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Techniques for Geothermal Liquid Sampling and Analysis

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C. H. Kindle
E. M. Woodruff

July 1981

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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TECHNIQUES FOR GEOTHERMAL LIQUID SAMPLING AND ANALYSIS

C. H. Kindle
E. M. Woodruff

July 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

In sampling and analyzing geothermal liquids, flow uncertainties, sampling biases, preservation difficulties and analytical interferences may lead to unreliable results. As part of a Department of Energy project in this field, Pacific Northwest Laboratory (PNL) was to encourage a common approach to geothermal sampling and analysis. Drawing from varied sources, a methodology has been developed that is particularly suited to liquid-dominated resources and adaptable to a variety of situations. It is intended to be a base methodology upon which variations can be made to meet specific needs or situations.

The approach consists of recording flow conditions at the time of sampling, a specific insertable probe sampling system, a sample stabilization procedure, commercially available laboratory instruments, and data quality check procedures. Readily available equipment is utilized whenever possible.

In order to reduce the possibility of sampling nonrepresentative flows, the following actions are taken:

- sampling after the well has been flowed at a high rate for at least 1 day
- recording recent flow history of the well
- recording pressure, temperature, and flow rate at time of sampling.

The sampling system includes the following components:

- insertion probe - for sampling from a selected point inside the pressurized system piping
- cooling coils - for reducing temperature while maintaining pressure
- regulating valve - for reducing pressure after cooling to avoid scaling and steam flashing
- filter - for removing suspended solids.

Most sample components can be stabilized in the field for analysis in the laboratory as soon as practical:

- CO_2 is determined from a sample stabilized with NaOH.
- H_2S is determined from a sample containing zinc acetate.
- Cations and NH_3 are stabilized by acidification.
- SiO_2 is diluted ten-fold to preserve it in solution.
- Hg samples are collected in glass bottles containing an acid-oxidizer mixture.
- pH is measured in the field.

For laboratory analyses, a combination of standard techniques and commercially available instruments produce satisfactory results. Specifically, these methods are:

- spectroscopy [inductively coupled plasma (ICP) and atomic absorption (AA)] - for cations
- colorimetry - for silica and ammonia
- ion chromatography - for anions
- selective ion electrode - for ammonia
- titrations - for sulfide, alkalinity, hardness, CO_2, chloride
- gravimetric - for suspended and dissolved solids
- turbidimetric - for sulfate.

Data quality checks are used to ensure that the analytical results are consistent. Charge balance (anion-to-cation ratio) and mass balance (total dissolved solids-to-analyzed consituents ratio) are calculated.

Differences among various analytical techniques were also addressed in this project using the results from a round-robin interlaboratory analysis of samples from the Salton Sea and East Mesa geothermal fields. The results were interpreted to indicate which methods may require extra attention to calibration if they are used for geothermal samples. The basic interlaboratory uncertainty demonstrated a coefficient of variation of 15 to 40%. An ongoing round robin among laboratories would help to identify and eliminate biases and still allow individual laboratories the flexibility to use methods of their own choice.

ACKNOWLEDGMENTS

The authors appreciate the work of several PNL staff members involved in preparing this report. D. W. Shannon and K. Pool reviewed and commented on the manuscript and supplied data for the evaluation. D. E. Robertson provided the methodology for determining mercury. L. P. White, M. W. Cole and D. D. DeMonia performed much of the analytical work. N. D. Tobin assisted with the statistical re-evaluation of the analytical round-robin data. Helpful input also was received from individuals too numerous to list. S. R. Gano provided editorial assistance.

Funding for this project was provided by the U.S. Department of Energy, Division of Geothermal Energy under the technical direction of R. R. Reeber (Washington) and A. J. Adduci (Oakland).

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1. INTRODUCTION

Accurate fluid measurements are important for utilizing geothermal energy because data on fluid characteristics can be applied to process design, materials selection, plant operation and maintenance, and reservoir engineerng evaluations. Because no standard system has been established for obtaining samples, maintaining integrity, or reducing interferences, geothermal results may be incomplete or unreliable. Certain sampling methods may bias the composition to favor one component over another. Furthermore, preservation is often a problem; components may precipitate out, undergo chemical change or evolve as a gas. In the laboratory, analytical methods also vary and may not always account for interferences.

This report summarizes a versatile sampling system and analytical methodology, which is particularly suited to liquid-dominated geothermal resources. The techniques have evolved since 1976 as part of a Department of Energy project oriented toward resolving sampling and analysis uncertainties. This project has included a field evaluation of alternative sampling methods; field experience using the techniques described to support geothermal corrosion studies and a binary-fluid electric generating plant monitoring project; round-robin evaluations of analytical techniques; support to non-electric (direct-use) applications; and laboratory tests, discussions, literature reviews, and handbook compilation of available sampling and analysis methods.

The sampling system consolidates several techniques in order to obtain samples that are as representative of the source as possible. The procedure is described here in sufficient detail to permit samplers to assemble and operate their own systems. In this procedure, the samples are rapidly stabilized to prevent deterioration prior to analysis. The analytical approach is centered around commercially available instrumentation and standard or published methods, and is therefore described in less detail. A simple format is also presented for calculating charge and mass-balance quality checks for internal data consistency.

Included in the report is an evaluation of the comparative performance of alternative analytical techniques based on a 20-laboratory round-robin comparison. The appendices contain more detailed information on the sampling method, the round-robin evaluation, data quality checks, and sources of published analytical methods.

Continuing attention is being given to the problems of geothermal sampling and analysis and the establishment of common techniques. Persons interested in commenting on these or other techniques should contact:

C. H. Kindle
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington 99352

2. UNIFORM APPROACH TO SAMPLING AND ANALYSIS

At least five different factors affect the accuracy of analytical determinations in geothermal liquids. These sources of variation include:

1. flow composition shift with time and nonhomogeneous (two-phase) flow
2. differences in sampling methods
3. sample stabilization processes
4. different analytical methods
5. differences between laboratories using the same methods.

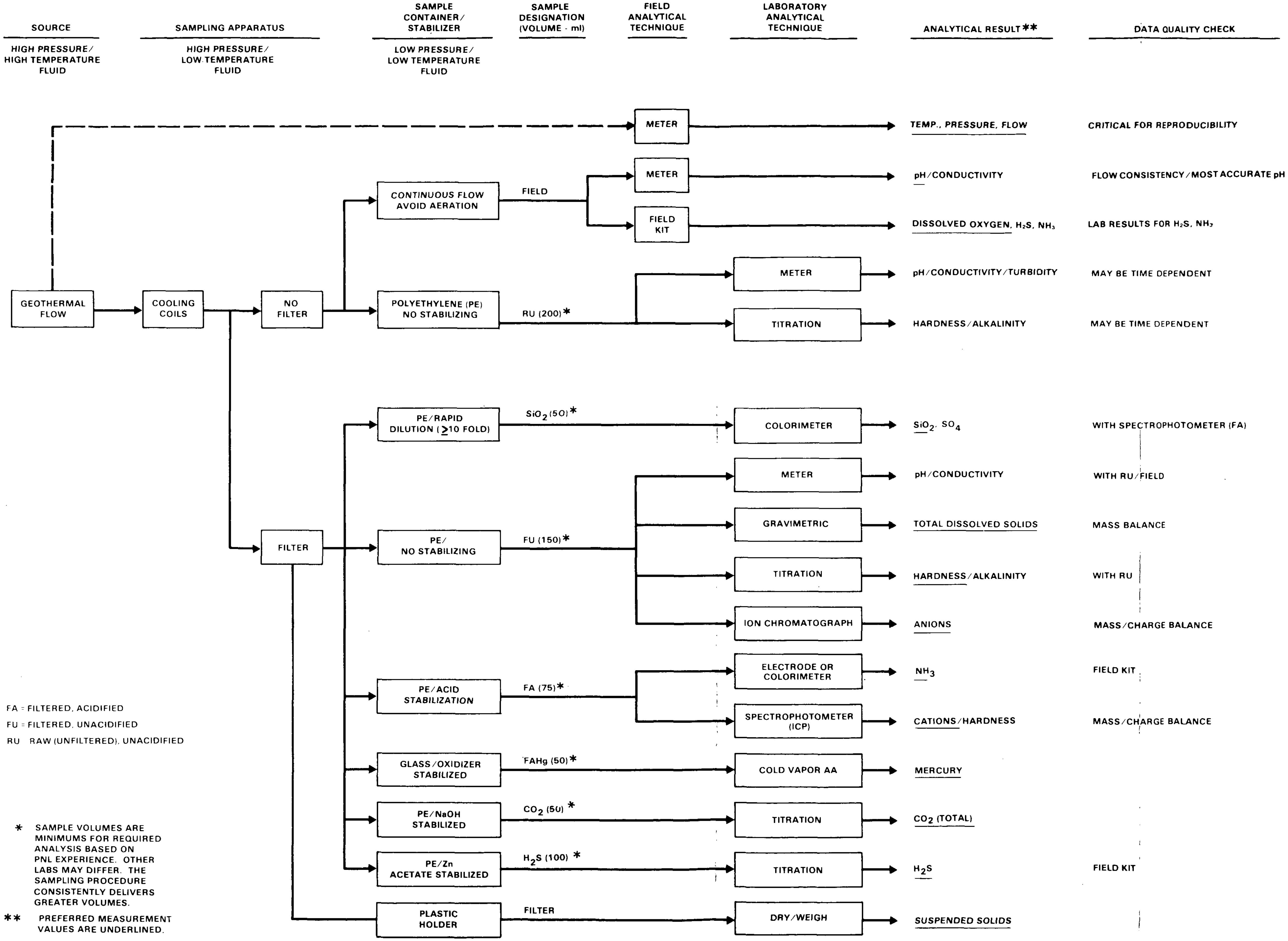
The concern about flow conditions (No. 1 above) has to be resolved on a site-specific basis. PNL's practice is to sample after flowing the well at production rate for at least one day. This technique avoids composition shifts that occur during well startup as a result of kill fluids or temperature gradient problems. Sampling methods presented here were developed for use in single-phase systems; two-phase sampling is discussed only briefly.

The uniform approach to sampling, sample stabilization, and analytical methods (Nos. 2, 3, 4 above) is discussed in more detail in this document, and is schematically related in Figure 1. The use of a sampling/analysis methodology based on this flowchart will improve the comparability and reliability of geothermal liquid composition data. Variations from this methodology, such as being unable to filter because of plugging or performing a precautionary dilution, can be handled in the field using this document and field conditions as a guide.

The problem of analytical differences between laboratories utilizing the same methods (No. 5 above) is discussed in the section on alternative analytical techniques. Increasing experience with geothermal samples should improve the situation. However, an ongoing, round-robin interlaboratory geothermal sample exchange would assist laboratories even more in identifying and eliminating biases. There is no such exchange now in operation.

Mitigating actions can be taken to minimize inaccuracies due to the above five variables. These actions are described in Table 1.

This uniform approach to sampling and analysis is oriented toward the use of a base support laboratory utilizing modern analytical techniques and reasonable control procedures. Field analysis is employed only for those measurements where preservation is not practical. The use of a field laboratory may reduce the need for some of the preservation steps.



FA = FILTERED, ACIDIFIED
FU = FILTERED, UNACIDIFIED
RU RAW (UNFILTERED), UNACIDIFIED

* SAMPLE VOLUMES ARE MINIMUMS FOR REQUIRED ANALYSIS BASED ON PNL EXPERIENCE. OTHER LABS MAY DIFFER. THE SAMPLING PROCEDURE CONSISTENTLY DELIVERS GREATER VOLUMES.

** PREFERRED MEASUREMENT VALUES ARE UNDERLINED.

FIGURE 1. Flowchart for Sampling Analysis

TABLE 1. Sources of Fluid Composition Variation and Mitigating Actions

Source of Variability	Example of the Extent of Variation	Mitigating Actions
1. Flow Composition Shifts a) with time b) with flow rate c) with position in two-phase flow	a) 65% Ca concentration reduction in 3 months at Salton Sea well (Needham et al. 1980) b) Carbonate concentration varies by 80% with changes in flow at East Mesa well (Riley et al. 1980) c) CO_2 concentration differs by factors up to 20 depending on sample point in two-phase flow (see text)	a) Flow the well for a day (or longer if possible) before sampling; record recent well flow history; resample later. b) Sample the well at production flow rates; record temperature, pressure, flow rate. c) Use full flow separator and sample resulting single phases; increase pressure to remake single phase; sample from different positions across diameter of pipe.
2. Sampling Differences	Varies with method and field conditions; 1c (above) would give a factor of 20. Most variations would be much more modest, particularly in single-phase work.	Use the method and equipment described (or a close variation); record sample point.
3. Sample Deterioration Before Analysis	Visual clouding within minutes after taking samples from Salton Sea brines, pH changes between field and laboratory.	Use the techniques described to check stabilization effectiveness; hold a duplicate sample for later analysis or submit a second field diluted set.
4. Analytical Method Differences	Using Reasonable Methods 15-40% is typical variation (text), worse with anions, and cations below ~ 1 mg/l.	Use techniques described; supervisory chemist should be knowledgeable; check results with data quality checks described.
5. Interlaboratory Differences		Supervisory chemist should be knowledgeable; laboratory participation in on-going round robins is desirable (best if there are geothermal samples in the exchange).

3. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are based on PNL's experience in geothermal liquid sampling and analysis:

SAMPLING SYSTEM

1. Inserting a sampling probe into the flowing stream avoids the possibility of contamination (corrosion products, dirt, scale) that is present in a normal service valve attached to the plant. The probe also permits easier identification of two-phase flows that bias sampling by allowing selection of a sampling position within the flow path to avoid trapped gas or stratified flow. Flow profiling is also possible.
2. Existing gate or ball valves are required for sample probe access to the pressurized flow. A 1/2-in. valve will provide enough clearance for most sample probes. Orientation to allow a tube to pass in a vertical direction is preferred if two-phase flow is a possibility.
3. The sample flow must be cooled under pressure to eliminate flashing within the sample collection system and facilitate handling. Cooling coils followed by a flow regulating valve permit pressure reduction without flashing or biasing the sample because of scale deposits and with a minimum of gas breakout.
4. Stainless steel is satisfactory for constructing the sample train. Precipitation of brine constituents in the sampling apparatus is negligible as far as biasing the sample.
5. The system is designed specifically for single-phase sampling but can accommodate limited quantities of gas and suspended solids normally found in geothermal sources.
6. The system can be adapted for operation with a pump to sample free flowing springs with the same filtering and stabilization steps used in pressurized systems. This maintains comparability of sampling techniques for a broad range of sources.

ANALYTICAL APPROACH

1. With few exceptions (described in the text), samples can be adequately stabilized in the field for subsequent analysis in an established laboratory.

2. For reliable pH values, the measurements must be made in the field. The flow should be cooled before being depressurized for pH measurement. Since pH is a function of dissolved CO_2 and the solubility of CO_2 is strongly temperature dependent, we propose a standard temperature of 25°C for the cooled sample flow.

3. The two types of atomic spectroscopy, absorption (AA) and emission (ICP), are both generally satisfactory for cation analyses.

4. Ion chromatography (pressurized ion exchange chromatography) is an acceptable technique for analyzing geothermal samples.

5. The flow rate, pressure, and temperature of the well at the time of sampling must be recorded to establish a basis for interpreting the sample composition.

6. The components of interest must be established before sampling because of the specific stabilization procedures required for certain components.

7. Results from different laboratories, using reasonable methods of their own choosing, will vary with a basic coefficient of variation (COV) of approximately 15 to 40% for cations and 10 to 50% for anions. This basic imprecision is better for a few major components (e.g., total dissolved solids - TDS, sodium, chloride), worse for cations at or below 1 to 0.1 mg/l concentrations, and generally exceeded for anions in concentrated brines.

8. The detailed conclusions from the round-robin evaluation of different analytical methods are in Section 7 "Alternative Analytical Techniques (Round Robin)."

4. GEOTHERMAL SAMPLING

Two major objectives must be satisfied in any geothermal sampling method:

1. Samples must be as representative of the source as possible.
2. A stabilization process must be initiated so the sample can be handled and transported to the laboratory without further changes affecting analytical results.

The sampling system described in this section has evolved into a step-by-step process that follows a convenient sequence designed to meet the two objectives stated above. The flow of operations has been incorporated in a uniform method for sampling single-phase geothermal flows and stabilizing samples for later analysis. The method is outlined in Appendix A and includes a data sheet for collection of field data that also serves as a check list or guide in completing the procedural sequence.

Development of this system included a field evaluation (Shannon et al. 1980) under controlled field conditions. During the evaluation, direct comparisons were made with other sampling methods. This test identified weaknesses in some other approaches while verifying the reproducibility of results obtained by using the methods described below.

SYSTEM COMPONENTS

The components of PNL's sampling system are illustrated in Figure 2. Briefly, the major elements are:

- insertion probe - provides access to a selected point inside system piping
- cooling coils - reduce temperature below boiling while maintaining pressure
- regulating valve - reduces pressure after cooling to avoid steam flashing and scaling
- filter - removes suspended solids to prevent their dissolution in samples stabilized by acidification.

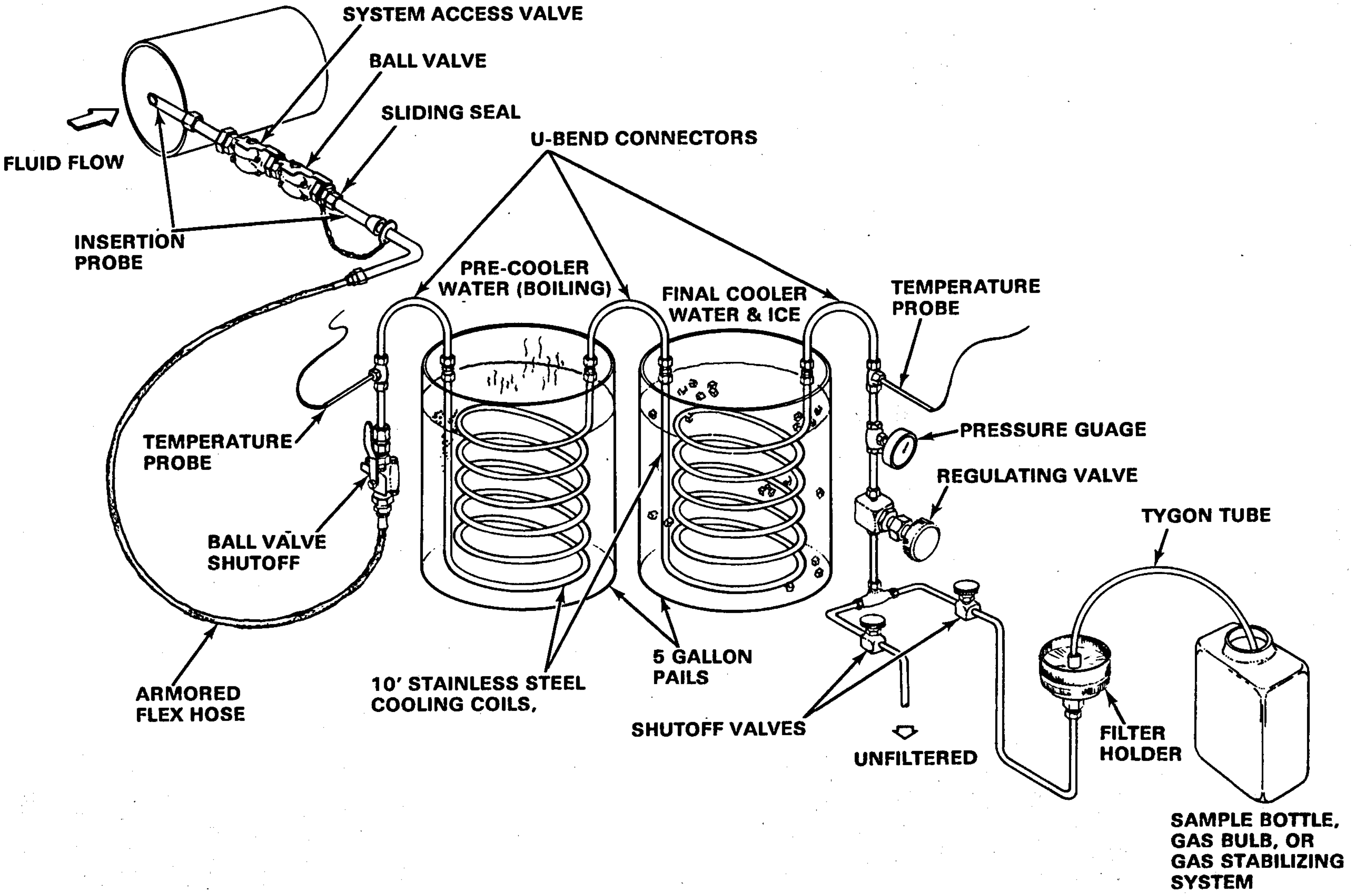


FIGURE 2. Geothermal Liquid Sampling Double Coil Assembly

System Access (Insertion Probe)

To accommodate the insertion probe, an unobstructed path through the valve is necessary. Gate or ball valves usually provide this path. The inlet tip of the probe then becomes the sample point and can be positioned at the center of flow in the pipe or numerous points traversing from side to side or top to bottom within the pipe for horizontal or vertical penetrations, respectively.

In selecting from several possible sample locations the following should be considered:

- proximity to fluid source - To be representative of a supply well, a point of access as close to the wellhead as possible is advisable. Some wellheads have sample lines installed, but their points of entry into the fluid stream can be difficult to verify. Of concern is whether access is directly into flow in the production string or involves the annulus between the casing and production string and the effect this may have on the gas content of the fluid produced. If this kind of uncertainty exists, use of the insertable probe immediately downstream from a wellhead is preferred.
- flow mixing - Flow can become stratified or zoned in long horizontal or vertical runs, particularly if there is entrained gas. A sample point downstream from an elbow, tee, or other bend takes advantage of internal mixing to produce more representative samples.
- mainline valves, orifices - Pressure reduction across flow restrictions can create conditions for steam flashing and the associated scaling or the release of dissolved gases even above the steam flash point. Most of these problems are avoided by selecting sample points upstream from restrictions; however, one precaution should be noted. A restriction sometimes creates a trap at the top of a pipe in which gas can collect and create a bubble on the upstream side. A probe inserted from the top will encounter gas only near the top wall and can be used to bleed the bubble off before the fluid is sampled.

Insertable Probe Assembly

The historical incentive for developing insertable probes came from the interest of sampling different positions across the flow stream. An early system, the "porcupine" method, consisted of permanently installed tubes of different lengths attached at intervals around the pipe circumference. A PNL handbook (Watson 1979) provides a description of this model as part of a compilation of various sampling and analytical methods that have been applied to geothermal situations (it is recommended to the reader). Hill (1975) established the concept of utilizing the sliding tube for sampling two-phase flow. An early version of the current model was a straight tube with a handle welded on at a right angle as an indicator of the direction the tip was pointing during sampling. A 90° bend at the exit end of the probe now serves as the directional indicator, and a safety chain has been added to prevent inadvertent probe extraction or expulsion (Figure 3).

A number of tube diameters from 1/8 in. to 1/2 in. (304 stainless steel tubing) were tested in PNL's studies. The 1/8-in. diameter tube was too flexible to maintain a fixed position after insertion in some systems. Although visual evidence of "whipping" was not possible, the sounds and vibrations emanating along the external portion of the tube suggested a very "active" tip inside the pipe. However, this should not cause any analytical problems,

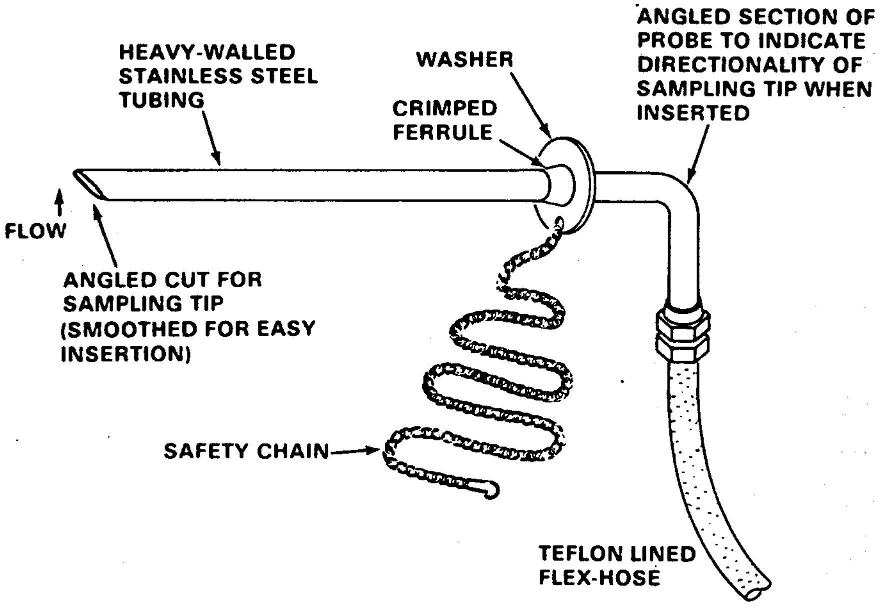


FIGURE 3. Sampling Probe

except for two-phase systems; the 1/8-in. tube is convenient and fits through 1/4-in. gate valves. Several wall thicknesses of 1/4-in. diameter tubing also were tested. Thin wall, 0.035 in., and intermediate wall, 0.065 in., both performed well when new but became bent after repeated use, which eventually impaired easy insertion. Changing to heavy wall, 0.083 in., in a 1/4-in. diameter tube reduced, but did not solve, this problem.

Currently, we use probes made from 3/8-in. diameter, 316 stainless steel tubing with a 0.065-in. wall thickness. These probes have remained straight with repeated use in the field and easily pass through 1/2-in. access valves. The inlet tips are formed by making a 45° cut and then grinding the tube wall to form a bevel away from the inside diameter of the tube. Each tip is rounded slightly to aid insertion through the sealing gland and reduce the possibility of hang-ups in passing through valves during insertion.

A tube ferrule is swaged onto the rear portion of the probe tube for a safety chain stop. Fittings normally permit swaging a ferrule with a nut at tube ends only. For mounting away from ends, a brass union of the tubing size is drilled (brass drills easily) to allow the tube to pass completely through to position the union/ferrule/nut assembly at any chosen location along the tube. Its position is a function of the overall tube length needed for the pipe size to be sampled, but the essential requirement is to stop tube retraction by restraining the safety chain when the tip of the probe tube is centered between the ball valve and the sealing gland (see Figure 2). Typical tube dimensions for probes inserted in 12-in. pipes (12 3/8-in. ID, 13-in. OD) are:

Overall tube length - 36 in.
Distance from entry to ferrule stop - 30 in.
Distance from entry to center of bend - 34 in.

To complete the probe, a washer with a ring attached is slipped on behind the ferrule; the tube is bent 90° in the direction of the opening at the inlet, and a nut and ferrule are installed at the exit end for flex hose attachment. An extra hole is drilled in the washer to accept a ring which in turn connects to the safety chain. The other end of the chain takes a snap to connect or disconnect to a matching washer and ring located between a ball valve and sealing gland that complete the probe assembly.

The ball valve is typically a Whitey "60" Series with a Teflon seal.(a) The sealing gland tested was a Conax PG gland (PG4-375-A-T) in which the gland is Teflon. The valve, gland, and probe tube remain assembled as a unit between sample jobs so the safety chain length always correctly matches the original configuration.

Armored Flex Hose

Early systems used loosely coiled 1/4-in. diameter tubes to connect probes to cooling coils. These tubes were difficult to pack and usually ended in being bent in a way that tended to lift or tilt the coils out of their buckets. The armored flex hose used in PNL's system solved the problems and made manipulations with the insertion probe much easier. Tests were conducted with Resistoflex R562 hoses, 6 ft long and 1/4 in. ID (Part No. R22105-5-72), that were lined with Teflon. The hoses are supplied with cadmium-plated carbon steel fittings on the ends that tend to corrode in geothermal fluids. However, no serious problems develop if the fittings are stored after being flushed with fresh water and dried. We have not observed any biases as a result of corrosion, although the potential does exist. A ball valve is attached to the exit end of the flex hose to serve as the master shut-off valve for the sampling system.

Temperature Probe

In-line temperatures are determined with stainless steel sheathed thermocouples inserted in matching tees and compression fittings designed for this purpose. Meters for direct reading of temperatures are available in many forms. Some of the more desirable meter and probe features for field use in geothermal sampling are:

- Sturdy waterproof case. Steam condensate can rain on geothermal sites even in the desert.
- Digital readout on meters are easier to see in direct sunlight if an LCD system is used rather than LED. Intense sunlight can cause an LCD window to "black out," but this can be restored to normal operation by shading it from the sun.

(a) Use of manufacturer or trade names does not imply PNL endorsement.

- Short thermocouple probes are less likely to bend and break during use.
- Probe leads should also be waterproof.

U-Bend Connector Tubes

These tubes and all other tubing components are fabricated from 1/4-in., 316 stainless steel tubing with a 0.035-in. wall thickness. The U-bends connect the coils and the inlet and outlet attachments. They apply a load down on the coils keeping them submerged in the cooling buckets. A typical jumper has a smooth 180° bend with a 4-in. space between ends.

In connecting U-bends to the coils and assembling other components, care must be taken to avoid leaks. Abnormally high oxygen levels (15 to 20 ppb) have been detected in samples and then traced to slow leaks at connections. Back diffusion at the fitting, even in pressurized systems, apparently allows sufficient oxygen to enter the sample stream for detection by dissolved oxygen field analysis kits sensitive in the 0 to 40 ppb range (CHEMetrics Inc., Dissolved Oxygen Test Kit, Model 0-40). Elimination of the leak by tightening or reassembling the loose fitting reduces oxygen to undetectable levels which is normal for fluid produced from deep wells.

Cooling Coils

Coils are typically formed from 10-ft lengths of 1/4 in. stainless steel tubing wound around an 8-in. pipe. For sampling fluids above 100°C, two coils are placed in series with the first cooled by allowing water in the bucket to boil. The second is cooled with ice and sufficient water to establish contact with the coil. During active sampling, the first bucket extracts heat from the sample flow that would otherwise consume a large amount of ice. The heat of vaporization of water is much greater than the heat of fusion. The flow is directed to the bottom of the coil and then spirals upward to assist in flushing entrained gas through the system. This also places the final loop of the second coil in contact with the coldest part of the bath (ice-water mixture). For systems producing fluid at 100°C or less, a single coil in an iced bucket provides sufficient cooling capacity. Single coils of 1/8-in. diameter tubing and 20 ft in length have been tested in an iced bucket. Although the rate of fluid delivery is reduced, the small size and single bucket are advantages when mobility is important.

Deposition Studies

Because mineral deposition in the sampling train could be a potential problem, studies were conducted on coils used during field evaluation of sampling methods to determine whether significant amounts of fluid constituents were accumulating. After the supply well (East Mesa 6-2 in the Imperial Valley, California) was sampled in triplicate, the coils were flushed with distilled water, disconnected, sealed and returned to the laboratory for subsequent study. Actual flow of 22 liters of well fluid was recorded during sampling. In the laboratory, internal deposits were stripped by flushing with an inhibited HCl solution made up using the following proportions:

200 ml concentrated HCl
200 ml distilled water
5 ml formaldehyde

Analyses of stripping solutions for three U-tubes and both cooling coils were totaled and normalized for the volume of source brine pased through the coils. The results in Table 2 show the original analyses for the triplicate brine samples, their standard deviation, and the comparable concentration per liter lost to deposition in the coils and U-bends.

No deposits that would measurably bias brine samples were found. Some dissolution of the stainless steel tubing by the stripping solution is reflected in the Fe analysis and was also noted in Cr and Ni results. Calcium and arsenic, which are normally found in scales produced by brines in the vicinity of East Mesa 6-2, were not lost in significant amounts in the sampling coils. Visual examination on a separate section showed no evidence of deposition.

Adaptations

The preceding description applies to most geothermal sampling requirements after a well has been completed and flow tests are under way or fluid is being delivered to a utilization system. For sampling springs or other gravity flows

TABLE 2. Coil Deposition Study

Element	Brine Analysis, mg/l	Amount Deposited in Coils, mg/l
As	0.58 ± 0.03	0.0104
B	7.2 ± 0.2	0.0004
Ba	0.3	0.001
Ca	10.7 ± 0.2	0.011
Fe	0.48 ± 0.03	1.7557
K	122 ± 1	0.0027
Li	4.65 ± 0.1	---
Mg	0.11 ± 0.02	0.0013
Na	1456 ± 22	0.0038
P	0.1	0.002
Sr	2.2 ± 0.06	0.0009

using the same apparatus, some means of pressurizing flow is necessary to pass it through the cooling coils with enough pressure for filtering and sparge tube stabilization of H_2S and CO_2.

On several occasions we have been able to position the cooling coils below artesian flow from wells and achieve cooling, but were unable to filter. The solution for this type of sampling has been to include a field-model peristaltic pump in the list of accessory equipment items. Features which make this unit(a) particularly suited for this purpose include:

- rechargeable battery
- an adapter for use with a 12-V car battery
- 115 VAC line cord
- compact size--11 1/2 x 7 in. x 8 in., and light weight (~15 lb)
- weighted tubing tip that can be added to inlet tube to aid in holding it submerged in a spring or wier.

(a) Portable Masterflex Sampling Pump, Horizon Ecology Corp., 7435 N. Oak Park Ave., Chicago, IL 60648.

By inserting the pump in the system between the cooling coils and the filter housing, heating the pump head is avoided although the silicone tubing with this type of pump is rated to 260°C.

Pails

Five-gallon paint pails are traditionally used for cooling baths. They last several months before rusting through if used continuously at one location. If moved from place to place their ability to nest and separate is soon lost to corrosion and the rims become deformed by beating them apart. Tapered stainless steel buckets that nest are now used. These buckets eliminate battering exercises and problems with corrosion.

Valves

Perhaps the most important factor in controlling flow in this type of sampling system is the location of the regulating valve on the cold side or in a downstream position with respect to the cooling coils. At this point, the fluid has cooled well below the steam flash point. The pressure drop across the valve can take place without the violent surging and unstable flow experienced in "hot side" regulation. Hot-side regulation is also plagued by scale that deposits in the valve and is dislodged by any motion of the valve stem. Thus, either an opening or closing motion of the valve immediately increases flow and slugs of steam are produced at the outlet. The PNL system uses Whitey SS-IRS4 regulating valves (others would likely perform as well).

Exit shut-off valves divert flow from filtered to unfiltered samples. These valves may be either stemmed valves (a typical example is the Whitey SS-14DKS4) or small ball or plug valves. Because of corrosion problems, copper based alloys (brass) are avoided.

To initiate and regulate flow the following sequence is followed:

1. close all valves
2. insert probe in seal
3. open probe valve and system valve
4. insert probe to sampling position, tighten seal and secure safety chain

5. open ball valve of flex hose exit
6. check for system leaks in coils
7. fill buckets with water and ice
8. open one exit shut-off valve
9. open regulating valve and adjust for desired temperature on exit temperature probe.

To stop the flow, the main inlet ball valve is used.

Filter and Filter Holder

The filter pore size recommended for geothermal sampling is 0.45 μm. A filter holder found convenient for assembling and disassembling in the field is the Millipore Swinnex. It accepts 47-mm diameter filters and should be oriented for vertical upward flow through the filter.

Exit Tubing

About 18 in. of Tygon tubing is attached to the stainless tube or filter outlet for convenience in filling sample containers.

Sample Bottles

Collection and shipment is made in rectangular or square polyethylene bottles for efficient packing. Lids are also polyethylene since other plastics often break during shipment. Closure designs with an extended lip on the bottle fitting into a matching groove in the cap survive shipment with fewer leaks than other designs. Kartell makes a wide mouth line of square bottles with this type of closure (Markson Cat. No. R14443, 1000 ml).

Miscellaneous Equipment

Other items supporting sampling operations which can be considered a minimum "tool kit" include:

Safety

Safety glasses
Heat resistant gloves (3 ply leather)
Coveralls - (burn protection for bare arms and legs)
Work gloves - leather or canvas
Surgeons gloves
Hard hats

Field Analysis

Kits for H_2S, NH_3, O_2
pH meter
Temperature meter and probes

Housekeeping

Plastic bags (can be used ice bags)
DI water (coil and utensil flush)
Plastic pail and 1 qt. plastic pitcher (for bailing excess meltwater)

Hardware

Assorted reducers, connectors, couplers, nuts, and ferrules for adapting to field requirements
Small wrenches for tube fittings
2 large crescent wrenches for probe and gland
Pliers
Tape for securing bottle tops
Tubing - tygon, 1/4 in. stainless steel
Tube clamps
Spare filter housing and o-rings
Duct tape, cord, baling wire (for tie downs), felt tip pen.
Knife
Measuring Tape (to measure insertion distances)

DIFFICULT SAMPLING SITUATIONS

This procedure recognizes that in the real world the sampler may encounter a geothermal source in which some gas breakout has occurred before the sample can be cooled. Breakout can occur even when sufficient pressurization is maintained to prevent steam flashing. Where breakout is appreciable the method described for collection (Appendix A, 12.1 to 12.5) will produce a gas sample in a reasonable amount of time. Interpretation of the results with respect to total flow should be done with caution, however, since the gas as collected in the gas bulb does not include the dissolved fraction passing through the bulb.

The sampling of two-phase flows to get a representative sample, even through compositing, is a difficult task. In part this difficulty is due to the wide variation in the types of two-phase flow that occur; the sample points and interpretations may differ for each type. Figure 4 relates the modes of two phase flow discovered during one study. Isokinetic sampling has

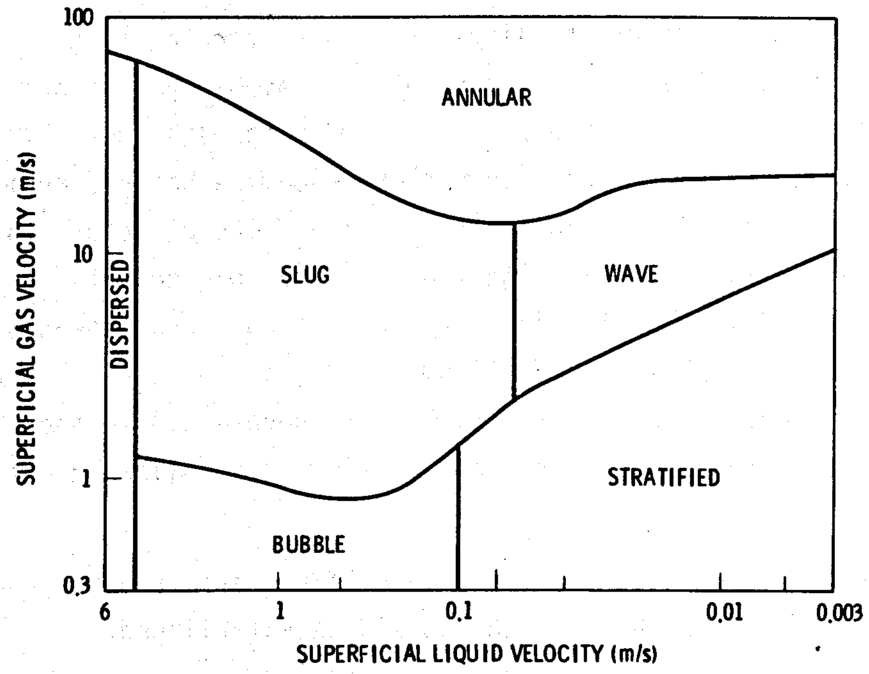


FIGURE 4. Two-Phase Mode Versus Flow Velocity (Freeston and Lee 1979)

been recommended (Riley et al. 1978), but at the end the data must be reassembled using unknown mass flow rates to give total flow composition. We have used the techniques described here and some simplifying assumptions to repeatedly sample a flow in a two-phase region. The results compared fairly well to the composition determined at a location of single phase flow for some components, but agreed poorly for others (such as CO_2 and Ca). However, this research exercise may not work quite so well in another location. In general, all techniques that sample from discrete locations in a two-phase flow will be biased to some extent. A full flow separator with subsequent single phase sampling avoids this problem. The methods to sample a two-phase flow are listed in decreasing order of reliability.

- full flow separator with subsequent single phase sampling
- multiple location probe sampling
    1. isokinetic
    2. nonisokinetic
- single location probe sampling
    1. isokinetic
    2. nonisokinetic
- nonprobe (valve) sampling.

The determination of gas-to-liquid ratios [referring to noncondensible gases (NCG)] involves the use of a separator. The design and operation of small separators is not standardized. Some operate with the pressure drop after the separator, some before; some operate on the hot geothermal fluid, while others cool the fluid prior to separation. These factors (pressure, temperature) are very critical to getting reproducible results. Figure 5 illustrates variability due to flow rate when using a non-isokinetic 1/4-in. probe to sample a two-phase flow. Figure 6 illustrates the temperature variability of NCG composition as a function of temperature. In the absence of standard separator design or operating practice, the following actions are recommended:

- The effect of variation in temperature, flow rate, and pressure on the NCG output of each separator should be established.

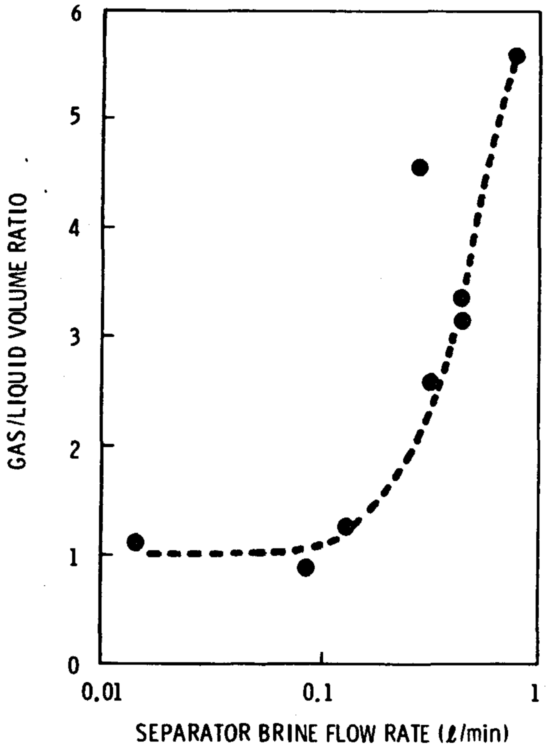


FIGURE 5. Example of NCG Gas/Liquid Ratio Sensitivity to Separator Flow Rate (data from Shannon et al. 1980)

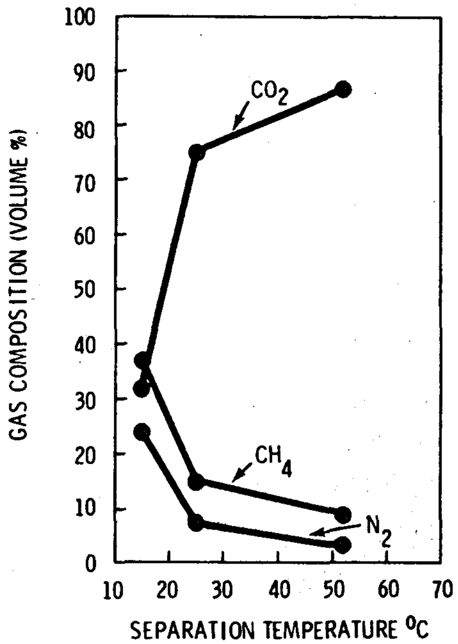


FIGURE 6. Effect of Separation Temperature on Free NCG Composition (data from Shannon et al. 1980)

- If two-phase flow is a possibility the sample probe should sample from more than one position.
- These parameters should be recorded whenever a separator is used.

ALTERNATIVE SAMPLING SYSTEMS

Other sampling systems in use range from dip bottles to evacuated flasks to selective absorption tubes. Watson (1979) includes a compilation of many sampling approaches. Some are used for specific fluid constituents or are adapted to transport by backpack and are beneficial. Others have been adapted from nongeothermal applications and can introduce large errors. Figure 7 illustrates one of the latter cases, in which hot pressurized brine was admitted into an evacuated stainless steel flask. To simulate a worst case, the flask was sealed and stored for 2 weeks before the sample was analyzed. The positive biases can be attributed to corrosion products from reaction with the flask; the negative bias can be attributed, at least in part, to precipitation during flashing when the sample was collected and no stabilization.

Another approach which is frequently utilized (unavoidably in some cases) is to withdraw a sample via an existing valve rather than using an insertable sample probe to get into the main stream. Figure 8 relates a situation encountered when using an insertable probe to sample two-phase flow. Without the probe, and just using valves at the top and bottom of the pipe, one sample would contain 500 mg CO_2/l and one more than 10,000 mg CO_2/l. Both would be defensible and reproducible. Use of an insertable sample probe in a traversing mode is critical to identifying segregated two-phase flow (which could heavily bias the sample).

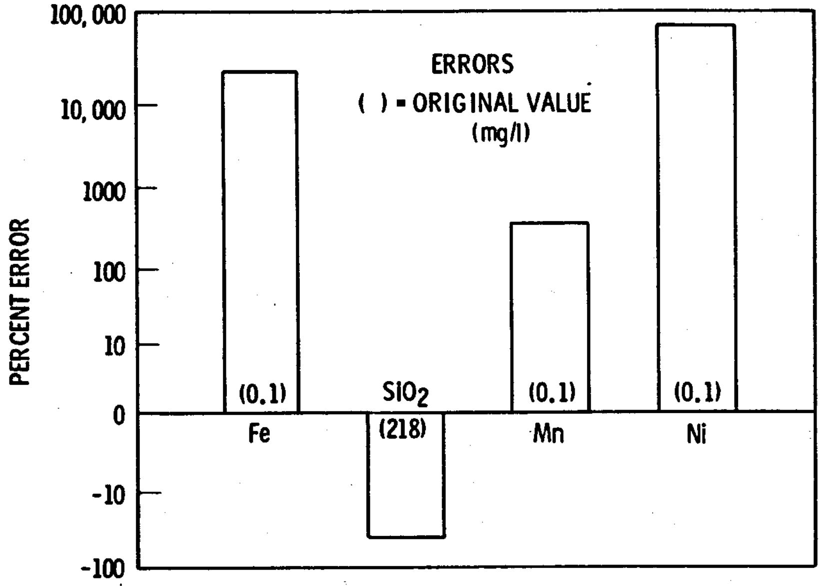


FIGURE 7. Worst Case Errors Encountered Using Evacuated Steel Flask Sampler (Kindle 1980; Shannon et al. 1980)

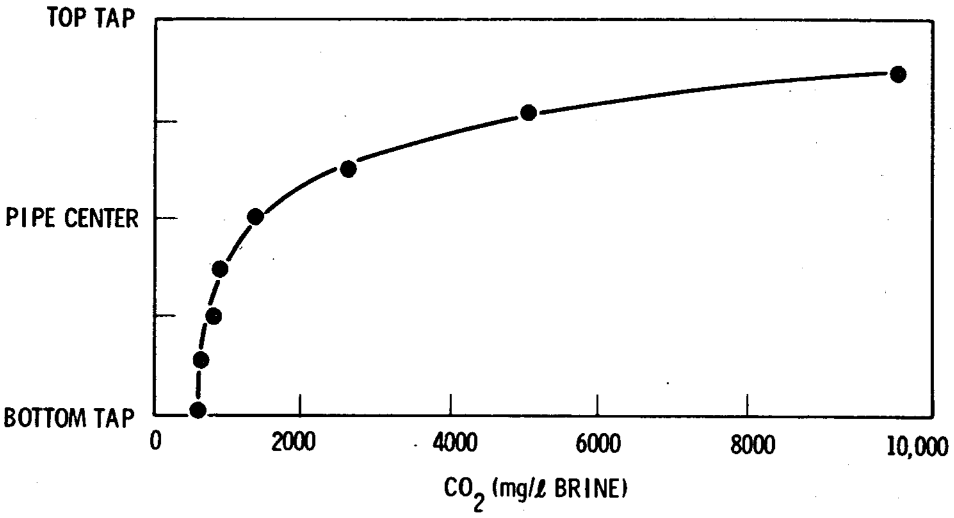


FIGURE 8. CO_2 Composition Versus Sample Point (Kindle 1980; Shannon et al. 1980)

5. SAMPLE STABILIZATION

Special preparations for stabilizing some samples for later analysis are necessary precautions. These preparations are made most conveniently and accurately in the laboratory prior to departure to the field. As Presser et al. (1974) states:

> The most commonly observed changes in untreated samples are in pH, iron, manganese, bicarbonate, ammonia, hydrogen sulfide, calcium, and sulfate. Silica concentrations in excess of 100 mg/l (milligrams per liter) may lead to difficulties owing to precipitation and polymerization. Polymeric silica is not reactive in the ammonium molybdate method that is often used for laboratory determination of silica.
>
> The changes in sample composition result from loss of carbon dioxide to the air space, oxidation and precipitation of iron and manganese, oxidation of hydrogen sulfide to sulfate, oxidation of ammonia, loss of calcium ion as calcium carbonate precipitates, and precipitation of silica. Waters inoculated with diatoms may also lose silica. Once a precipitate forms, there is no accurate way to restore the initial composition of the solution. Constituents that will probably be unaffected by storage include sulfate (if no hydrogen sulfide was originally present), lithium, sodium, potassium, magnesium, fluoride, chloride, bromide, iodide, and boron.

A stabilization sequence is described below. The specific container volumes used depend on the needs of the laboratory except that the sparge tube (glass tube with frit on end) stabilization efficiency will likely depend on the height of the stabilizing solution above the glass frit.

1. For CO_2 preservation, the sample flow is directed into 1-liter bottles that are exactly half filled with 2N NaOH stabilizing solution to start (Figure 9). The flow is passed to the bottom through a glass tube with a glass frit sparger to ensure that any gaseous CO_2 contacts the NaOH before exhausting. PNL's collection efficiency using the single sparge bottle is shown in Figure 10.

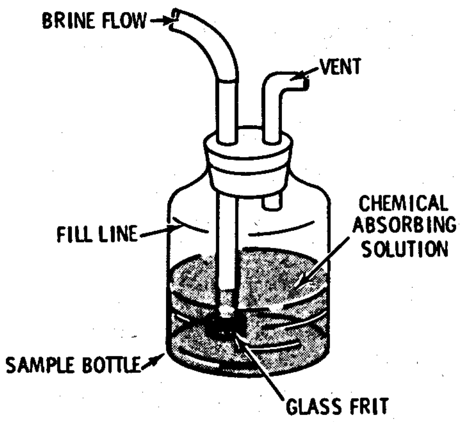


FIGURE 9. Gas Stabilization Device

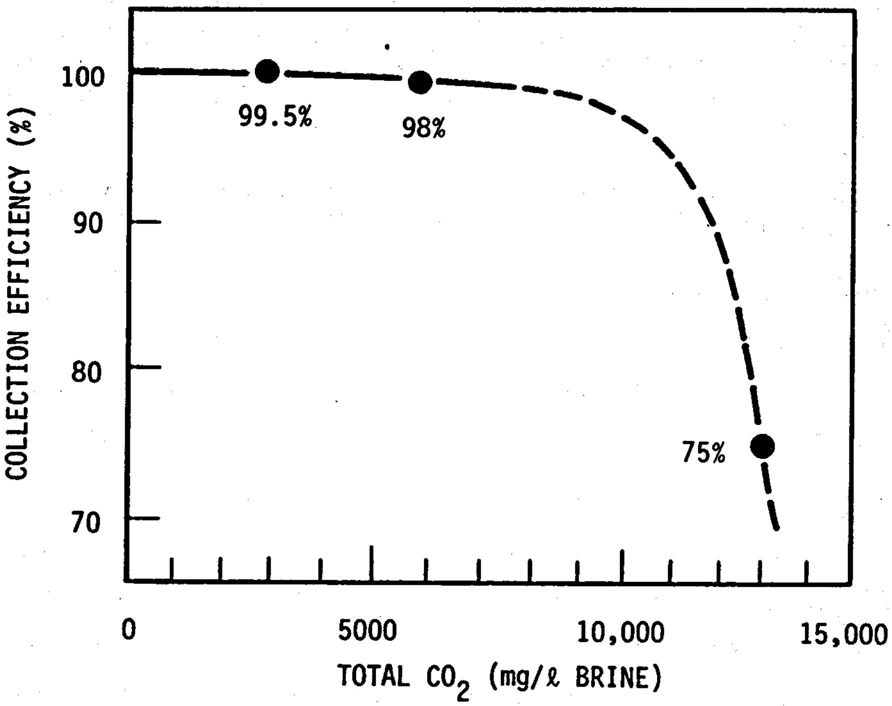


FIGURE 10. Single Sparge Bottle Efficiency (data from Shannon et al. 1980)

This efficiency would vary with the gas flow rate. The PNL flow rate is an empirically judged, moderate bubbling rate. For persons new to the technique, a couple of trial determinations using two bottles in series is recommended. Unstabilized solutions will rapidly lose CO_2 to the atmosphere before the analysis can be done.

2. For H_2S preservation, the same sparge technique is applied only using 500 ml of 0.5 N zinc acetate in a single bottle. This zinc acetate stabilization was used during the round robin sample exchange (Section 7). Despite the delays of sample shipping and laboratory scheduling, the average results showed no loss of sulfide compared to the composition value of the two synthetic samples. However, there is a rapid deterioration rate in samples exposed to natural light (Figure 11). (Figure 11 is included to illustrate the sensitivity to light; it is not intended to relate long-term stability for all geothermal waters.)

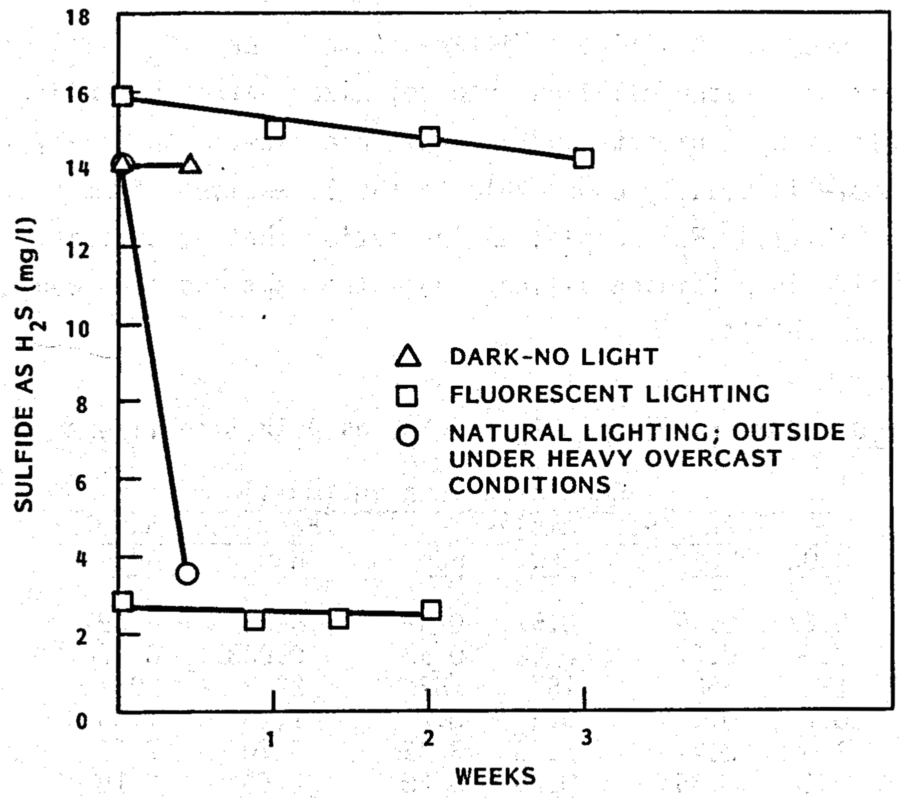


FIGURE 11. Instability of Sulfide in the Presence of Light, Zinc Acetate Preservation

3. Cations are stabilized by acidification and the container is labeled FA (filtered, acidified). Ten ml of concentrated HNO_3 or HCl are put in the 1-liter sample bottle (to 1% of its volume) and this bottle is sealed until used in the field. Limited testing indicates no difference between the two acids at least down to our routine analytical limits in stabilizing cations (Table 3). HNO_3 seems to be used more commonly than HCl. Where there is particular interest in cations that form marginally soluble chlorides (eg., Ag), HNO_3 would be preferable.

4. For mercury analysis the sample is stabilized by 1% (volume) of a 5% $KMnO_4$ solution, 1% (volume) of concentrated HNO_3, and 2% (volume) of a 5% $K_2S_2O_8$ solution. Glass bottles (labeled FAHg) are used to collect and store the samples to prevent possible biases from a plastic container. A bias caused by mercury diffusing through the wall into the sample is shown in Figure 12. The mercury sample is analyzed as soon as possible.

5. Dilution is used to stabilize a filtered sample for SiO_2 analysis. The ten-fold or greater dilution into deionized water is performed in the field using a pipette and a volumetric flask. The analysis of this sample is usually comparable to the Si analysis from the filtered, acidified (FA) sample, an indication that acidification is also effective in retaining silica. An extra cautious step would be to dilute and acidify.

TABLE 3. Comparison of HNO_3 and HCL as Acid Stabilizers

	Concentrations in (mg/l)					
	Raft River Samples				East Mesa Sample	
	HNO_3	HCL	HNO_3	HCL	HNO_3	HCL
B	0.47	0.45	0.57	0.57	8.53	8.69
Ba	0.08	0.07	0.52	0.52	0.863	0.876
Ca	159	150	187	187	29.2	29.3
Fe	0.1	0.1	0.2	0.2	1.28	1.38
Li	3.01	2.74	3.46	3.46	6.70	7.17
Mg	0.40	0.36	0.29	0.28	2.05	2.18
Na	1470	1400	2040	2040	2417	2535
Si	32.3	32.0	29.3	29.8	105.6	109.4
Sr	0.96	0.94	6.80	6.78	6.77	6.83

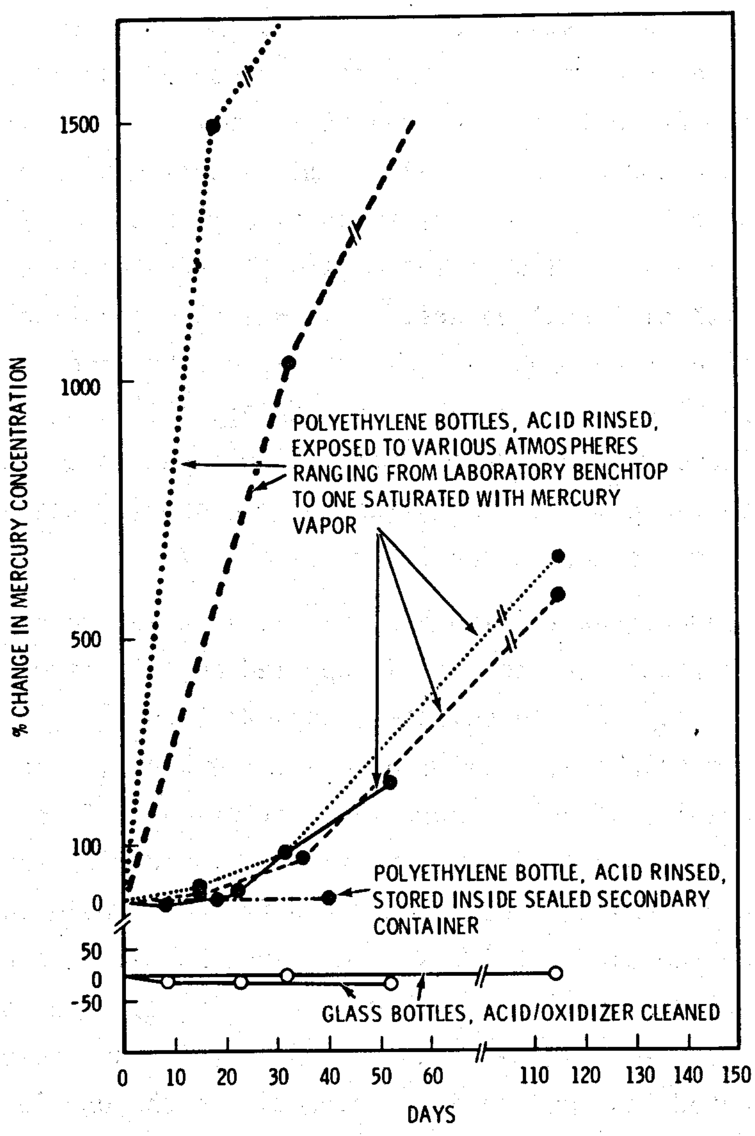


FIGURE 12. Comparison of Polyethlyene to Glass as a Storage Container for Saline Solutions when Mercury Concentrations are Quantified. Initial concentrations were 2-25 x 10^{-3} ppb. (Data from Bothner and Robertson 1975).

6. Acidification is used to stabilize NH_3 as NH_4^+ and measure it in the filtered, acidified (FA) sample. Flowing the cooled liquid sample directly into the FA container is adequate to mix and stabilize; a sparge tube is unnecessary (Table 4). Limited comparisons of ammonia preservation options indicated a deterioration rate of 0-3%/week when using HCl stabilization (1% by volume) without refrigeration. This rate may vary with different waters. This HCl stabilization was utilized during the round robin; the ammonia results were among the more precise reported (not typical of something undergoing degradation). While there was some deterioration indicated in comparing results to synthetic composition values for one sample, the difference was less than a standard deviation (Section 7).

7. For SO_4 the filtered, unacidified (FU) sample is used; no preservation technique (except filtering) is applied on this sample. In some fluids sparingly soluble sulfates, such as $BaSO_4$, may be above their equilibrium solubility limit; however, the kinetics of precipitation are apparently sluggish under many situations. To check for any loss in the SO_4 concentration, the field-diluted SiO_2 sample can be compared to the undiluted FU value. A difference would indicate a bias that can be remedied, if it is of concern, by taking a diluted and highly HCl acidified sample either in the SiO_2 split or separately. Figure 13 demonstrates $BaSO_4$ solubility in NaCl solutions. It is not advocated that HCl be added directly to the undiluted sample (making it a FA sample) as a means of improving the solubility.

TABLE 4. Equivalence of Two Ammonia Collection Practices. Sampling Rate 220 ml/min; liquid temperature 26°C; liquid pH adjusted; NH_3 concentration, mg/l

	Liquid Sample pH		
Collection Practice	pH 4.1	pH 6.9	pH 10.1
Sample Runs into Open (FA) Bottle	0.63	0.62	0.59
Sample Delivered Via Sparge Tube to Bottom of (FA) Bottle	0.65	0.62	0.57

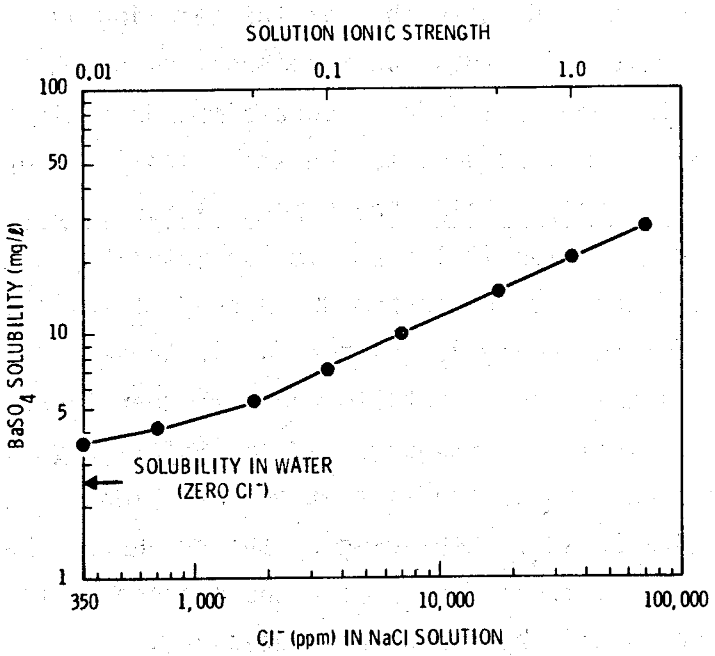


FIGURE 13. $BaSO_4$ Solubility Versus Ionic Strength; 25°C NaCl Solutions (plotted data from Davis and Collins 1971)

The acid seems to act to speed up the kinetics of precipitation to reach the solubility limit: four FA-HCl samples (East Mesa 8,000 ppm TDS) lost 15 to 20% of the SO_4 after 8 months compared to identical FU samples; Harrar (1981) reports slight acidification to cause rapid $BaSO_4$ precipitation in a Salton Sea brine.

8. Once they are filled, the sample bottles are placed into a large cardboard container and covered with the box lid. This serves to keep the samples out of the light as well as being convenient for organizing the field operation.

There are other stabilization approaches, or variations (for example, EPA 1979; Presser et al. 1974; Hankins 1980; Kroneman 1981). Some specify certain acids for preserving certain constituents; cooling samples to 4°C; acidifying samples to a precise pH; or delaying no more than 1 day before completing certain analyses (e.g. NH_3).

The experience to date indicates that if the sampling is conducted and the samples stabilized as described, subsequent composition changes will be gradual enough to allow adequate opportunity for accurate measurements (with a possible qualification for H_2S). However, despite the stabilization steps indicated in this discussion, the samples still should be analyzed as soon as practical in order to minimize degradation in the particular water being analyzed since the range of geothermal water types is broad. A prudent initial test would be to perform a second, delayed analysis (either duplicate samples or later reanalysis depending on the constituent) to check whether there is any deterioration involved in the particular resource and analytical sequence. This is particularly true for those constituents that may have legal (environmental) implications such as H_2S or NH_3. Depending on the resource, the constituents of interest, the analytical factor, and the purpose of the testing, there may be some cases where stabilization is not necessary.

6. ANALYTICAL SYSTEM

The approach that PNL takes to the analytical end of the measurement process is described in two sections:

1. Analytical techniques
2. Data quality check

The purpose of this discussion is to relate analytical techniques found to be reliable over a wide range of geothermal sources.

The analytical techniques described here do produce satisfactory results, but are not necessarily unique in that regard. A laboratory experienced in geothermal analysis using other techniques may also do very well. Section 7 discusses other options.

ANALYTICAL TECHNIQUES

Standard techniques and commercially available instruments are generally acceptable for analyzing geothermal samples. These techniques and instruments range from classical wet chemical acid titrations to modern spectroscopic and ion chromatographic techniques. The specific methods used by PNL are:

Spectroscopic: Inductively Coupled Plasma (ICP) and Atomic Absorption (AA) for cations
Colorimetric: for silica and ammonia
Ion Chromatography: for anions
Selective Ion Electrodes: for pH and ammonia
Titrations: sulfide, alkalinity, hardness, CO_2, chloride
Gravimetric techniques: suspended and dissolved solids
Turbidimetric: sulfate

The use of the ICP is of particular benefit to a laboratory which analyses a broad range of samples. The simultaneous multi-element readout minimizes the chance that a dramatic change in one component will go unnoticed.

The techniques are described briefly below and referenced to standard methods where available.

Inductively Coupled Plasma (ICP)

ICP, an atomic emission spectroscopic technique, is routinely used for metallic cations. Field-filtered and acidified samples are analyzed directly on the Jarrell-Ash instrument without any other treatment except for dilution when instrumental limitations require it.

The ICP analyzes the following cations: Al*, Ag, As*, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg*, Mn, Mo, Na, Ni, P*, Pb, Sb, Se*, Si, Sn*, Sr, Th, Ti, Tl*, U*, Zn, Zr. [The marked elements (*) are ones that we have found to require particular care in calibration.]

Exceptions for cation analysis are:

1. Mercury - use cold vapor atomic absorption (CVAA) in order to get the necessary sensitivity.
2. Silicon - use the colorimetric method for silica (the comparison with the ICP FA sample is usually very close).
3. Potassium - compare with the AA if the ICP sensitivity is limited.

Many ICP instruments require the selection of a particular analytical wavelength for each element at the time of purchase. This choice is then hard-wired at the factory and permanently fixed. The wavelengths that were specified for PNL's instrument are listed in Appendix B. For a single sodium and a single potassium wavelength (as opposed to our dual wavelengths) we recommend the wavelengths identified as "low-potassium" and "high-sodium" as appropriate to the widest range of geothermal fluids.

Atomic Absorption (AA)

Mercury is analyzed exclusively with a cold vapor atomic absorption (CVAA) technique to give sensitivities below 10 parts per trillion on a 250 ml sample. The technique is a variation from both the standard APHA method (Part 301A[VI], APHA 1979) and the EPA equivalent (Method 245.1, EPA 1979); also see Bothner and Robertson (1975). PNL has adopted the use of acid-rinsed glass to contain the sample (rather than plastic) and the addition of all the stabilizing oxidizing agents ($K_2S_2O_8$, HNO_3, $KMnO_4$) at the time of field collection (rather than later in the laboratory). The laboratory steps are correspondingly fewer, but still involve hydroxylamine sulfate reduction of excess permanganate, and stannous chloride reduction of mercuric ions. We have also used a straight AA for determination of potassium.

Selective Ion Electrodes (SIE)

SIE methods are used to measure pH and ammonia concentrations. Vendors operating instructions are followed in the laboratory. However, delayed pH measurements made in the laboratory are completely unreliable for characterizing the geothermal liquid exactly as it is when it flows through the plant. The pH measurement must be made at the time of sampling on the cooled (recommend 25°C), newly depressurized liquid. The conditions of the measurement should be noted.

Ion Chromatography

Ion exchange liquid chromatography with conductimetric detection is used to simultaneously determine the following anions: chloride, fluoride, nitrate, phosphate, and sulfate. Procedural details and suggestions supplied by the vendor (Dionex) are followed. In addition, chloride is determined by silver nitrate titration and sulfate by a barium based turbidimetric technique.

Wet Chemistry

Volumetric Methods

1. Total sulfide/H_2S: The iodometric titration with standard iodine, and thiosulfate for back titrating, is similar to that described in part 428D, APHA (1979).
2. Alkalinity: A neutralization titration to a pH 4.5 endpoint using standard acid as titrant determines total alkalinity as described in Part 403, APHA (1979). The alkalinity value (similar to the pH value) may be time dependent due to the evolution of CO_2 from the sample. For this reason, reported alkalinity numbers may be suspect for many geothermal systems. The information obtained from a traditional alkalinity value could probably be exceeded by the knowledge of the total CO_2, pH, and a delayed alkalinity value. However, a

traditional alkalinity value is best determined in the field at the time of sampling rather than in the laboratory.

3. Total CO_2: An acid titration on the NaOH stabilized sample from pH 8.3 to 4.5 is used similar to D-513, ASTM (1980). A Mettler automatic titrator is used, although a manual titration would be equivalent.

4. Hardness: The standard EDTA method is used (Part 309B, APHA 1979). As a check, hardness is also calculated from spectroscopic analytical data obtained for multivalent cations.

Gravimetric Methods

1. Suspended Solids: This determination is made by weighing the matter (after drying to 105°C) which does not pass a 0.45 μm filter. Procedure details similar to those outlined in Part 208C, APHA (1979) are followed.

2. Total Dissolved Solids: The filtrate is evaporated to dryness in two steps, one 90°C and one 180°C, using a tared crucible. See Part 208B, APHA (1979) for procedural details.

Colorimetric Analyses

1. Silica: The colorimetric molybdosilicate analysis using absorption at 410 nm is performed with a Hach Spectrometer. Details are described in Part 426B, APHA (1979). Silica is also measured using the ICP.

2. Ammonia: A direct Nessler colorimetric determination is utilized in addition to, or in place of, the SIE analysis. This colorimetric method depends on the absorption at 425 nm; again the Hach Spectrometer is utilized. Rochelle salt is used as the stabilizing reagent. See Part 418B, APHA (1979) for details.

3. Dissolved Oxygen: The technique is the field determination using CHEMetrix field kits. Care should be taken to make sure that oxygen is not introduced in the sampling equipment or operation; specifically, fittings on valves and tubing need to be very snug.

Miscellaneous Analyses

1. Conductivity: This parameter is determined by use of a calibrated conductivity cell and bridge. See Part 205, APHA (1979).
2. Turbidity: This general water parameter is determined using an absorptometric technique Hach Spectrometer. Results are expressed in formazin turbidity units, FTU, which are similar to Jackson candle units. The basic procedure is in HACH Chemical (1976). This measurement can be time dependent.

DATA QUALITY CHECK

The data quality check is a measure of the internal consistency of the analytical data, and is necessary to ensure that results are consistent. Appendix C details PNL's procedure. Basically it consists of two parts:

- charge balance (anion to cation ratio)
- mass balance [total dissolved solids (TDS) to analyzed constituents ratio]

For both of these parts the ratios would be 1.00 for a complete and accurate analysis, but in practice they vary. A value in the 0.95 to 1.05 range appears to be satisfactory. Laboratories that analyze fairly consistent types of samples may do better. Reservoir engineering programs, where small changes in concentrations are interpreted, may require a better balance.

Both the mass and charge balances are primarily sensitive to the major components, and a small error here will affect the quality check even though the majority of the results are accurate and consistent. Conversely, accurate results on the major components can cover up poor results on other constituents. In the calculation of the charge balance, some of the species will change as the pH varies from one sample to another. When analyzing the liquids for only a few specific components, these quality checks may not be usable for lack of required data. If the sample is high in volatile salts, the mass balance may be adversely affected by mass losses during the drying step of the gravimetric TDS determination. Experience shows that these quality checks record their poorest values on samples having less than 1000 ppm TDS and a HCO_3^- value that is a large fraction of the TDS value. The mass balance and charge balance, calculated as described here and in Appendix C, seem to move in parallel, and to a similar degree, when indicating a large inconsistency or incomplete analysis. The charge balance is the more definitive and widely used of the two quality checks descibed here.

Figure 14 relates the internal consistency experienced during a field exercise in the Raft River, Idaho, Known Geothermal Resource Area (KGRA) using the analytical techniques described. This figure reflects results of the initial analysis; no reruns to obtain a better fit were performed.

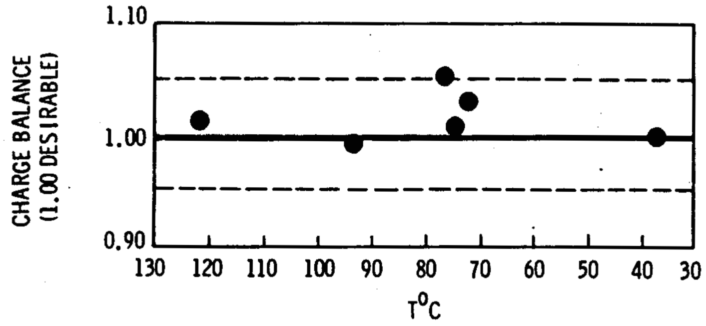


FIGURE 14. Analytical Charge Balance Versus Temperature of Geothermal Water, Raft River, Idaho, Case Study

7. ALTERNATIVE ANALYTICAL TECHNIQUES (ROUND ROBIN)

This section describes the comparative performance of alternative analytical techniques on geothermal samples as determined in a multi-laboratory, round-robin test organized by PNL. The raw data (Shannon 1979) was first interpreted by Watson 1980. The reinterpretation presented here was made because some of the conclusions and statements in Watson 1980 could not be beneficially utilized. A side-by-side comparison of the two interpretations is given in Appendix D.

The round-robin involved 20 laboratories analyzing four samples: two of ~4,000 ppm TDS and two of ~240,000 ppm TDS (sea water is ~33,000). One sample at each level was synthetic; the actual samples were taken from the East Mesa (Well 6-2) and the Salton Sea (Woolsey No. 1 Well) areas. HCl was used as the acid stabilizer. The samples were shipped by mail or commercial carrier to the participants, most of whom were west of the Mississippi. The participating laboratories, with varying degrees of geothermal experience, used procedures of their own choice. Figure 15 represents the precision of the results. The scatter of results and the difficulty of control or knowledge about how particular laboratories exercised procedures are similar to problems encountered during an international water analysis round robin (Ellis 1976).

The published data were interpreted by two techniques. An easily applied statistical tool, the Q-test (Dean and Dixon 1951), identified deviant results with a 90% confidence level. This treatment compared the mean results of a method (or sole result if only one laboratory used the method) with the mean (or sole) results of other methods in an attempt to identify the deviant method. The Q-test operated only if three or more values (each from a separate method) were available. Several methods were classified deviant by a second technique: comparing the results to known compositions in the synthetic samples. This approach was consistent with the available data.

An analytical method was declared deviant if its average result was "flagged" by either of the evaluation techniques for one or more of the four samples (it is the intent here to evaluate analytical methods suitable for the range of geothermal fluids, not just one particular type of fluid). A method was declared acceptable if it was used on both the low and high TDS samples

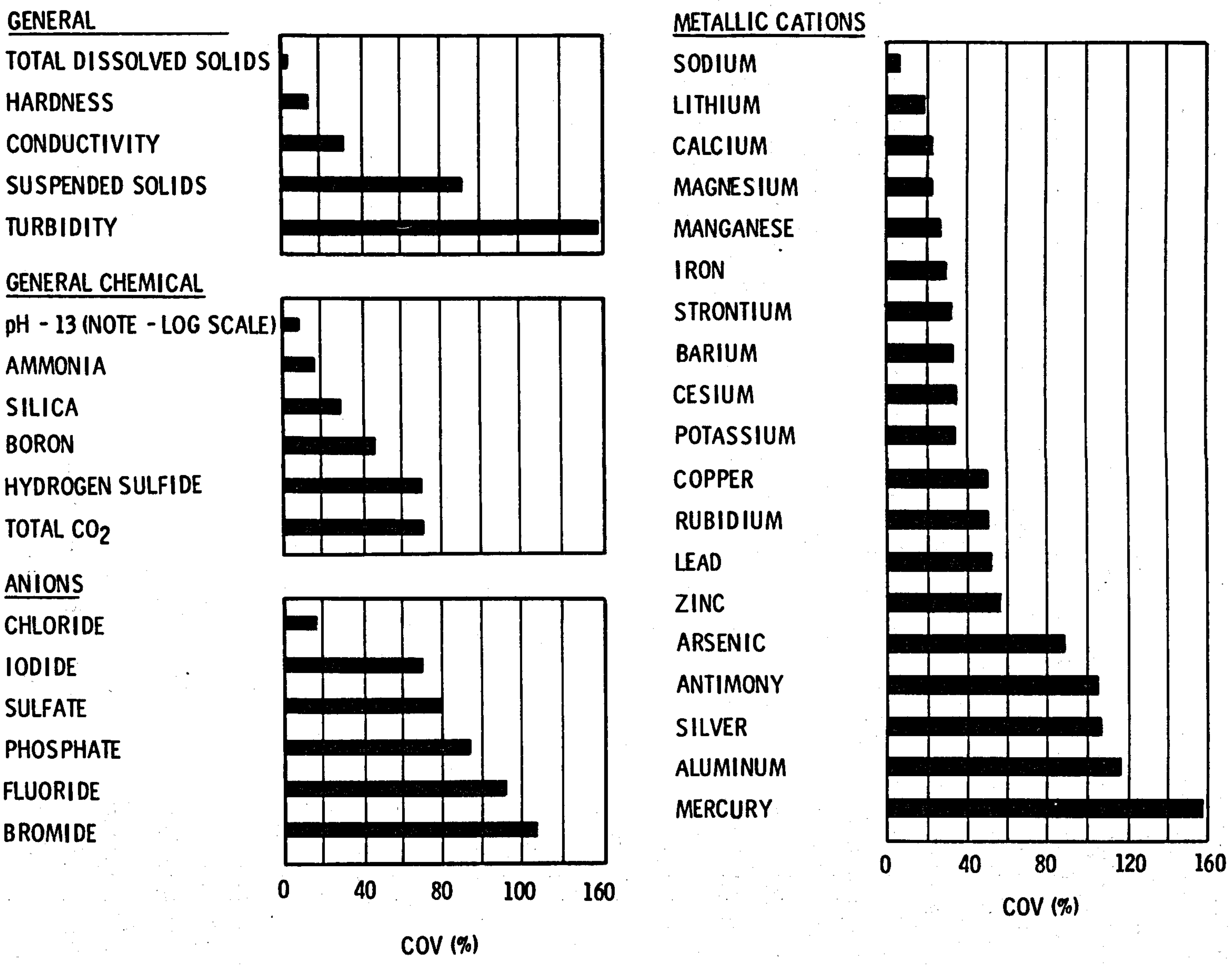


FIGURE 15. Precision of Round-Robin Analytical Results Expressed as a Percent Coefficient of Variation

and was not identified as deviant. The details of how the data were analyzed and a description of the Q-test are given in Appendix E.

The results of this interpretation are shown in Table 5. A general interpretation of Table 5 is suggested in Table 6. The analytical method abbreviation code is in Table 7. A complete summary of these methods has been published (Watson 1979). Appendix F cross references these analytical methods to several published sources where more detailed procedures are available.

The lack of control in the round robin and the lab-to-lab variation indicates that those methods identified as "deviant" should be calibrated with care if they are to be used. Any stronger conclusion exceeds both the quality of the underlying data and the intent of this interpretation.

In order to quantify the interlaboratory differences that are to be expected between laboratories, the coefficient of variation (COV) was plotted as a function of concentration for each round robin set--one point for the high TDS samples and one for the low TDS samples. To smooth the data, both the COV and the concentrations are average values from each round-robin set since the concentrations of the synthetic sample mimicked the real sample for most constituents. Starting with the sets demonstrating the worst precision (highest COV), the conclusions of Table 5 were applied to discard results from "deviant" methods. The result is Figure 16, which essentially is this interpretation of suitable methods applied to a detailed Figure 15.

Two distinct groups form once the results from "deviant" methods are discarded. The band that ranges from 15 to 40% COV (Group A), and is independent of concentration, represents the basic difference between laboratories using reasonable methods to analyze geothermal samples. Since this band is constant over a wide concentration range it is interpreted that interlaboratory and/or intermethod differences are the dominant source of variation for cation analyses on a given sample down to a concentration range of approximately 1 mg/l (assuming reasonable choice of methods).

TABLE 5. Suitability of Analytical Methods for Geothermal Brine Constituents Based on Round Robin Results

CONSTITUENT			
METHOD RESULT: DEVIANT	UNABLE TO EVALUATE	METHOD RESULT: ACCEPTABLE	ANALYTICAL METHOD
Sb	B, SO_4	Al, Ba, Ca, Cs, Cu, Fe, Pb, Li, Mg, Mn, K, Rb, Si, Ag, Na, Sr, Zn	AA
	Hg		AA CV
	Cu, Pb, Mn,	Al, Fe, Zn	AA EXT
Al, Ba, Cu, Pb, Rb, Sr		Cs, Zn, Sb, Ag, As	AA GF
Sb	As		AA H EV
	As		AA A GEN
Ba			ABSORPT
NH_4	CO_2 (Total) Alkalinity, HCO_3		ACID TIT
		Cl	Ag TIT
		F	AMA DIST
		Br, I	API PHOT
		I	As COLOR
		PO_4	ASC COLOR
		NH_4	AUTO ANAL
	CO_2 (Total) Hardness, HCO_3		CALCULATE
		B	CAR COLOR
Br	Fe		COLOR
		B	CUR COLOR

NOTE: 1. RESULT CLASSIFIED DEVIANT IF SO IDENTIFIED FOR ONE OR MORE OF THE FOUR SAMPLES.
2. UNDERLINED ENTRIES BASED ON SINGLE DATA POINTS.

TABLE 5. (contd)

CONSTITUENT			
METHOD RESULT: DEVIANT	UNABLE TO EVALUATE	METHOD RESULT: ACCEPTABLE	ANALYTICAL METHOD
$\underline{\mathrm{NH}}_4$			DIR NES
		NH_4	DIST NES
$\underline{\mathrm{NH}}_4$			DIST TIT
	Hardness, Ca, Mg		EDTA TIT
$\underline{\mathrm{B}}$, $\underline{\mathrm{Cs}}$, $\underline{\mathrm{Si}}$, $\underline{\mathrm{Na}}$, $\underline{\mathrm{Sr}}$	Hq, Rb, Ag	As, Ca, Cu, Fe, Li, Mg, Mn, K, $\underline{\mathrm{Sb}}$, $\underline{\mathrm{Ba}}$ $\underline{\mathrm{Pb}}$, $\underline{\mathrm{As}}$	EM SPEC
$\underline{\mathrm{Si}}$, $\underline{\mathrm{Ba}}$, $\underline{\mathrm{SO}}_4$	Fe	Cs, Li, K, Rb, Na, Sr, $\underline{\mathrm{Al}}$, $\underline{\mathrm{B}}$, $\underline{\mathrm{Ca}}$	FLAME EM
$\underline{\mathrm{Si}}$	Susp. Solids, T.D.S.,	SO_4, $\underline{\mathrm{Cl}}$	GRAVI
		Turbidity	HACH MET
$\underline{\mathrm{Si}}$			HB COLOR
		Cl	Hg TIT
Si, $\underline{\mathrm{Sb}}$, $\underline{\mathrm{As}}$, $\underline{\mathrm{PO}}_4$, $\underline{\mathrm{K}}$		$\underline{\mathrm{Na}}$, Mg, Mn, Ag, Sr, Zn, Al, Ba, B, Ca, Cu, Fe, Pb	ICP
		H_2S	IODO TIT
		$\underline{\mathrm{Br}}$, $\underline{\mathrm{Cl}}$, $\underline{\mathrm{F}}$, $\underline{\mathrm{Li}}$, $\underline{\mathrm{K}}$, $\underline{\mathrm{Na}}$, $\underline{\mathrm{SO}}_4$, NH_4	ION EXC
Br, $\underline{\mathrm{Cl}}$, NH_4		F, I	ION SP EL
$\underline{\mathrm{Br}}$			IP COLOR
$\underline{\mathrm{H_2S}}$			LAUTH VIO
	I		LEU COLOR
		$\underline{\mathrm{H_2S}}$	MB COLOR
	Conductivity		METER

NOTE: 1. RESULT CLASSIFIED DEVIANT IF SO IDENTIFIED FOR ONE OR MORE OF THE FOUR SAMPLES.
2. UNDERLINED ENTRIES BASED ON SINGLE DATA POINTS.

TABLE 5. (contd)

CONSTITUENT			
METHOD RESULT: DEVIANT	UNABLE TO EVALUATE	METHOD RESULT: ACCEPTABLE	ANALYTICAL METHOD
PO_4			MPA MET
		Si	MS COLOR
Ca	Al, Cl, I, Hg, K, Ag	Sb, Br, Cs, Rb, Na, Sr, Zn, Ba, As	NEUTRON
		Turbidity	NEPHEL
I		Br	OXI TIT
	pH		pH MET
	CO_2 (Total)		PRE EVO
	PO_4		Sn CO DI
		PO_4	Sn COLOR
	CO_2 (Total)		Sr GRAVI
		F	SPECT
Sb, Cs, Cu, Pb, Li, B, Rb, S, Zn, Si	PO_4, K, Ag	Al, Ba, Fe, Mn, Br, Ca, I, Mg, Na, Sr	SSMS
	CO_2 (Total)		T CARBON
		SO_4	TURBID
		F	VIS DIST
	Turbidity		VIS MAT
Al, Cu, Fe, Mn, PO_4 K	Sb, Hg, Sr	Si, Br, Cl	XRF

NOTE: 1. RESULT CLASSIFIED DEVIANT IF SO IDENTIFIED FOR ONE OR MORE OF THE FOUR SAMPLES.
2. UNDERLINED ENTRIES BASED ON SINGLE DATA POINTS.

TABLE 6. Recommended Interpretation for Table 5

Method Result: Deviant	Unable to Evaluate	Method Result: Acceptable
1) No underlining – the average result from the method deviated: 1) statistically from the results of other methods or 2) from composition values for a synthetic brine. Choosing an alternate method or careful calibration with representative standards is recommended	No Interpretation	1) No underlining – on average this method's results were consistent with other methods' for all samples.
2) Underlining – the result(s) of using this method was (were) deviant on one or more samples because of a single lab's result. Be aware of a potential problem.		2) Underlining – the sole lab analyzing this parameter by this method reported a consistent result for all samples.

TABLE 7. Abbreviation Code for Analytical Methods

AA	Atomic Absorption
AACV	Cold vapor atomic absorption
AA EXT	Atomic absorption, extraction method
AA F G	Atomic absorption, graphite furnace
AA H EV	Atomic absorption, hydride evolution
AA A GEN	Atomic absorption, arsine generation
ABSORPT	Absorptometric
ACID TIT	Acid titration
AG TIT	$AgNO_3$ titration
AMA DIST	Amadac F and distillation
API PHOT	API photometric
AS COLOR	Arsenious ceric colorimetric
ASC Color	Ascorbic acid colorimetric
AUTO ANAL	Auto analyzer
CALCULATE	Calculation
CAR COLOR	Carmine colorimetric
COLOR	Colorimetric
CUR COLOR	Curcumin colorimetric
DIR NES	Direct nesslerization
DIST NES	Distillation and nesslerization
DIST TIT	Distillation into H_2SO_4 and titration with NaOH
EDTA TIT	EDTA titration
EM SPEC	Emission spectroscopy
FLAME EM	Flame emission spectroscopy
GRAVI	Gravimetric
HACH MET	Hach meter
HB COLOR	Heteropoly-blue colorimetric
HG TIT	$Hg(NO_3)_2$ titration
ICP	Inductively coupled plasma
IODO TIT	Iodometric titration
ION EXC	Ion (exchange) chromatography
ION SP EL	Ion specific (selective) electrode
IP COLOR	Iodine-permanganate colorimetric
LAUTH VIO	Lauth's Violet (a variation on MB COLOR)
LEU COLOR	Leuco crystal violet colorimetric
MB COLOR	Methylene blue colorimetric
METER	Conductivity meter
MPA MET	Molybdophosphate acid method
MS COLOR	Molybdosilicate colorimetric
NEUTRON	Neutron activation
NEPHEL	Nephelometer
OXI-TIT	Hypochlorite oxidation and titration
PH METER	pH meter
PRE EVO	Precise evolution
SN CO DI	$SnCl_2$ colorimetric with digestion
SN COLOR	$SnCl_2$ colorimetric
SR GRAVI	Strontium gravimetric
SPECT	SPADNS spectrophotometric
SSMS	Spark source mass spectrometry
TOT CARBON	Total carbon analyzer
TURBID	Turbidimetric
VIS DIST	Alizarin visual and distillation
VIS MAT	Visual matching
XRF	X-ray fluorescence (of liquid sample)

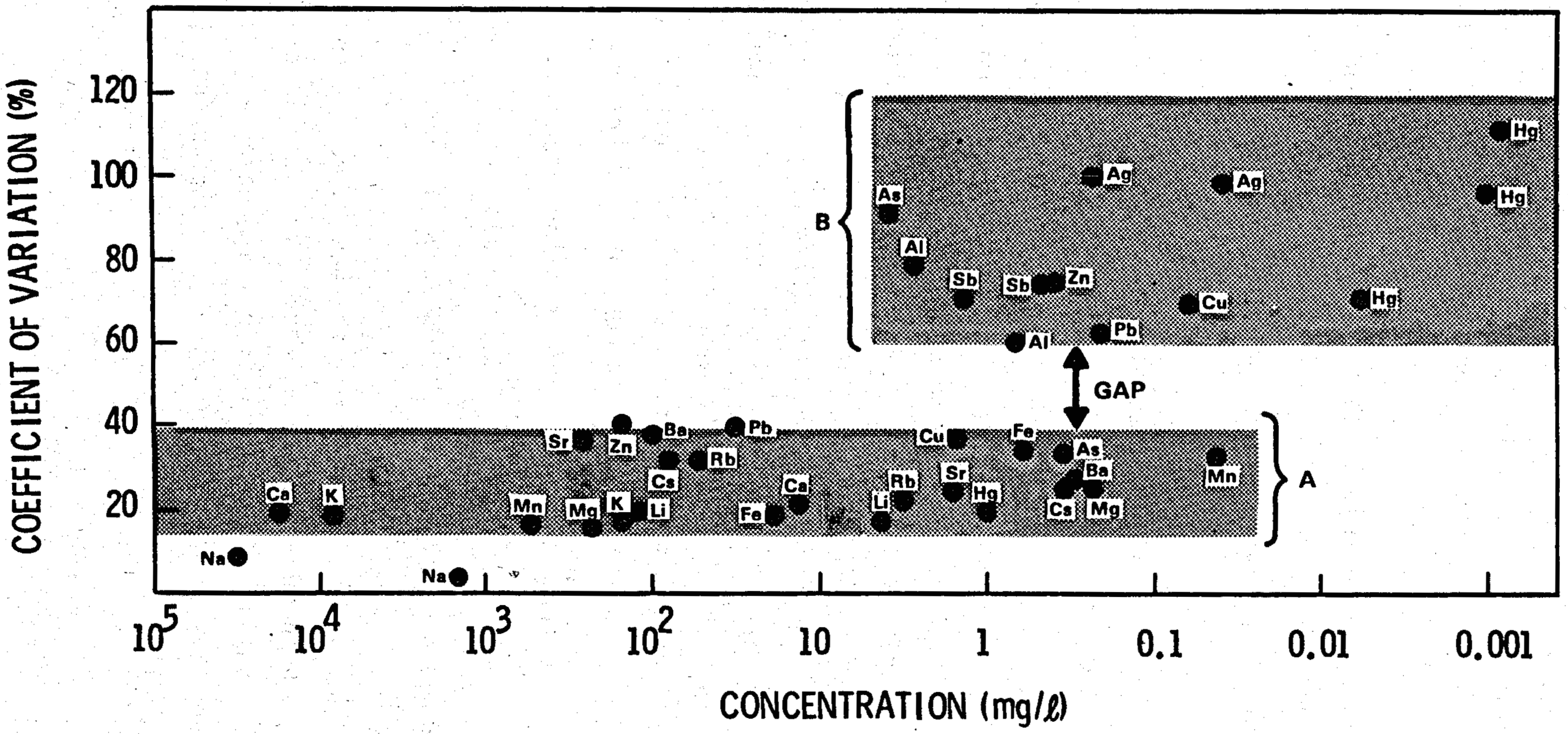


FIGURE 16. Interlaboratory Precision Vs Concentration of Cations. Data from "Deviant" Methods Discarded as Described in Text.

The gap in Figure 16 may be an artifact of the particular interpretation presented here; however, it may illustrate that other sources of variation become dominant below a concentration range of ~1/mg/l (Group B). These factors may include.

- ongoing precipitation in the sample that becomes the dominant source of error at low concentrations
- normal statistical uncertainties as instrumental detection limits are approached
- interferences/calibration difficulties at low concentrations in the (spectroscopic) methods commonly used.

A similar treatment was applied to the anion results and again two groups formed (Figure 17). A lower band (A) again can be postulated, although with fewer data points, in a similar range (10 to 50%) to that found for the cation data. The higher group again indicates that again sources of error other than lab-to-lab variation become dominant. However, for the anions, this second group forms at higher average concentration than the more precise data, which rules out the possiblity that it is due to normal statistical uncertainties as detection limits are approached. Since these salts are usually very soluble, this indicates that interferences and/or calibration difficulties are a likely cause of uncertainty in anion measurements in concentrated brines.

Listed below are some general conclusions from the round robin:

1. The wide range of results made it difficult to evaluate the methods.
2. Specific ion electrode results demonstrated problems and inconsistencies
   a. NH_4 and Cl results were subjectively the best over the entire range although both were classified "deviant" (Care in calibration is appropriate). The NH_3 specific ion electrode indicated some negative bias in the less concentrated brines (~14 ppm NH_4, ~4000 ppm TDS).

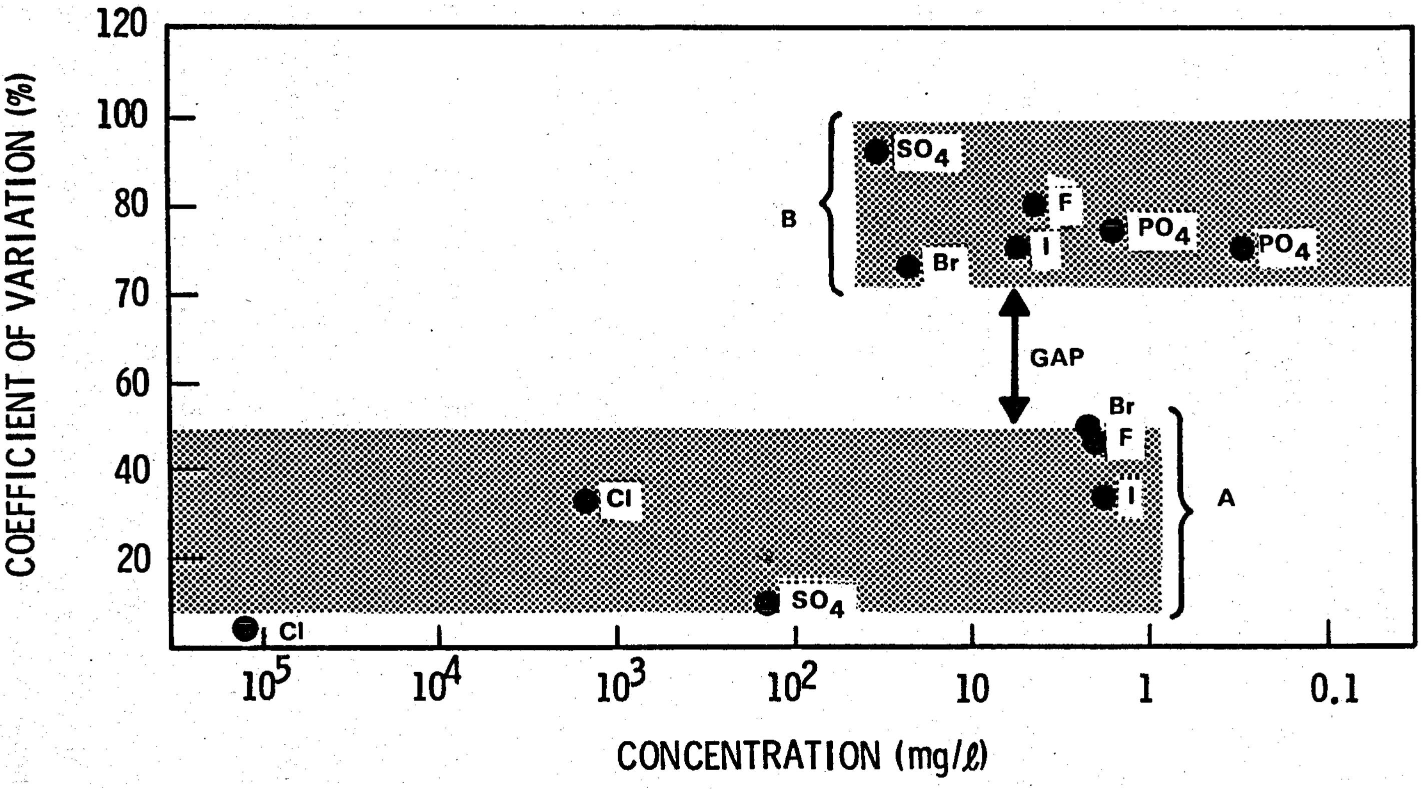


FIGURE 17. Interlaboratory Precision Vs Concentration of Anions. Data from "Deviant" Methods Discarded as Described in Text

b. As the brine became more concentrated, consistency deterioriated for I and F. Up to three orders of magnitude separated some results on the same concentrated brine sample.

c. The Br results were deviant and imprecise for all four samples.

d. The spread of reported hydrogen ion concentrations increased seven-fold in going from the low to high TDS brine (in logarithmic pH units the range was 1.37 for low TDS and 2.24 for high TDS brine). A pH meter that reads to 0.1 pH units is just as satisfactory as one that reads to 0.01 pH units. pH should be a field measurement.

3. For determining total solids content, the more precise measure is a total dissolved solids (TDS) gravimetric determination; conductivity variation was significantly greater. Conductivity meter calibration practices could be examined and possibly tightened if the values are to be used quantitatively.

4. Direct X-ray fluorescence (XRF) analysis of the brines was generally unreliable in giving accurate values. Only one laboratory consistently tried this approach.

5. Spark Source Mass Spectrometry (SSMS) had problems when used as the basic analytical tool. For selected components its results were adequate.

6. Ion (exchange) chromatography was used on a limited basis and gave acceptable results for all eight species reported.

7. Atomic spectroscopy, AA and ICP, gave acceptable results for most cations. The analysis of antimony (Sb) was the only one identified as deviant for both methods.

8. The determination of total CO_2 in high TDS samples requires extra care in checking for interferences.

9. There was no evidence of any deterioration of any of the constituents of the synthetic brine samples based on reported results and

synthetic make-up values. Where there was a lesser concentration indicated it was within one standard deviation of the original value.

10. The interlaboratory precision of the iodometric titration (the most popular method) on zinc preserved H_2S samples was strongly a function of concentration (Figure 18) indicating a functional limit of >1 mg/l, at least on an interlaboratory basis. Individual laboratories may wish to test their own performance (it should be significantly better) to establish minimum concentration limits. The average result for the two synthetic samples showed no deterioration from make-up values; since the precision of the actual samples falls on the same curve it implies that the actual samples suffered no deterioration either (the poor precision limits the strength of this statement).

11. Results from different laboratories, using reasonable methods of their own choosing, will vary with a basic coefficient of variation

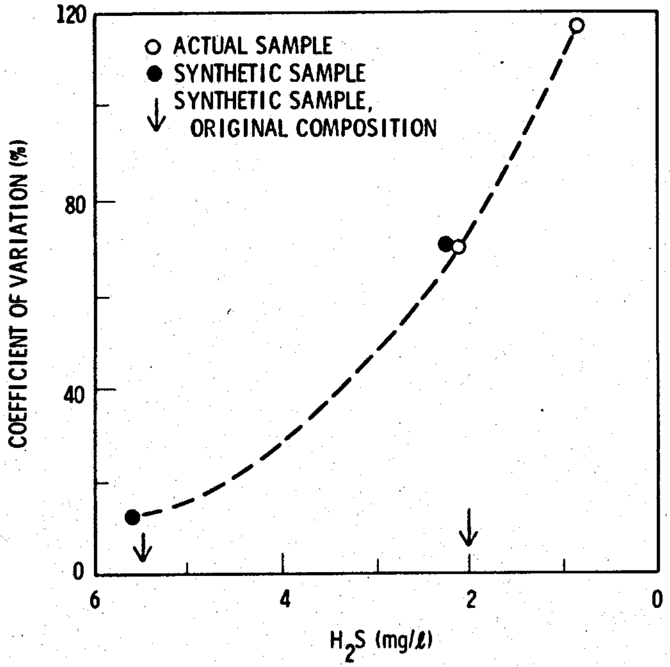


FIGURE 18. Iodometric H_2S Determination; Interlaboratory Precision Versus Concentration

(COV) of approximately 15 to 40% for cations and 10 to 50% for anions. This basic COV is: lowered for a few components (e.g., total dissolved solids - TDS, sodium, chloride, ammonia), exceeded for cations at or below 1 to .1 mg/l concentrations, and is generally exceeded for anion measurements in concentrated brines.

12. There was no evidence of ammonia deterioration in the samples. If the data from the "deviant" methods is discarded the results indicate no loss of ammonia (Table 8).

TABLE 8. Ammonia Stability

	Synthesis Value	Multi-Lab Average	Coefficient of Variation (%)
Low TDS Samples	14.0	12.84	10
	--	16.23	6
High TDS Samples	448	449	8
	--	369	8

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APPENDIX A

PROPOSED STANDARD METHOD
SAMPLING SINGLE-PHASE GEOTHERMAL FLOWS AND STABILIZING FOR LATER ANALYSIS

APPENDIX A

SAMPLING SINGLE-PHASE GEOTHERMAL FLOWS

1. Scope

1.1 This method covers extraction of representative samples from pressurized single-phase geothermal flows and stabilization of inorganic constituents for subsequent analysis.

1.2 This method covers the collection of discrete samples; it does not cover continuous sampling.

2. Specific Exclusions

2.1 This does not address sampling total noncondensible gases (NCG) for use in simulating how NCG will partition between dissolved and gaseous states under particular plant operating conditions. Specifically it does not address quantifying gases such as N_2, CH_4 and certain other trace gases that are soluble in cold, depressurized brine (Section 12).

3. Equipment Specifications

3.1 The reference to specific sizes of equipment is illustrative and is not meant to be binding.

4. Purpose

4.1 The goal of sampling is to obtain a portion of the main body of fluid that is truly representative of the geothermal resource. Critical factors necessary to achieve this are: adequate geothermal flow, points of sampling, sampling techniques, fluid homogeneity, and maintenance of chemical integrity prior to analysis.

4.2 A totally representative sample should not be an absolute prerequisite to the selection of a sampling point. With adequate interpretation, a nonrepresentative sample can yield valuable data about trends and can indicate areas where more representative data would be available. Samples collected from a single point in a system must be recognized as being potentially nonrepresentative to some degree. Therefore, it becomes important to recognize the degree of representation in the sample and to make it a part of the permanent record. Otherwise, an artificial degree of precision is assigned to data when it is recorded.

4.3 The samples must be collected, stabilized, packed, shipped, and manipulated prior to analysis in a manner that safeguards against change in the particular constituents or properties to be examined.

5. Purity of Reagents

5.1 It is recommended that the highest purity acid (HNO_3 or HCl), $KMnO_4$, and $K_2S_2O_8$ available shall be used for stabilizing metallic constituents to minimize the introduction of additional elements and therefore improve the end data by minimizing the blank (and the detection limit) and maximizing the precision.

5.2 All chemicals shall be of reagent grade purity or better. Unless otherwise indicated, it is intended that all reagents shall meet or exceed the purity specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[1]

Note — It is advantageous to use NaOH that is "CO_2-free" in order to improve the precision of the CO_2 analysis.

6. Method Summary

6.1 Fluid is extracted from a pressurized geothermal flow using a probe inserted into the main flow through a seal and a straight-throated valve. The fluid is cooled under full flow pressure. The system is dropped to atmospheric pressure, and the full sample stream is run into a series of separate sample containers. These are designed or contain chemicals to stabilize specific chemical-physical parameters for later measurement.

6.2 This procedure is applicable to sampling pressurized geothermal fluid from sources such as well heads, pipe, processing streams and tanks on an intermittent basis.

6.3 The use of this procedure is intended to permit the practiced operator to sample single phase flows to obtain chemical and physical characteristics of the fluid. The use of this method and appropriate supporting analytical techniques will provide the following data:

6.3.1 Liquid

6.3.1.1 Elemental Composition

6.3.1.2 pH

6.3.1.3 Dissolved Solids

6.3.2 Gases - Dissolved or Flashed

6.3.2.1 Quantity

---

[1] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

6.3.2.2 Chemical Composition (partial)

6.3.3 Suspended Solids

6.3.3.1 Quantity

7. Abbreviations

7.1 FU - Filtered, Unacidified Fluid

7.2 FA - Filtered, Acidified Fluid

7.3 FAHg - Filtered, Acidified for Mercury Analysis (see text)

7.4 RU - Raw, Unacidified Fluid (Unfiltered)

7.5 DI - Deionized

8. Equipment

8.1 The equipment size specifics mentioned are meant to be illustrative.

8.2 The sampling-line equipment is recommended to consist of:

8.2.1 Insertion sampling probe with flex hose and cooling coil(s).

8.2.2 Cooling bath(s).

8.2.3 Inlet and outlet valve and temperature components with suitable fittings to attach to system.

8.2.4 Sparge tube and fitting to use in sample container (2-hole rubber stopper and glass tube with medium glass frit is adequate).

8.2.5 Two pails and bailing cup to remove excesses from cooling buckets and sample line.

8.2.6 Ice.

8.2.7 Water.

8.3 The sample containers shall consist of:

8.3.1 One 500 ml gas bulb.

8.3.2 One 100 ml plastic bottle (for SiO_2 sample dilution).

8.3.3 One 1-liter bottle, for total CO_2 determination, containing 500 ml (2 N) NaOH (for CO_2 stabilization).

8.3.4 One 1-liter bottle containing 500 ml (0.5N) zinc acetate solution (for H_2S).

8.3.5 Three 1-liter bottles for FU, FA, and RU samples (FA bottle to contain 10 ml concentrated HCL or HNO_3).

8.3.6 One 250 ml glass bottle (FAHg for mercury analysis) containing 3 ml of 5% $KMnO_4$ solution, 3 ml of concentrated HNO_3, and 5 ml of 5% $K_2S_2O_8$ solution.

8.4 The measurement tools shall include:

8.4.1 pH meter and probe and buffer solutions. If inline probe is used, verify that probe and housing will withstand full system pressure or mount downstream of regulating valve.

8.4.2 5 ml pipette and 50 ml volumetric flask (for $\geq$10 fold SiO_2 dilution).

8.4.3 DI water in squeeze bottle (with supply for refill).

8.4.4 1000 ml graduated cylinder.

8.4.5 Conductivity meter.

8.4.6 Clip board with data sheet.

8.4.7 Thermometer for water and air temperature.

8.4.8 (1) pre-weighed 0.45 micron filter in protective holder - tared to 10^{-4} grams for suspended solids.

9. Geothermal Flow Conditions

9.1 Geothermal wells frequently experience chemical composition shifts during shutdown and start-up operations. Before sampling, examine and record the recent flow history of the well to minimize the possibility that the fluid composition is atypical. A rule of thumb is to flow the well at full production rates for at least 24 hours prior to sampling.

9.2 The short term chemical consistency during sampling can be monitored on a macro scale using the conductivity of the flowing sample stream.

10. Sample Train Set-up

10.1 Assemble equipment and connect sample train components.

10.2 Attach insertion probe to flex hose with probe valve closed.

10.3 Attach ball valve/pressure gland to system valve. (Note: If sampling without using an insertable probe, attach flex hose directly to sample valve without using probe/gland.)

10.4 Check all valves to assure they are closed.

10.5 Connect cooling coils to flex hose and insert probe to desired position in pipe as follows:

10.5.1 Measure distance probe is to be inserted and mark probe.

10.5.2 Insert probe into pressure gland and tighten.

10.5.3 It is highly recommended that a safety chain or other device be used to assure that the probe is not expelled by internal pressure in the geothermal system.

10.5.4 Open access valve (frequently a gate valve).

10.5.5 Loosen pressure gland and insert probe to mark. Probe opening should face upstream.

10.5.6 Tighten pressure gland.

10.5.7 Readjust safety chain to secure probe at this position.

10.6 Slowly open inlet ball valve fully open.

10.7 Check visually for leaks--system is pressurized to the outlet regulating valve--correct any leaks.

10.8 Fill water bucket and insert coils in buckets.

10.9 Ice the ice bucket and add water to etablish coil contact.

10.10 Open outlet regulating valve slowly and regulate flow to obtain an outlet temperature between 20 and 30°C. The proposed standard temperature for recording pH values is 25°C.

10.11 Flush system with at least three litres of brine while recording the initial sampling data.

11. Unfiltered Fluid Sample (RU)

11.1 Continue the sample flow as started above.

11.2 Determine and record pH at stabilized exit temperature.

11.3 Determine and record conductivity at stabilized exit temperature (Optional).

11.4 Fill the RU bottle.

11.5 Seal and label RU bottle.

12. Gas Sample

12.1 Continue the sample flow started above. This step collects a gas sample that exists over the cooled, depressurized flowing brine sample.

12.2 Measure and record brine temperature and range of variation during the gas collecting step. Control temperature as precisely as possible (25°C ± 1 recommended) to minimize gas composition shifts. (Substantial gas-liquid solubility changes with temperature exist.)

12.3 Fill glass bulb with geothermal liquid-brine (make sure all air bubbles are out by putting outlet end up).

12.4 Invert bulb and place outlet of bulb into bucket of water.

12.5 When bulb is full of gas and gas bubbles are seen in the bucket of water, close outlet, then inlet stopcocks on gas bulb and disconnect tygon tube from sample cooling coil. Label bulb.

13. Filtered Flow Samples

13.1 Filtered samples are advantageous for improved storage/integrity where stabilization is used because suspended solids may dissolve in the stabilized solution and bias the chemical composition.

13.2 Close ball valve and insert weighed filter and holder into line--restart flow. While the filter is in line it is necessary to measure the flow. Use of the graduated cylinder and the fill volume of the sample bottles is a convenient way to accomplish this.

13.3 From this filtered flow fill the following sample containers, seal and label:

13.3.1 FU bottle.

13.3.2 Make SiO_2 dilutions by withdrawing brine using the pipette from the FU bottle while it is filling. Add the brine to volumetric flask half filled with DI water. Fill to mark with DI water and empty diluted sample into SiO_2 plastic sample bottle and label.

13.3.3 FA bottle.

13.3.4 FAHg bottle (a glass bottle with oxidizer in it for Hg stabilization - see text).

13.4 Collect total CO_2 and H_2S samples as follows:

13.4.1 Attach sparge tube and fitting to sampling train outlet.

13.4.2 Check temperature.

13.4.3 Sparge gas + liquid into CO_2 bottle (half-filled with NaOH) until full to 1-liter mark.

13.4.4 Rinse off sparge tube into the sample bottle.

13.4.5 Repeat with H_2S bottle (half-filled with zinc acetate solution).

13.4.6 Rinse off sparge tube into the sample bottle.

Note: If sampling at a high rate, or if the CO_2/H_2S content is high or unknown, two stabilization bottles with sparge tubes should be used in series instead of the single one mentioned in 13.4.3 and 13.4.5.

13.5 To quantify the suspended solids in the cooled flow:

13.5.1 Stop the flow and record the flow volume that passed through the filter.

13.5.2 Remove filter holder and pass DI water through it in the same direction as the geothermal fluid. This serves to remove traces of the brine which would otherwise contribute solids as it dried. It may be necessary to apply pressure or vacuum to move the DI water through a fine or plugged filter.

14. Shutdown

14.1 Measure sample stream conductivity at the same temperature as when sampling started - Step 11.3 (Optional).

14.2 Record all well and sample train parameters at end of sampling.

Note: This provides some indication of the flow's chemical consistency during sampling.

14.3 Carefully remove sample probe and close sample valve on the system.

14.4 Disconnect flex hose from insertion probe and flush with DI water. Blow the sampling train dry using tygon tube as mouth piece.

15. Data Sheet

15.1 A sample data sheet is shown in Figure A.1.

Date: ____________ Location: ______________________________

Geothermal Flow: Sample Point: ______________________________

Access (Probe or ?) __________ Well or Process: ______________________

Temp. ______ °(F or C) Pressure ________ psi

Flow Rate ________ (   ) Air Temp. ______

Start Time: __________

Sample Temp: ________; pH ________ at ________ (Temp) at ________ (Time)

Conductivity ______ at ______ (Temp) at ________ (Time)

Raw-unfiltered (R), Unacidified (U) Samples

	ID Code	Sample Temp.	Time	Comments
RU				
Gas Bulb				

Filtered (F) Samples, some Acidified (A)

Tared Filter ID: ________________; Time on: __________

	ID Code	Sample Temp	Time	Comments
FA				
FU				
SiO_2				
FAHg				
CO_2				
H_2S				

Filter; Time Off ____________, Total Volume Through ____________

Sample: Conductivity ______ at ______ (Temp) at __________ (Time)

Shut Down: Flow; Pressure __________, Temp __________, Flow Rate ________

Time Completed: ________ Recorded by: ____________________

Remarks/Other Measurements:

FIGURE A.1. Geothermal Sampling Data Sheet

APPENDIX B

ICP WAVELENGTHS

APPENDIX B

ICP WAVELENGTHS

ELEMENT	WAVELENGTH (Å)	ELEMENT	WAVELENGTH (Å)
Al	3092	Na (high conc.)	3303*
Ag	3280	Na (low conc.)	5896
As	1936	Ni	2316 x2
B	2497	P	2149 x2
Ba	4934	Pb	2203
Ca	3179	Sb	2175
Cd	2265	Se	1960
Co	2286	Si	2881
Cr	2677	Sn	1899
Cu	3247	Sr	4215
Fe	2599	Th	2837
K (low conc.)	7664*	Ti	3349
K (high conc.)	4047	Tl	3775
Li	6707	U	3859
Mg	3832	Zn	2062 x2
Mn	2576	Zr	3391
Mo	2020		

---

*Better choice for single wavelengths.
x2 Indicates 2nd order.

APPENDIX C

DATA QUALITY CHECK PROCEDURE

APPENDIX C

DATA QUALITY CHECK PROCEDURE

1. Scope

1.1 This specification covers the minimum requirements for control in reporting the analytical work on a geothermal liquid sample.

1.2 This adapts and extends ASTM standard D-596-69(74) to geothermal samples.

2. Application

2.1 This specification covers only the minimum requirements for a quality control check on the reporting of analytical data. It does not cover the quality assurance program within the actual working laboratory or field sampling activities.

3. Summary

3.1 This specification covers the quality control check to be made on the results of the completed chemical analysis to assess the degree of internal consistency.

3.2 The internal consistency of the analytical results will be determined by:

3.2.1 Charge balance (ideal value: 1.00).

3.2.2 Mass balance (ideal value: 1.00).

3.3 Discussion - The attainment of the ideal value of 1.00 for either the mass or charge balance serves as a quality check on the overall analysis. A 1.00 value says simply that either the analysis is correct or a large error in an individual value is precisely compensated for by errors in other individual values.

3.4 Rationale - This quality check compares the results of individual determinations for consistency with macro values. It checks to see if the sum of the parts adds up to the whole.

3.5 Sensitivity - This quality check is particularly sensitive to major components. The pH or oxidation potential will affect which species are present for inclusion in the charge, mass balances. Hydrogen and hydroxyl ions (H^+, OH^-) are negligible for geothermal waters. Experience with particular waters will indicate other ions that are negligible for that water type.

4. Definitions

4.1 Charge Balance: a ratio of the sums of the negative (anion) and positive (cation) ionic charges, quantified as milliequivalents per liter, detected in the fluid. Specifically the charge balance is defined as the ratio:

$$\text{CHARGE BALANCE} = \frac{\Sigma\ \text{Anion Concentrations (meq/l)}}{\Sigma\ \text{Cation Concentrations (meq/l)}}$$

4.2 Mass Balance: a ratio of the observed mass of dissolved solids and the total calculated mass based on the results of the individual analyses. Specifically the mass balance is defined as the ratio:

$$\text{MASS BALANCE} = \frac{\text{Total Dissolved Solids (mg/l)}}{\Sigma\ \text{Individual Solid Concentrations (mg/l)}}$$

4.3 Total Dissolved Solids - That matter, dispersed in the geothermal fluid to give a homogeneous single phase, which is nonvolatile when dried to a residue.

4.4 Solid concentration - The concentration of nonvolatile ionic and molecular species present in the fluid.

5. Standard Specification

5.1 All reports of analytical determinations on geothermal fluids shall include a statement, for that individual sample, specifying:

5.1.1 Charge balance.

5.1.2 Mass balance.

5.2 Both charge and mass balance shall be reported to the hundredth column (x.xx).

6. Charge Balance

6.1 Anions - All quantified anions are to be included in the charge balance. A partial listing of anions found in geothermal liquids is below, along with the multiplicative factor to convert from (mg/l) to (milliequivalents/liter).

6.1.1 Chloride, Cl^- (0.0282).

6.1.2 Sulfate, $SO_4^=$ (0.0208).

6.1.3 Bicarbonate, HCO_3^- (0.0164).

6.1.4 Carbonate, $CO_3^=$ (0.0333).

6.1.5 Fluoride, F^- (0.0526).

6.1.6 Nitrate, NO_3^- (0.0161)

6.1.7 Biphosphate, $HPO_4^{=}$ (0.0208)

6.1.8 Bisulfide, HS^- (0.0302)

6.2 Cations - All quantified cations are to be included in the charge balance. A partial listing of cations found in geothermal liquids is below along with the multiplicative factor to convert from (mg/l) to milliequivalent/liter).

6.2.1 Sodium, Na^+ (0.0435).

6.2.2 Potassium, K^+ (0.0256).

6.2.3 Calcium, Ca^{++} (0.0499).

6.2.4 Strontium, Sr^{++} (0.0228).

6.2.5 Lithium, Li^+ (0.144).

6.2.6 Magnesium, Mg^{++} (0.0823).

6.2.7 Iron, Fe^{++} (0.0358).

6.2.8 Ammonium, NH_4^+ (0.167).

6.3 Charge balance shall be reported as the ratio of the sum of the anionic charges to the sum of the cationic charges.

7. Mass Balance

7.1 The mass balance shall be the ratio of the directly determined total dissolved solids (TDS) to the sum of the individually determined solids present.

7.2 The individually determined solids shall be those species tabulated for the charge balance plus nonvolatile molecular components such as silica.

8. Partial Analysis

8.1 In the event of only a partial analysis being performed on the major components of a sample, the following items shall be noted to comply with this quality control standard:

8.1.1 Charge balance.

8.1.2 Mass balance.

8.1.3 Note that the analysis is incomplete.

8.1.4 Note identifying the incomplete portion of the analysis.

9. Worksheet

9.1 A sample worksheet for calculating the charge and mass balances is shown in Figure C.1.

NAME: ________________
REPORT DATE: __________
PROJECT: _____________
SAMPLE ID: ____________

MASS AND CHARGE BALANCES

CHARGE BALANCE =(meq/ℓ anions)÷(meq/ℓ cations)=	
MASS BALANCE $= \frac{(\text{mg}/\ell)\ \text{TDS}}{(\text{mg}/\ell)\ \text{Total Solids}} =$	

CHARGE BALANCE

PARAMETER	ANIONS			PARAMETER	CATIONS		
	mg/ℓ	Factor	(meq/ℓ)		mg/ℓ	Factor	(meq/ℓ)
HCO_3^-		0.0164		NH_4^+		0.167	
$CO_3^=$		0.0333		Ca^{++}		0.0499	
HS^-		0.0302		Fe^{++}		0.0358	
$SO_4^=$		0.0208		K^+		0.0256	
F^-		0.0526		Li^+		0.144	
NO_3^-		0.0161		Mg^{++}		0.0823	
$HPO_4^=$		0.0208		Na^+		0.0435	
Cl^-		0.0282		Sr^{++}		0.0228	
TOTAL		╳		TOTAL		╳	

MASS BALANCE

Σ Anions (mg/ℓ)	
Σ Cations (mg/ℓ)	
SiO_2 (mg/ℓ)	
Total Solids	

TDS (mg/ℓ)-Experimental	

FIGURE C.1. Sample Worksheet

APPENDIX D

COMPARISON OF ROUND-ROBIN INTERPRETATIONS

CHLORIDE CONTENT (PPM) OF GEOTHERMAL ROUND ROBIN SAMPLES BY METHOD*

	Round-Robin Results	
	Low TDS GRR-1	High TDS GRR-2
	REAL SAMPLE	REAL SAMPLE
Ag TIT	(1939)	(127,900)
	2038	131,200
	2009	130,600
	1957	130,500
	1955	127,000
	1937	125,300
	1917	122,700
	1880	
	1820	
Hg TIT	(1904)	(131,000)
	2000	140,000
	1932	132,000
	1909	130,000
	1773	122,100
	-34-	
XRF	(1269)	(133,000)
	1957	
	580	
NEUTRON	(1288)	-
GRAVI	(1970)	(128,900)
ION SP EL	(2000)	-(140,000)-
ION EX	(1975)	(132,000)

---

* Data of Shannon (1979), Tables 1 and 3, no synthetic sample results
( ) Method Value, or average
\- - Statistically omitted or deviant, this paper
____ Underlined methods classified by single datum

METHOD EVALUATION FOR CHLORIDE

KINDLE AND WOODRUFF[(a)]
METHOD RESULT: ACCEPTABLE

Ag TIT
GRAVI
Hg TIT
ION EX
XRF

UNABLE TO EVALUATE

NEUTRON

METHOD RESULT: DEVIANT

ION SP EL

WATSON (1980)[(b)]
WITHIN 95% CONFIDENCE LIMIT

GRR-1	GRR-2
NEUTRON (SIC)	Ag TIT
	Hg TIT
	GRAVI
	ION EX

OUTSIDE 95% CONFIDENCE LIMIT

GRR-1	GRR-2
Ag TIT	XRF
Hg TIT	ION SP EL
XRF	
NEUTRON (SIC)	
GRAVI	
ION SP EL	
ION EX	

(a) Explained in text and Appendix F. Deviant results: (1) Rejected with 90% confidence that they were deviant using Q-test, or (2) determined for synthetic samples by comparison to known values.
(b) J. C. Watson, "Round Robin Evaluation of Methods for Analysis of Geothermal Brine," GEOTHERMAL SCALING AND CORROSION, ASTM STP 717, L. A. Casper and T. R. Pinchback, Eds., ASTM, 236-258 (1980)

SILICA CONTENT (PPM) OF GEOTHERMAL ROUND ROBIN SAMPLES BY METHOD*

	Round Robin Results			
	Low TDS GRR-1		High TDS GRR-2	
	SYN 250	REAL	SYN 44.9	REAL
AA	(249) 276 265 264 257 228 206	(244) 295 271 269 255 210 165	(39.7) -583- 49.2 43.2 42.8 41 37.5 36.2 27.8	(396) 475 438 409 407 400 375 370 297
HB COLOR	(228) 250 206	(223) 237 230 203	-(216)- 401 30	-(262)- 279 244
MS COLOR	(239) 300 226 219 210	(239) 290 230 219 218	(37.7) 45 38 37.9 36.8 31	(376) 500 400 355 355 268
FLAME EM	(260) 300 220	-(391)- 535 247	(25.7)	(428)
ICP	-(1)- 1 0.5	(232) 260 204	--	(407)
SSMS	--	PRESENT	(42.8)	-(173)- 286 60
EM SPEC	-(3)-	(428)	--	--
GRAVI	--	--	-(17)-	(166)

---

* Data of Shannon (1979), Tables 1 and 3
Synthetic make up value
( ) Method value or average
\- - Result statistically thrown out for this paper, or deviant
____ Underlined methods classified by single datum

METHOD EVALUATION FOR SILICA

KINDLE AND WOODRUFF[(a)]

METHOD RESULT: ACCEPTABLE

AA
MS COLOR

UNABLE TO EVALUATE

METHOD RESULT: DEVIANT

EM SPEC
GRAVI
HB COLOR
ICP
FLAME EM
SSMS

WATSON (1980)[(b)]

WITHIN 95% CONFIDENCE INTERVAL

GRR-1	GRR-2
HB COLOR ICP	MS COLOR

OUTSIDE 95% CONFIDENCE INTERVAL

GRR-1	GRR-2
AA MS COLOR FLAME EM SSMS EM SPEC	AA HB COLOR FLAME EM ICP SSMS GRAVI

(a) Explained in text and Appendix F. Deviant results: (1) Rejected with 90% confidence that they were deviant using Q-test, or (2) determined for synthetic samples by comparison to known values.

(b) J. C. Watson, "Round Robin Evaluation of Methods for Analysis of Geothermal Brine," GEOTHERMAL SCALING AND CORROSION, ASTM STP 717, L. A. Casper and T. R. Pinchback, Eds., ASTM, 236-258 (1980)

DISSOLVED AMMONIA CONTENT (PPM) of GEOTHERMAL ROUND ROBIN SAMPLES BY METHOD*

	Round-Robin Results			
	Low TDS GRR-1		High TDS GRR-2	
	SYN 14	REAL	SYN 448	REAL
DIR NES	(15.5)	(16)	(508)	-(463)-
	16	18	569	584
	15	17.9	448	341
		14.8		
		13.5		
ION SP EL	-(10.4)-	(13.7)	(420)	(343)
	12	17	464	370
	11.7	14.2	436	341
	10.8	14.0	361	332
	9.9	13.6	-135-	329
	7.8	9.9		-139-
DIST NES	(12.4)	(15.1)	(441)	(377)
	13.7	16	493	420
	12.5	14.8	430	380
	10.9	14.6	400	331
AUTO ANAL	(14.1)	(16.8)	(444)	(366)
ION EX	(13.0)	(16.8)	(480)	(358)
ACID TIT	(16.5)	(20.3)	-(165)-	(342)
DIST TIT	(20.6)	-(33.0)-	(414)	(319)

- Data of Shannon (1979), Tables 1 and 3

( ) Method Value, or Average
- - Deviant Value or Statistically Omitted for this Paper
Synthetic Make-Up Value
___ Underlined Methods Classified by Single Datum

METHOD EVALUATION FOR AMMONIA

KINDLE AND WOODRUFF[(a)]

METHOD RESULT: ACCEPTABLE

AUTO ANAL
DIST NES
ION EX

UNABLE TO EVALUATE

METHOD RESULT: DEVIANT

ACID TIT
DIR NES
ION SP EL
DIST TIT

WATSON (1980)[(b)]

WITHIN 95% CONFIDENCE INTERVAL

GRR-1	GRR-2
AUTO ANAL	AUTO ANAL
ION EX	ION EX

OUTSIDE 95% CONFIDENCE INTERVAL

GRR-1	GRR-2
ACID TIT	ACID TIT
NES	NES
ION SP EL	ION SP EL

(a) Explained in text and Appendix E. Deviant results: (1) Rejected with 90% confidence that they were deviant using Q-test, or (2) determined for synthetic samples by comparison to known values.

(b) J. C. Watson, "Round Robin Evaluation of Methods for Analysis of Geothermal Brine," GEOTHERMAL SCALING AND CORROSION, ASTM STP 717, L. A. Casper and T. R. Pinchback, Eds., ASTM, 236-258 (1980)

APPENDIX E

METHODOLOGY, GEOTHERMAL ROUND-ROBIN EVALUATION

APPENDIX E

METHODOLOGY GEOTHERMAL ROUND ROBIN EVALUATION

BASIS

1. Use "Q-test" (Dean and Dixon 1951) to statistically identify deviant results at 90% confidence level.
2. Q-test is applied in series to a set of data to try to identify additional deviant results even after one result is already discarded.
3. The mean values of method's results were treated as single values having no standard deviation.
4. For synthetic samples compare results to known value to establish deviant value in addition to applying Q-Test.

METHODOLOGY

1. To arrive at result per method per species per sample.
    - A. If single result use that value.
    - B. If multiple results:
        - 1) Apply Q-test to omit flyers.
        - 2) Use mean value of remaining data.
2. Use Q-test on results of 1 to identify deviant methods.
    - A. If mean value was deviant, so identified in Table 5.
    - B. If single value was deviant, so identified in Table 5.
    - C. If mean value was Q-test deviant solely because of a single datum, then that method was identified as a single value deviant. This resulted several times when there were two widely different values for one method; the Q-test only works on three or more values. The HB color method for silica was classified this way based on the GRR-2 synthetic sample, Appendix D.
3. Use wide or consistent variation from composition values to identify deviant results in synthetic samples. An example is the ion selective electrode method for ammonia in GRR-1, Appendix D. Same classification as under 2.

4. For the purpose of applying the Q-test the results on the synthetic and real samples are assumed to be coupled within, but not between, each round robin. This is a further attempt to isolate individual laboratory biases, since both samples within a round robin were presumably analyzed concurrently and identically. For example if one method were found deviant on the GRR-1 synthetic sample that method's data would be excluded from the GRR-1 real sample data set, but not from the GRR-2 statistical analysis. GRR-1 and GRR-2 were interpreted separately and then the results combined.

5. Less than values were generally ignored entirely or classified as "unable to evaluate". Only if the less than value fitted well with other data was it included (such as ICP method on silica, Appendix D). All CO_2 (TOTAL) determinations were put into this category because of the scatter on the high TDS samples.

6. The "unable to evaluate" classification was also used if:
   A. An acceptable value resulted from a method used in only one GRR.
   B. Less than three methods were used to analyze that parameter. (The statistical test doesn't operate on fewer than three data points.)
   C. The data subjectively did not match with the evaluation process.

7. "Unable to evaluate" methods were included in the statistical evaluation process. Specifically, the results of methods classified "unable to evaluate" were included in the statistical evaluation that led to the classification of other methods.

Q-TEST

The Q-test as stated by Day and Underwood (1967) is performed as follows:

1. Calculate the range of the results.

2. Find the difference between the suspected result and its nearest neighbor.

3. Divide the difference obtained in step 2 by the range from step 1 to obtain the rejection quotient, Q.

4. Consult a table of Q values. If the computed value of Q is greater than the value in the table, the result can be discarded with 90% confidence that it was indeed subject to some factor which did not operate on the other results.

VALUES OF REJECTION QUOTIENT, Q

Number of Observations	$Q_{0.90}$
3	0.90
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

APPENDIX F

ANALYTICAL METHODS USED IN GEOTHERMAL ROUND ROBIN, IDENTIFICATION AS "STANDARD" METHODS

APPENDIX F

ANALYTICAL METHODS USED IN GEOTHERMAL ROUND ROBIN,(a) IDENTIFICATION AS "STANDARD" METHODS

Analytical methods used in analyzing geothermal fluids are cross referenced to methods published by five agencies: ASTM, API, EPA, APHA, and USGS. The parameters measured are indicated as to whether at least one of the methods corresponded to a method published by one of these "standardizing" organizations:

1) American Society for Testing and Materials - ASTM
2) American Petroleum Institute - API
3) Environmental Protection Agency - EPA
4) American Public Health Association - APHA
5) United States Geological Survey - USGS

Analysis	ASTM	API	EPA	APHA	USGS
Alkalinity	X	X	X	X	X
Aluminum			X	X	
Ammonia	X		X	X	
Antimony					
Arsenic	X		X	X	X
Barium		X	X	X	X
Bicarbonate, Carbonate	X			X	X
Boron	X		X	X	X
Bromide	X	X	X	X	X
Calcium	X	X	X	X	X
Carbon Dioxide	X		X	X	X
Cesium					
Chloride	X	X	X	X	X
Conductivity	X	X	X	X	X
Copper	X		X	X	X
Fluoride	X	X	X	X	X

(a) Based on PNL's manual "Sampling and Analysis Methods for Geothermal Fluids and Gases," PNL-MA-572 (1979).

Analysis	ASTM	API	EPA	APHA	USGS
Hardness	X		X	X	X
Hydrogen Sulfide		X	X	X	X
Iodine	X	X	X	X	X
Iron	X		X	X	X
Lead	X		X	X	X
Lithium	X				X
Magnesium	X	X	X	X	X
Manganese	X		X	X	X
Mercury	X		X	X	
pH	X	X	X	X	X
Phosphate	X	X	X	X	X
Potassium	X		X		X
Rubidium					
Silica	X		X	X	X
Silver			X	X	X
Sodium	X		X		X
Strontium	X				X
Sulfate	X	X	X	X	
Sulfide		X	X	X	X
Suspended Solids	X		X	X	X
Total Dissolved Solids (TDS)	X		X	X	X
Turbidity	X		X	X	X
Zinc	X		X	X	X

CROSS REFERENCED METHODS IN DETAIL

ANALYSIS	ASTM	API	EPA	APHA	USGS
1. ALKALINITY (ACID TIT.)	D 1067-70	2.21-2.22	00710	403	BOOK 5
2. ALUMINUM					
A. ATOMIC ABSORPTION-DIRECT			01105	301 IV	
B. ATOMIC ABSORPTION-GRAP. FURN.					
C. ATOMIC ABSORPTION-EXTRACTION				301 V	WRI
D. FLAME EMISSION					
E. X-RAY FLUORESCENCE					
F. INDUCTIVELY-COUPLED PLASMA					
G. SPARK SOURCE MASS SPEC					
H. NEUTRON ACTIVATION					
I. EMISSION SPEC					
3. AMMONIA					
A. DISTILLATION PROCEDURE	D 1426-74		00610	418A	
B. TITRATION					
C. NESSLER	D 1426-74A,B		00610	418B	
D. COLORIMETRIC PHENATE (AUTO.)			00610		
E. AMMONIA ELECTRODE			00610		WRI
F. ION-EXCHANGE CHROMATOGRAPHY					
4. ANTIMONY					
A. ATOMIC ABSORPTION-DIRECT					
B. ATOMIC ABSORPTION-HYDRIDE EVOLUTION					
C. X-RAY FLUORESCENCE					
D. INDUCTIVELY-COUPLED PLASMA					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPECTROMETRY					

	ASTM	API	EPA	APHA	USGS
5. ARSENIC					
A. SILVER DIETHYLDITHIOCARBAMATE	D 2972-74		01002	404A	BOOK 5
B. ATOMIC ABSORPTION-DIRECT					
C. ATOMIC ABSORPTION-(HYDRIDE EVOL.)				301A	
D. INDUCTIVELY COUPLED PLASMA					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPEC					
6. BARIUM					
A. TURBIDIMETRIC		3.32			
B. ATOMIC ABSORPTION			01007	303	BOOK 5
C. FLAME EMISSION					
D. ICP					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPEC					
7. CARBONATE, BICARBONATE					
A. ACID TITRATION	D 513-71C			407B	BOOK 5
B. $CaCO_3$ SATURATION CALCULATION				203	
8. BORON					
A. CARMINE COLORIMETRIC	D 3082-74A			405B	BOOK 5
B. CURCUMIN COLORIMETRIC			01022	405A	
C. FLAME EMISSION					
D. ICP					
E. SPARK SOURCE MASS SPEC					
F. EMISSION SPEC					

	ASTM	API	EPA	APHA	USGS
9. **BROMIDE**					
A. HYPOCHLORITE OXIDATION-TITRATION	D 1246-77C		71870		BOOK 5
B. CHROMIC ACID OXID. & EXTRACTION		3.14			
C. COLORIMETRIC (IODINE-PERMANGANATE)	D 1246-77B				BOOK 5
D. COLORIMETRIC-PHENOL RED				406	
E. BROMIDE ELECTRODE					
F. X-RAY FLUORESCENCE					
G. ION EXCHANGE CHROM.					
H. SPARK SOURCE MASS SPEC					
I. NEUTRON ACTIVATION					
10. **CALCIUM**					
A. EDTA TITRIMETRIC	D 511-76B	2.4	00910;00916	306C	BOOK 5
B. ATOMIC ABSORPTION	D 2576-70 D 511-76C		00916	301A	BOOK 5
C. FLAME EMISSION					
D. ICP					
E. NEUTRON ACTIVATION					
F. EMISSION SPEC					
11. **CARBON DIOXIDE**					
A. TITRIMETRIC	D 513-71 C, D, E			407B	
B. STRONTIUM GRAVIMETRIC					
C. PRECISE EVOLUTION	D 513-71 A, B				
D. CALCULATION				203 407 A, B, C	
E. INFRARED CARBON ANALYZER			00680		

	ASTM	API	EPA	APHA	USGS
12. CESIUM					
A. ATOMIC ABSORPTION					
B. FLAME EMISSION					
C. NEUTRON ACTIVATION					
D. EMISSION SPECTROMETRY					
13. CHLORIDE					
A. SILVER NITRATE TITRATION	D 512-67B	2.8		408A	BOOK 5
B. MERCURIC NITRATE TITRATION	D 512-67A		00940	408B	BOOK 5
C. TITRIMETRIC (CONDUCTOMETRIC)					
D. GRAVIMETRIC					
E. CHLORIDE ELECTRODE					
F. X-RAY FLUORESCENCE					
G. ION-EXCHANGE CHROM					
H. NEUTRON ACTIVATION					
14. CONDUCTIVITY					
A. CONDUCTIVITY METER	D 1125-77A,B,C	2.91	00095	205	BOOK 5
15. COPPER					
A. ATOMIC ABSORPTION (DIRECT)	D 2576-70 D 1688D		01042	301	BOOK 5
B. AA-MIBK EXTRACTION					
C. X-RAY FLUORESCENCE					
D. ICP					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPEC					

	ASTM	API	EPA	APHA	USGS
16. **FLUORIDE**					
A. ALIZARIN (PRE-DISTILLATION)				414A, 414D	
B. COLORIMETRIC	D 1179-72A		00950;00951	414C	
C. AMADAC F COLORIMETRIC					
D. FLUORIDE ELECTRODE	D 1179-72B			414B	BOOK 5
E. ION-EXCHANGE					
F. SPARK SOURCE MASS SPEC					
17. **HARDNESS**					
A. EDTA TITRATION	D 1126-67B		00900	309B	BOOK 5
B. CALCULATION				309	BOOK 5
18. **HYDROGEN SULFIDE**					
A. TITRIMETRIC (IODINE)		3.10.1	00746	428D	BOOK 5
B. COLORIMETRIC (METHYLENE BLUE)		3.10.2		428C	
C. LAUTH'S VIOLET COLORIMETRIC					
19. **IODINE**					
A. TITRIMETRIC (FOR BROMIDE ALSO)	D 1246-77C	3.16	71865		BOOK 5
B. COLORIMETRIC (ARSENIOUS-CERIC-FERRIC THIOCYANATE)				415B	
C. LEUCO CRYSTAL VIOLET METHOD				415A	
D. COLORIMETRIC (ARSENIOUS-CERIC)	D 1246-77A				BOOK 5
E. PHOTOMETRIC		3.15			
F. IODINE ELECTRODE					
G. X-RAY FLUORESCENCE					
H. SPARK SOURCE MASS SPEC					
I. NEUTRON ACTIVATION					

	ASTM	API	EPA	APHA	ESGS
20. IRON					
A. COLORIMETRIC-PHENANTHROLINE	D 1068-77A			310A	
B. AA	D 2576-70F D 1068-77C		01045	301-A-II	BOOK 5
C. AA-MIBK EXTRACTION				301-A-III	
D. FLAME EMISSION					
E. X-RAY FLUORESCENCE					
F. ICP					
G. SPARK SOURCE MASS SPEC					
H. NEUTRON ACTIVATION					
I. EMISSION SPEC.					
21. LEAD					
A. ATOMIC ABSORPTION-DIRECT	D 2576-70 D 3559-77A		01051	301-A-II	
B. AA-MIEK EXTRACTION				301-A-III	BOOK 5
C. ICP					
D. SPARK SOURCE MASS SPEC					
E. EMISSION SPEC					
22. LITHIUM					
A. ATOMIC ABSORPTION-DIRECT	D 3561-77				BOOK 5
B. FLAME EMISSION					
C. ION-EXCHANGE CHROMATOGRAPHY					
D. SPARK SOURCE MASS SPEC					
E. EMISSION SPEC					

	ASTM	API	EPA	APHA	ESGS
23. MAGNESIUM					
A. EDTA TITRIMETRIC	D 511-76B	2.4		313C	BOOK 5
B. AA-DIRECT	D 2576-70 D 511-76C		00927	301-A-II	BOOK 5
C. ICP					
D. SPARK SOURCE MASS SPEC					
E. NEUTRON ACTIVATION					
F. EMISSION SPEC					
24. MANGANESE					
A. AA-DIRECT	D 2576-70 D 858-77B		01055	129	BOOK 5
B. AA-MIBK EXTRACTION	D 858-77C				BOOK 5
C. X-RAY FLUORESCENCE					
D. ICP					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPEC					
25. MERCURY					
A. COLD VAPOR AA	D 3223-73		71900	301A	
B. X-RAY FLUORESCENCE					
C. NEUTRON ACTIVATION					
D. EMISSION SPEC					
26. pH					
A. pH METER	D 1293-65	2.1	00400	424	BOOK 5

	ASTM	API	EPA	APHA	ESGS
27. PHOSPHATE					
A. COLORIMETRIC (STANNOUS CHLORIDE)				425E	
B. COLORIMETRIC (ASCORBIC ACID REDUCTION)	D 515-72A	3.9	70507	425F	BOOK 5
C. MOLYBDOPHOSPHORIC ACID SPECTRO METHOD (MODIFIED)					
D. X-RAY FLUORESCENCE					
E. ICP					
F. SPARK SOURCE MASS SPEC					
28. POTASSIUM					
A. POTASSIUM ELECTRODE					
B. AA-DIRECT	D 3561-77		00937		BOOK 5
C. FLAME EMISSION					
D. X-RAY FLUORESCENCE					
E. ICP					
F. ION-EXCHANGE					
G. SPARK SOURCE MASS SPEC					
H. NEUTRON ACTIVATION					
I. EMISSION SPEC					
29. RADIOACTIVE ISOTOPES					
A. GENERAL GAMMA SPECTROMETRY					
B. LEAD-210 ISOTOPE					
C. RADON-226 (EMMANATION)	D 3454-75T			705	
D. RADON-226 (PRECIPITATE/MOUNT)					
E. THORIUM					
F. URANIUM					

	ASTM	API	EPA	APHA	ESGS
30. RUBIDIUM					
A. AA-DIRECT					
B. FLAME EMISSION					
C. SPARK SOURCE MASS SPEC					
D. NEUTRON ACTIVATION					
E. EMISSION SPEC					
31 SILICA					
A. GRAVIMETRIC	D 859-68A			426A	
B. COLORIMETRIC (HETEROPOLY BLUE)	D 859-68B,C		00955	426C	BOOK 5
C. COLORIMETRIC (MOLYBDOSILICATE)	D 859-68B,C		00955	426B	
D. AA-DIRECT				301A	BOOK 5
E. FLAME EMISSION					
F. ICP					
G. SPARK SOURCE MASS SPEC					
H. EMISSION SPEC					
32. SILVER					
A. AA-DIRECT			01077	301A	
B. AA-APDC/MIBK EXTRACTION				301A	BOOK 5
C. ICP					
D. SPARK SOURCE MASS SPEC					
E. NEUTRON ACTIVATION					
F. EMISSION SPEC					

	ASTM	API	EPA	APHA	ESGS
33. SODIUM					
A. AA-DIRECT	D 3561-77		00929		BOOK 5
B. SODIUM ELECTRODE	D 2791-77A				
C. FLAME EMISSION					
D. ICP					
E. ION EXCHANGE					
F. SPARK SOURCE MASS SPEC					
G. NEUTRON ACTIVATION					
H. EMISSION SPEC					
34. STRONTIUM					
A. AA-DIRECT	D 3354-74				BOOK 5
B. FLAME EMISSION					
C. X-RAY FLUORESCENCE					
D. ICP					
E. SPARK SOURCE MASS SPEC					
F. NEUTRON ACTIVATION					
G. EMISSION SPEC					
35. SULFATE					
A. GRAVIMETRIC	D 516-68A	2.71	00945	427A, B	
B. TURBIDIMETRIC	D 516-68B	2.72	00945	427C	
C. ATOMIC ABSORPTION-INDIRECT (WITH BARIUM CHLORIDE)					
D. FLAME EMISSION-INDIRECT (WITH BARIUM CHLORIDE)					
E. ION EXCHANGE					

	ASTM	API	EPA	APHA	ESGS
36. SULFIDE					
A. TITRIMETRIC (IODINE)		3.10.1	00746		BOOK 5
B. ANTIMONY TEST (QUALITATIVE)				428	
C. COLORIMETRIC (METHYLENE BLUE)		3.10.2		428C	
D. SULFIDE ELECTRODE					
E. X-RAY FLUORESCENCE					
F. SPARK SOURCE MASS SPEC					
G. NEUTRON ACTIVATION					
37. SUSPENDED SOLIDS					
A. GRAVIMETRIC	D 1888-67A		00530	308D	BOOK 5
38. TOTAL DISSOLVED SOLIDS - TDS					
A. GRAVIMETRIC	D 1888-67A		70300	208B, C	BOOK 5
39. TURBIDITY					
A. ABSORPTOMETRIC					
B. VISUAL MATCHING				214B	
C. NEPHELOMETRIC	D 1889-71		00076	214	BOOK 5
40. ZINC					
A. ATOMIC ABSORPTION-DIRECT	D 2576-70		01092	301A	BOOK 5
B. AA-APDC&ANBK EXTRACTION				301A	
C. ICP					
D. SPARK SOURCE MASS SPEC					
E. NEUTRON ACTIVATION					
F. EMISSION SPEC					

ABBREVIATION		REFERENCES
ASTM	1.	1977 Annual Book of ASTM Standards, Part 31, Water, American Society for Testing and Materials, Philadelphia, PA (1976).
API	2.	API Recommended Practice for Analysis of Oil Field Water, American Petroleum Institute, Dallas, Texas (1968).
EPA	3.	Methods for Chemical Analysis of Water and Wastes, Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio (1976).
APHA	4.	Standard Methods for the Examination of Water and Wastewater, 14ed., American Public Health Association, Washington, D.C. (1975).
USGS	5.	Brown, Eugene, M. W. Skongstad, M. J. Fishman, Methods for Collection and Analysis of Water Samples for Dissolved Gases, Book 5, Chapter A1, United States Geological Survey, Washington, D.C. (1974).
USGS/WRI	6.	Presser, T. S. and I. Barnes, Special Techniques for Determining Chemical Properties of Geothermal Water, WRI-22-74, United States Geological Survey, Menlo Park, California (1974).