (a/c)/(A/C), \quad (2)$$

where: a = area under methane peak for FID-GC standard, c = concentration, in ppm, of methane standard, A = area under methane peak for sample, C = concentration of methane in sample as determined by TCD-GC, and N = normalization factor for sample being analyzed by FID-GC. Multiply area under peaks by N (Equation 2) for each of hydrocarbons determined in order to make quantitative comparison between hydrocarbons in sample and those in standards.

Preliminary studies indicate that benzene is sufficiently soluble in caustic solution such that headspace hydrocarbon analysis is not quantitative. A plot of gas-phase benzene concentration vs. temperature over a range of temperatures from 18°C to 78°C shows no deviation from a linear curve, indicating that more benzene can be extracted from caustic solution with increasing temperature. Therefore, benzene determination is to be considered semiquantitative because of inability to completely extract benzene from caustic solution. Concentration of methane and other hydrocarbons in headspace does not increase significantly with increasing temperature, indicating that these hydrocarbons are not very soluble in caustic solution and partition strongly into the headspace.

Wet Chemistry - Dissolved Gases

Ammonia

NH_3 is very soluble in H_2O, but is considerably less soluble in NaOH solution. The NH_3 analysis is; therefore, the first of wet chemical procedures to be performed before possible loss of NH_3 from solution occurs. NH_3 concentration is determined by gas-sensing electrode (Orion Model 95-10 Ammonia Electrode and Orion Model 407A specific ion meter). Results of analyses by this method compare favorably with distillation and titration techniques.

Dry NH_4Cl salt for several hours at 60°C in vacuum oven. Make 1000 ppm NH_3 standard, which will last for several days, from NH_4Cl. Make 200 ppm, 20 ppm, 2 ppm, and 0.2 ppm standards from serial dilution of 1000 ppm standard. Diluted standards should be made fresh each day and kept sealed when not in use.

Assemble gas-sensing electrode according to instruction manual. To counteract electrode drift caused by differences in osmotic strength between electrode internal filling solution and sample solutions, an adjusted solution is prepared by adding 2.2 g $NaNO_3$ to 50 mL of commercial filling solution . Each day electrode should be cleaned and reassembled with new membrane and internal filling solution. For analysis of samples that contain little or no steam condensate, the electrode is assembled using approximately 30 drops of adjusted internal filling solution. For samples containing approximately equal amounts of NaOH and steam condensate, 15 drops each of adjusted and unadjusted filling solution are used. Plug electrode into meter and let it sit in pH 4 buffer for 2 hours. Electrode operation should be checked daily as outlined in instruction manual.

Pipet 10 mL of 4 N NaOH and 10 mL of standard in a 30-mL beaker. Immerse tip of electrode and stir standard solution with small magnetic stir bar. Read mV scale after three minutes. Record this diluted standard concentration and mV reading. Analysis of standards should yield a straight line on a semilog plot of concentration vs. mV reading. Analyze samples and standards from low concentration to high concentration when possible and place electrode

tip in pH 4 buffer before going from high to low concentration. Shake sample in gas bottle, then open bottle, and pipette 15 mL samples into 30-mL beaker. Immerse electrode, stir for 3 minutes, then record mV reading. Reanalyze standards after every nine samples, or more frequently if electrode measurement drifts. End procedure with set of standard analyses. After completing analyses, use standard calibration curve to determine NH_3 concentration (in ppm) of samples. Record concentration and volume used on worksheet.

Density

Label small (15 or 30-mL) plastic bottles with sample number and weigh empty bottle with cap. Record weight. Using volumetric pipette, add 15 to 25 mL of sample to bottle and weigh again. Calculate density of solution (caustic+sample) and record on worksheet. Seal bottle and save aliquot as reserve fluid for possible replicate wet chemical analyses.

Carbon dioxide and carbon-13

The method used by this laboratory for CO_2 determination requires access to a light stable isotope extraction line. CO_2 is liberated from an aliquot of sample solution by reaction with phosphoric acid in an evacuated flask, and the quantity of CO_2 extracted is measured in a calibrated manometer. This method has the advantages of saving time and reducing sources of contamination that are common to gravimetric determinations of CO_2 in caustic solution. Precipitation, filtration, drying, grinding, and sieving are avoided. Analyses of CO_2 by titration or gravimetric determination are not routinely performed; therefore, are not discussed. Detailed discussions of these other methods are reported in Giggenbach and Goguel (1989) and McCrea (1950).

In one arm of a sidearm flask, add approximately 8 mL of 100% phosphoric acid (H_3PO_4). Recipe for acid is described in Coplen et al. (1983). If necessary, warm sample solution to dissolve sodium carbonate crystals before extracting aliquot from bottle. To other arm of flask, quickly add an aliquot of sample solution and a small volume (generally 100µl/aliquot) of 30% hydrogen peroxide (H_2O_2). H_2O_2 is added to oxidize any H_2S that is present in aliquot since H_2S can contaminate analysis. If sample contains a lot of H_2S, then more H_2O_2 may need to be added to a new aliquot. An indication of abundant H_2S is the presence of a yellow precipitate (sulfur) in the sample solution after addition of H_2O_2 or the smell of H_2S upon opening the flask after analysis. If approximate concentration of CO_2 in gas is known from historical analyses, then proper volume of aliquot can be determined. If CO_2 concentration is unknown, then use 0.5 mL of sample solution for first attempt at analysis. Make sure that sample size is not too small for mass spectrometric analysis or too large for precise measurement in manometer (optimum amount of liberated CO_2 is about 200 µmoles). Record volume of sample aliquot on worksheet. Seal sidearm flask with stopcock and attach to manifold on a light stable isotope extraction line. Freeze sample and evacuate flask, gently heating acid to remove dissolved air. After evacuation, close stopcock and remove flask from vacuum line. Carefully react H_3PO_4 with sample to liberate CO_2 from solution. Let reacted solution sit for approximately twenty-four hours with occasional agitation of solution by turning flask. Return sidearm flask to isotope extraction line and gently heat reacted solution in sealed flask to exsolve any residual CO_2 from solution. Because the sample aliquot may contain steam condensate and since water is generated as product of reaction that liberates CO_2, a trap to remove water is added to extraction line during transfer of gas to manometer. Transfer dry CO_2 gas to calibrated manometer and measure number of µmoles of CO_2. At present, the computer program used here calculates CO_2 concentration from $SrCO_3$ precipitated; therefore, determine the equivalent weight of $SrCO_3$, in grams, from µmoles of CO_2 extracted and record on worksheet. Transfer gas sample to vessel for transport to mass spectrometer for $\partial^{13}C$ analysis. Isotopic value resulting from $\partial^{13}C$ analysis is not used in total gas composition calculation, but is recorded in

Comments Section of worksheet for use in geothermometry calculations and fluid source determinations.

Hydrogen sulfide (total sulfur) and sulfur-34

Empty remaining sample solution into graduated cylinder and record volume. Check volume at this time by adding up volumes of aliquots used for analyses and compare to calculated total volume, where the calculated volume is determined by the following equation:

$$V_{calc} = ((wt\ bottle+NaOH+tape+sample) - (wt\ bottle+tape))/density\ sample. \quad (3)$$

Ideally, the difference between calculated and measured volumes should be 1 mL or less. Check to see that pH of sample is greater than 11 by putting a small drop on pH paper. If necessary, add 10 N NaOH until pH is greater than 11. Transfer quantitatively to a beaker that will have ample volume for additional reagents. To oxidize H_2S (as S^{2-} in caustic solution) to SO_4^{2-}, add 2-3 mL 30% H_2O_2 per 40 mL of sample and stir. The reaction is exothermic so allow sample to cool. Add 2-3 mL more H_2O_2 per 40 mL of sample, cover with watchglass and let sit overnight. Agitate sample slightly and sample should effervesce. If solution does not effervesce, add more H_2O_2. Heat beaker on hot plate until solution begins to effervesce, then cool slightly. Remove CO_2 by adding HCl (1 volume concentrated HCl:1 volume purified H_2O) until pH is 2. Cover and let sit overnight. If solution is cloudy, filter solution with 0.45 µm pore size paper. If gas sample has been stored for more than six months prior to analysis, glass from sample bottle may be dissolved in caustic solution. Polymerization of colloidal silica upon acidification interferes with the gravimetric analysis of H_2S, so SiO_2 must be removed. If filtering is too slow, use 1.2 µm, followed by 0.45 µm pore size paper. Transfer sample quantitatively to clean beaker. Heat solution to below boiling and add 15 mL of 0.5 M $BaCl_2$ solution. Stir briefly, cover with watch glass and let sit overnight. Using ashless filter paper, filter $BaSO_4$ precipitate from solution. Place filter paper and sample in fired, weighed ceramic crucible and fire again, taking care to slowly ash filter paper. Place crucible on its side in flame for air to circulate in crucible so that $BaSO_4$ is not reduced to BaS in firing process. When sample is sufficiently fired, remove from heat, cool, and weigh sample+crucible. Record weight of $BaSO_4$ precipitate on worksheet. Transfer $BaSO_4$ to vials and retain for $\partial^{34}S$ analysis if necessary. (Sulfur isotopic analyses are not performed in this laboratory.)

Total sulfur can also be determined by titration or colorimetry. Giggenbach and Goguel (1989) and Fishman and Friedman (1985) describe an iodometric titration technique. Fishman and Friedman (1985) describe a turbidimetric method which can be used after oxidizing sulfide to sulfate under acid conditions. Neither of these methods provides for preservation of H_2S for $\partial^{34}S$ analysis.

Water as steam condensate

The concentration of steam condensate is determined from subtracting masses of all previously determined components, including headspace gases, from mass of sample collected. This value is determined from data entered into a computer program that calculates the total gas composition.

4. CALCULATION OF GAS COMPOSITION

When determining concentration of H_2 and He, ratio these gases to standards analyzed on the Ar-carrier GC and ratio the other residual major gases (O_2, Ar, N_2, CH_4) gases to standards analyzed on He-carrier GC. H_2 and He are determined with high sensitivity on the GC that uses Ar carrier gas and the other residual major gases are determined with high sensitivity on GC that uses He carrier gas. Remember that if N_2 concentration is greater than 60% in residual sample, ratio N_2 to air standard to determine its concentration. Calculation of residual major gas composition should sum to 100±3%.

When analytical work is completed, data listed on worksheets in Appendices A and B are entered interactively into a computer program that calculates gas composition and outputs results similar to those displayed in Appendix C. In addition to data from worksheets, volume of TCD-GC inlet system must be known as well as Henry's Law distribution coefficients for gas species being analyzed. Total gas composition in mole percent without water (steam), total gas composition in mole percent with steam, and total gas composition in weight percent with steam are calculated.

After normalizing hydrocarbon analysis to methane as determined from TCD-GC, hydrocarbon concentrations are given in ppm. At present, this computer calculation does not incorporate hydrocarbon determinations into total gas analysis. In general, CH_4 is the most numerically significant hydrocarbon present and other hydrocarbons are insignificant to total gas calculation. In cases where there are abundant (more than 2%) hydrocarbons present (other than methane), hydrocarbon concentrations should be included in total gas analysis.

Information obtained from a gas analysis can be very useful. The total gas analysis can be used to help characterize a geothermal system, calculate reservoir temperatures, make recommendations for exploration drilling, make engineering decisions regarding type and size of power installations, characterize steam separation processes in reservoir and wellbore, and monitor effects of reservoir development.

REFERENCES CITED

Coplen, T. B., Kendall, C., and Hopple, J., 1983, Comparison of stable isotope reference samples, Nature, v. 302, p. 236-238.

Ellis, A. J., Mahon, W. A. J., and Ritchie, J. A., 1968, Methods of collection of geothermal fluids, 2nd ed., New Zealand DSIR Rept. CD 2103, 51 p.

Ellis, A. J. and Mahon, W. A. J., 1977, Chemistry and Geothermal Systems, Academic Press, New York, 392 p.

Finlayson, J. B., 1970, The collection and analysis of volcanic and hydrothermal gases, Geothermics, Special Issue 2, p. 1344-1354.

Fishman, M. J. and Friedman, L. C., eds., 1985, Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations in the United States Geological Survey, Book 5, Chapter A1, USGS Open-File Rept. 85-495, 709 p.

Giggenbach, W. F., 1975, A simple method for the collection and analysis of volcanic gas samples, Bulletin Volcanologique, v. 39, p. 132-145.

Giggenbach, W. F. and Goguel, R. L., 1989, Collection and analysis of geothermal and volcanic water and gas discharges, 4th ed., New Zealand DSIR Rept. No. CD 2401, 81 p.

Janik, C. J., Nehring, N. L., Huebner, M. A., and Truesdell, A. H., 1982, Carbon-13 variations in fluids from the Cerro Prieto geothermal system, in Proc., 4th Symposium on the Cerro Prieto Geothermal Field, Baja Calif., Mexico, v. 2, August 1982, Guadalajara, Mexico, p. 535-541.

McCrea, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale, J. Chem. Phys., v. 18, p.849-857.

Nehring, N. L. and D'Amore, F., 1984, Gas chemistry and thermometry of the Cerro Prieto, Mexico geothermal field, Geothermics, v. 13, p.75-89.

Nehring, N. L. and Truesdell, A. H., 1978a, Collection of chemical, isotope, and gas samples from geothermal wells, in Proc., 2nd Workshop on Sampling and Analyses of Geothermal Effluents, Feb 1977, Las Vegas, NV, EPA-600/7-78-121, p. 130-140.

Nehring, N. L. and Truesdell, A. H., 1978b, Hydrocarbon gases in some volcanic and geothermal systems, Geothermal Resources Council Transactions, v. 2, p. 483-486.

Sheppard, D. S. and Giggenbach, W. F., 1985, Methods for the analysis of geothermal and volcanic waters and gases. New Zealand DSIR Rept. CD 2364, 78 p.

Sheppard, D. S. and Truesdell, A. H., 1985, A GC-System for the Analysis of Residual Geothermal Gases, Chromatographia, v. 20, p. 681-682.

Shevenell, L., Goff, F., Gritzo, L., and Trujillo, P.E., Jr., 1985, Collection and analysis of geothermal gases, LANL Rept. LA-10482-OBES, 25 p.

Truesdell, A. H. and Pering, K. L., 1974, Gas collection and analysis from geothermal systems, USGS Open-File Rept. 74-361, 4 p.

Trujillo, P. E., Counce, D., Grigsby, C. O., Goff, F., and Shevenell, L., 1987, Chemical analysis and sampling techniques for geothermal fluids and gases at the Fenton Hill Laboratory, LANL Rept. LA-11006-MS, 84 p.

Sample Number_____CP77-25*_____ GC Analyst____Nehring_____

Field_____Cerro Prieto, MX_____ Date analyzed__14 July 78, 23 Aug 78____

Description__Well M19-A_____

Collector____Truesdell/Nehring_____ Date collected__27 April 1977_____

Gas Chemistry					*Wet Chemistry*	
HE Carrier			$P_{std1cc@7psi}$	$P_{sample1cc@11psi}$	vol bottle (mL)......................	315.0
%	Gas	Std	StdCount	SampleCount	wt bottle (g)...........................	144.3
---	H_2	30.0	36205	67165	wt bottle+NaOH....................	260.7
6.71	N_2	29.8	808086	286015	wt bottle+NaOH+tape..........	---
52.40	CH_4	30.2	656705	1791005	wt bottle+NaOH+tape+samp	413.5
0.18	Ar	0.99	16899	4880	psia residual...........................	16.95
0.00	O_2	1.91	70649	0	T(°C) residual........................	24.0
---	C_2H_6	6.11	---	---	vol NH_3...............................	10.0
					vol CO_2..............................	5.0
AR Carrier			$P_{std1cc@7psi}$	$P_{sample1cc@13psi}$	vol H_2S..............................	223.0
%	Gas	Std	StdCount	SampleCount	vol total............(244.7 calc)..	244.0
0.00	He	1.00	11257	0	density NaOH+samp (g/mL)	1.10
37.70	H_2	30.0	392504	915178	ppm NH_3............................	72.0
---	O_2	1.91	2253	0	μmoles CO_2 (as wt $SrCO_3$)	0.1818
---	N_2	29.8	43072	19575	wt $BaSO_4$............................	0.8283
---	CH_4	30.2	81726	284855	vol NaOH reserved or lost....	---

97.00

Comments: $\partial^{13}C$ = -6.4 (Janik et al., 1982)

*Total Gas Analysis calculated from this data and published in Nehring and D'Amore (1984).

Appendix B: HYDROCARBON GAS ANALYSIS WORKSHEET

Sample Number_____CP77-25*_____   GC Analyst_____Nehring_____

Field_____Cerro Prieto, MX_____   Date analyzed___12 September 1978_____

Description__Well M19-A_____

Collector_____Truesdell/Nehring_____   Date collected__27 April 1977_____

method: internal std__X__ external std_____

Gas	ppm Std	10.0 cc STP StdCount	10.0 cc STP SampleCount
methane	100.00	27566	27218568
ethene	0	0	10
ethyne	0	0	0
ethane	100.00	53204	3885508
propene	0	0	0
propane	100.00	72752	995016
propyne	0	0	0
2-methylpropane	0	0	62552
1-butene	0	0	0
n-butane	100.00	96108	198094
2-butene	0	0	0
1-butyne	0	0	0
2-butyne	0	0	0
2,2-dimethylpropane	0	0	0
2-methylbutane	0	0	29349
1-pentene	0	0	0
n-pentane	100.00	114589	29305
2-pentene & cyclopentane	0	0	14901
2,2-dimethylbutane	0	0	22798
3-methylpentane	0	0	18431
2-methylpentane	0	0	0
1-hexane	0	0	0
n-hexane & cyclohexane	100.00	107812	58248
benzene	0	0	1252810

Comments: Internal std used for FID calculations.

*Total Gas Analysis calculated from this data and published in Nehring and D'Amore (1984).

Appendix C: TOTAL GAS ANALYSIS

Field: Cerro Prieto
Name: M-19A
Sample #: CP77-25*
Description: Gas+SC
Date Collected: 27 April 77
Collected by: Truesdell/Nehring
Date of run: 26 Mar 79

TCD-GC

TC-He 14 July 78 — Pstd=7.0, Psam=11.0
TC-Ar 23 Aug 78 — Pstd=7.0, Psam=13.0

Gas	%-std	ctstd (He)	ctsamp (He)	ctstd (Ar)	ctsamp (Ar)	Mol % Res gas
He	1.00	nd	nd	11257	0	0.00E+000
H2	29.99	36205	67165	392504	915178	3.77E+001
Ar	0.99	16899	4880	nd	nd	1.82E-001
O2	1.91	70649	0	2253	0	0.00E+000
N2	29.80	808086	286015	43072	19575	6.71E+000
CH4	30.20	656705	1791005	81726	284855	5.24E+001
C2H6	6.11	nd	nd	nd	nd	0.00E+000
Total						9.70E+001

nd-not determined

WET CHEMISTRY

vol bottle (mL)	315.0
wt bottle (g)	144.3
wt bottle+NaOH	260.7
wt bot.+NaOH+samp	413.4
vol CO2	5.0
vol H2S	223.0
vol NH3	10.0
vol Total	244.0
density	1.10
wt SrCO3	0.1818
wt BaSO4	0.8283
NH3 ppm	72.00
Temp Res (C)	24.00
PSIA Res	16.95

Gas	mol	mol/1000 mol H2O
H2O	8.372E+000	4.834E+000
CO2	4.047E-002	4.651E-001
H2S	3.894E-003	1.359E-001
NH3	1.137E-003	4.464E-001
Res	3.737E-003	5.881E+000
Total	8.421E+000	

TOTAL GAS ANALYSIS

Gas	wt % w/H2O	Mol % w/H2O	Mol % w/o H2O
H2O	9.871E+001	9.942E+001	8.219E+001
CO2	1.166E+000	4.806E-001	7.909E+000
H2S	8.686E-002	4.624E-002	2.310E+000
NH3	1.268E-002	1.351E-002	0.000E+000
He	0.000E+000	0.000E+000	0.000E+000
H2	1.857E-003	1.671E-002	2.858E+000
Ar	1.778E-004	8.074E-005	1.381E-002
O2	0.000E+000	0.000E+000	0.000E+000
N2	4.599E-003	2.979E-003	5.095E-001
CH4	2.056E-002	2.326E-002	3.978E+000
C2H6	0.000E+000	0.000E+000	0.000E+000
Total	1.000E+002	1.000E+002	9.977E+001

FID GAS ANALYSIS 12 Sept 78

CCStd=10.0 CCSamp=10.0

gas	rel. area	std (ppm)	ct std	ct sample	CH4/gas	ppm res (mol)	ppm total w/o H2O
methane	1.0	100	27566	27218568	1	524129.7	39783.55
ethene	1.6	0	0	10	4354971	0.1	0.01
ethyne	1.3	0	0	0	0	0.0	0.00
ethane	1.6	100	53204	3885508	11	46762.9	3549.49
propene	2.1	0	0	0	0	0.0	0.00
propane	2.1	100	72752	995016	57	9124.0	692.55
propyne	1.9	0	0	0	0	0.0	0.00
2-methylpropane	1.9	0	0	62552	827	634.0	48.12
1-butene	2.6	0	0	0	0	0.0	0.00
n-butane	2.7	100	96108	198094	371	1412.8	107.24
2-butene	2.6	0	0	0	0	0.0	0.00
1-butyne	2.1	0	0	0	0	0.0	0.00
2-butyne	2.7	0	0	0	0	0.0	0.00
2,2-dimethylpropane	2.1	0	0	0	0	0.0	0.00
2-methylbutane	4.1	0	0	29349	3802	137.8	10.46
1-pentene	3.2	0	0	0	0	0.0	0.00
n-pentane	3.1	100	114589	29305	2879	182.0	13.82
2-pentene & cyclpentane	3.2	0	0	14901	5845	89.7	6.81
2,2-dimethylbutane	1.9	0	0	22798	2268	231.1	17.54
3-methylpentane	1.3	0	0	18431	1920	273.0	20.72
2-methylpentane	1.2	0	0	0	0	0.0	0.00
1-hexene	2.0	0	0	0	0	0.0	0.00
n-hexane & cyclohexane	1.6	100	107812	58248	748	701.0	53.21
benzene	1.6	0	0	1252810	35	15077.8	1144.47

Comments; Internal std method used for FID calculations.
$\partial13C$ = -6.4 (Janik et al, 1982)

*Data from Nehring and D'Amore (1984)