



GEOHERMAL SAMPLING AND ANALYSIS

Halldór Ármannsson, Magnús Ólafsson and Finnbogi Óskarsson

ISOR – Iceland GeoSurvey
Grensásvegur 9, 108 Reykjavík
ICELAND

halldor.armannsson@isor.is, magnus.olafsson@isor.is, finnbogi.oskarsson@isor.is

ABSTRACT

Sampling and analysis provide the data for all geochemical interpretation and thus it is imperative that these tasks be performed by trained personnel with insight into possible errors. Different types of containers (glass or plastic, amber or transparent) and different pre-treatment (dilution, filtering, freezing, addition of chemicals) is needed for the various constituents determined. Some constituents need analysis shortly after collection either on the spot or in a near-by laboratory which may be a field laboratory. The most common analytical techniques employed for geothermal fluid samples that are likely to be available in most laboratories are titrimetry, UV-Vis spectrophotometry, atomic absorption spectrophotometry (AAS), ion chromatography (IC), electrometry and gas-solid chromatography (GSC). In recent years inductively coupled plasma has become widely used both with atomic emission spectrometry (ICP/AES) and mass spectrometry (ICP/MS) but this requires expensive equipment and these instruments, particularly the latter, tend to be run by large commercial laboratories on a commercial basis and it is quite common that samples are sent there for analysis, especially for major cations and trace elements. Stable isotopes are analysed for by mass spectrometry (MS) and radioactive isotopes by radiometry. These techniques are not available to all laboratories and are frequently carried out on a commercial basis. From the returns in the inter-laboratory comparison of analytical techniques carried out by the International Atomic Energy Agency in 2002 involving 31 laboratories working with geothermal samples it is clear that AAS is the most used technique for cation analysis but titrimetry and UV-Vis spectrophotometry for anion analysis.

1. INTRODUCTION

The collection of samples for chemical analysis is the first step in a long process which eventually yields results that provide building blocks in the model of a geothermal system. It is imperative that this step is properly carried out because all subsequent steps depend on it.

There are several hidden dangers inherent in the collection of geothermal sample. The terrain may be treacherous and dangerous chemicals need to be handled. Thus there is an obvious need for well trained personnel with insight into possible errors and interferences to carry out this task. The most common mistakes made during sampling involve the use of improper containers, improper cleaning and lack of or improper treatment for the preservation of samples.

2. CONTAINERS

For lightness, ruggedness and tolerance of bumps in the field plastic bottles (HDPE/PP) are the best. Most plastics are however relatively permeable and let atmospheric air easily through, possibly setting off oxidation reactions, and liquids may easily evaporate through them causing concentration of constituents and possible oversaturation. Many plastics are also rife with possible adsorption sites for sample constituents and may thus decrease their concentrations.

Glass is fragile and relatively heavy but can fairly easily be made airtight. Thus glass containers are preferable for the preservation of constituents affected by atmospheric air. Constituents that are sensitive to light are collected into amber bottles.

If containers have not been specifically pre-cleaned and prepared for a certain task they should be rinsed at least three times with the sample fluid prior to collection.

3. SAMPLE PRESERVATION

Some constituents will not survive intact from sample collection to analysis without special precautions. Common reasons for concentration changes are interaction with suspended matter, adsorption on the walls of the containers, biological activity, redox reactions, polymerisation and precipitation. Different preservation methods are needed for the various processes and thus the total sample will comprise several sub-samples. Preservation methods may be physical or chemical and the more common ones are listed in Table 1. In the case of chemical addition, the amount of chemicals added may need to be adjusted to suit the composition of the sample. The amounts of nitric acid and zinc acetate given in Table 2 should be adequate in most cases, however larger amounts may be needed for samples with high buffer capacity or high concentrations of hydrogen sulphide.

It is desirable that samples be kept relatively cool apart from the inconvenience of handling boiling hot water and steam. Fluid that is well above ambient temperature is therefore cooled to ambient temperature using a cooling device, usually a cooling coil immersed in cold water, during collection. Steam samples collected into NaOH or KOH in double-port bottles may by-pass the cooling device as steam condensation will take place inside the bottle if it is cooled in water.

4. COLLECTION

The collection of samples of non-boiling water can be divided into two categories, samples from natural springs and samples from hot water wells. When collecting samples from hot springs it is desirable that the water be free-flowing from the sample spot. If not, a sampling pump is needed. Water temperature and discharge as well as wellhead pressure if available are reported.

The collection of representative samples from high-temperature drillholes is done either by using the separator on the wellhead separating the whole discharge or with a small Webre separator. Natural steam discharge may occur in many different forms, such as gentle discharge from a large area of hot ground or major discharge from large fumaroles. The most useful information is often obtained from steam discharged from powerful fumaroles. The temperature of the fumarole is reported.

It has been shown that the most representative samples are collected from the flow of a two-phase well at about 1.5 m distance from the T-joint at the well top.

The various sub-samples collected are described in detail in Table 2 but the total procedure for collection from high-temperature wells is shown in Figure 1. Samples are collected into plastic bottles unless otherwise specified.

TABLE 1: Preservation methods for geothermal samples

Type	Method	Purpose	Used for
Physical	Filtration	Prevent interaction with suspended matter	Anions, cations
	Freezing	Prevent biological activity	Nutrients
	Airtight container	Prevent interaction with atmospheric air	Volatiles
	On-site analysis	Prevent reactions of reactive constituents	Reactive constituents
Chemical	Base addition	Absorption of acid gases	CO ₂ , H ₂ S in vapour, δ ³⁴ S in H ₂ S in vapour
	Acidification	Prevent adsorption on walls of containers	Cations
	Precipitation	Prevent a constituent from reaction to change the concentration of another	Sulphide to preserve sulphate
	Sterilization	Prevent biological activity, using HgCl or formaldehyde	δ ³⁴ S and δ ¹⁸ O in SO ₄ , prevents biological oxidation of sulphide
	Dilution	Prevent polymerization and precipitation	Silica
	Redox	To change oxidation state of a volatile constituent to make it less volatile	Hg
	Ion exchange	Concentrate and further prevent adsorption on walls of container of trace constituents	Trace cations
	Extraction	Concentrate and further prevent adsorption on walls of container of trace constituents	Trace cations

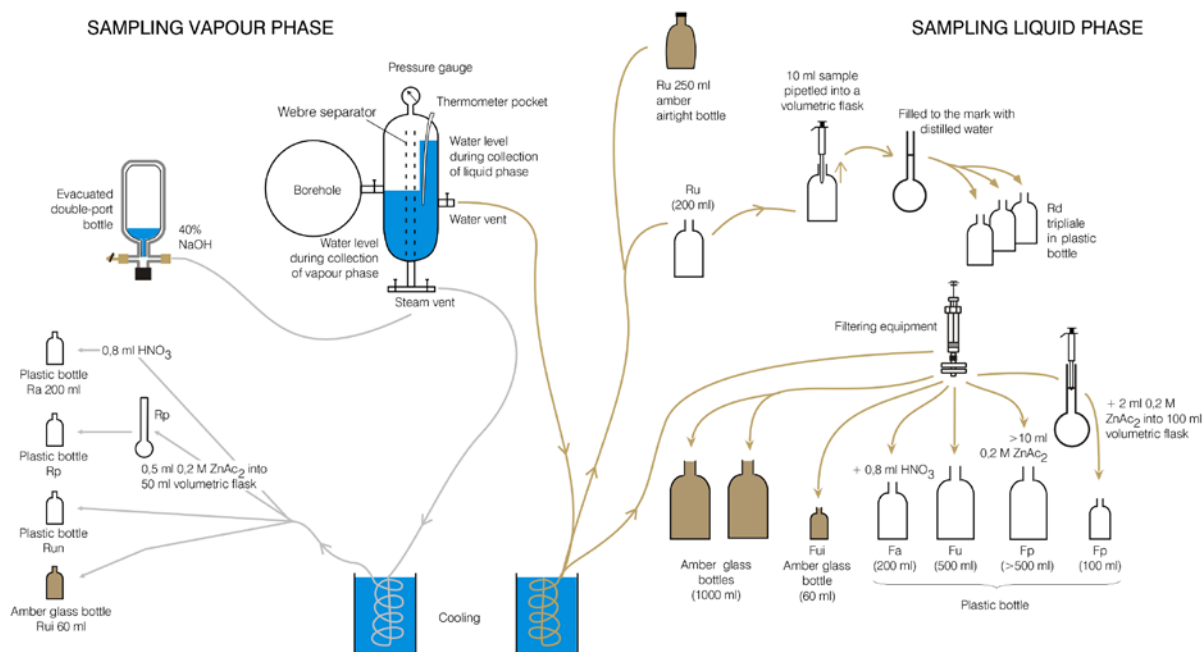


FIGURE 1: Overview of collection of a sample from a two-phase geothermal well for chemical analysis.

TABLE 2: Treatment and sub-samples from geothermal sampling

Phase	Treatment	Specification	To determine
Vapour	None; amber glass bottle	Ru	$\delta^2\text{H}$, $\delta^{18}\text{O}$
	0.5 mL 0.2 M ZnAc_2 added to sample in 100 mL volumetric glass flask to precipitate sulphide	Rp	SO_4
	None	Ru	Anions
	0.8 mL conc. HNO_3 (Suprapur) added to 200 mL sample	Ra	Cations
	Added to 50 mL 40% NaOH in evacuated double port bottle	Gas sample, Ai	CO_2 , H_2S in NaOH , residual gases in gas phase, $\delta^{34}\text{S}$ in H_2S in vapour
Liquid	None	Ru	Mg , SiO_2 if < 100 ppm
	Dilution; 10 to 50 mL of sample added to 90 to 50 mL of distilled, deionised water	Rd (1:10 to 1:1)	SiO_2 if > 100 ppm
	None; amber glass bottle with ground glass stopper	Ru	pH, CO_2 , H_2S (if not in field), NH_3
	Filtration (0.45 or 0.20 μm)	Fu	Anions
	Filtration; 2 mL 0.2 M ZnAc_2 added to sample in 100 mL volumetric glass flask and ≥ 10 mL to ≥ 500 mL bottle containing ≥ 25 mg SO_4 to precipitate sulphide	Fp, Fpi	SO_4 , $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in SO_4
	Filtration; 1 \times 60 mL and 2 \times 1000 mL amber glass bottle, with ground glass stoppers	Fui, Fuc, Fut	$\delta^2\text{H}$, $\delta^{18}\text{O}$, ^{13}C , ^3H
	Filtration; 0.8 mL conc. HNO_3 (Suprapur) added to 200 mL sample	Fa	Cations

The vents on the Webre separator are opened and the fluid is allowed to flow from the borehole through the separator. Care is taken that the pressure in the separator does not deviate much from that of the wellhead. For the collection of the vapour phase the water level inside the separator is kept low until preferably a mixture of water and steam issues through the water vent. A blue cone should form at the steam vent showing that dry steam is being issued. To check the efficiency of the separation a small sample of condensed steam may be drawn and the concentration of a non-volatile component such as Na or Cl determined, compared with the concentration of the same component in the liquid phase and the percentage of carry-over calculated. If $t < 70^\circ\text{C}$ it may be desirable to determine the dissolved oxygen concentration of the water to estimate its corrosion potential. This determination is carried out during sampling as described below.

When sampling fumaroles care has to be taken that a discrete, directed outflow is chosen and diffuse ones avoided at all costs. A good guide to the suitability of an outflow for sampling is sulphur deposits. A funnel is placed atop the outflow and care taken that no atmospheric air is drawn in. The funnel is connected to a titanium tube which is directed to a lower point where the sample is collected. When sampling springs care has to be taken to obtain a sample as near to the outflow as possible. An indicator such as ink may be used if it is difficult to find. Normally the water sample will be drawn with a pump into an evacuation flask. The filtering apparatus is fitted between the sample and the pump when appropriate. If a gas sample is required two evacuated flask one with taps on both ends below and a double port gas bottle containing 40% NaOH above are arranged in series. The taps are opened slowly, first on the two-ended flask and care taken that water does not enter the double port bottle (Figure 2). Sampling techniques are described in more detail by Ármansson and Ólafsson (2006).

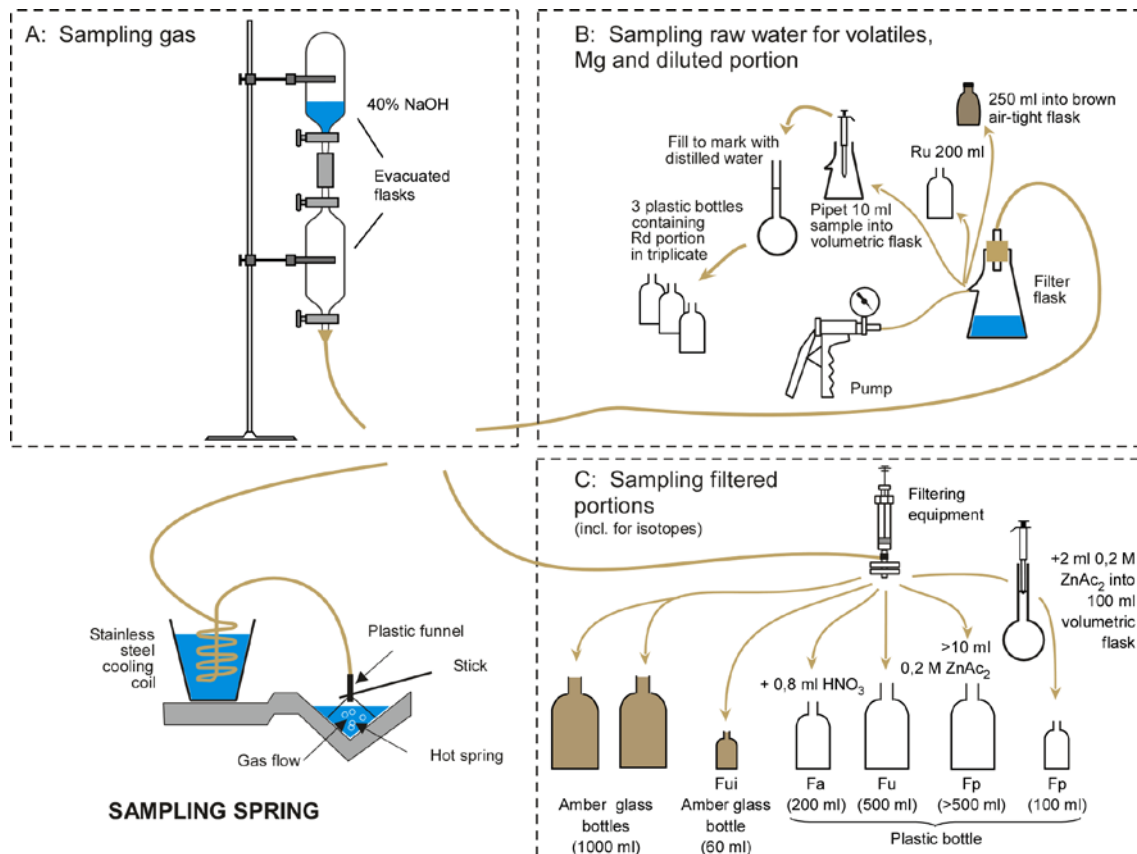


FIGURE 2: Collection of sample from a spring

5. ANALYSIS

5.1 Main laboratory

The choice of an analytical technique depends on several factors, i.e. the availability of instruments, potential servicing facilities for different types of instruments, the presence of trained personnel, and the speed, reliability and cost of the different methods.

5.2 Field laboratory

In a field laboratory facilities for the determination of volatile constituents (pH, CO₂, H₂S, NH₃, O₂), urgent constituents (e.g. SiO₂), constituent used for separation efficiency checks (Na or Cl) and apparatus for specific tests if required e.g. analytical balance, drying oven) and a supply of deionised water.

5.3 Determination of volatile constituents in water

It is recommended that analysis for oxygen and hydrogen sulphide be carried out in the field. pH should also be determined in the field as various processes can affect the pH value on the samples way to the laboratory, in particular loss of volatiles and silica polymerisation.

It is convenient to determine oxygen colourimetrically using ampoules, e.g. those from CHEMetrics, Inc., containing Rhodazine D for concentrations 0-100 ppb, but Indigo carmine for higher concentrations. Oxygen may also be determined by a Winkler iodometric titration. Hydrogen sulphide is determined titrimetrically using mercuric acetate and dithizone (Ármannsson and Ólafsson 2006).

Mercury can behave as a volatile constituent. Even though it is usually present as Hg^{2+} it is easily reduced to elemental Hg which is extremely volatile. Therefore it is recommended that an oxidizing agent such as KMnO_4 be added upon collection to samples for mercury analysis. The analysis is either carried out by reduction, gold amalgamation of elemental mercury, heating and flameless atomic absorption spectroscopy (AAS), or by atomic fluorescence spectrometry (AFS).

5.4 Silica analysis

Silica is one of the most important constituent analysed in geothermal water, as it is extensively used for geothermometry, as well as for prediction of scaling. According to the IAEA Interlaboratory Comparison 2003 (Urbino and Pang 2004), the majority of the participating laboratories analysed silica by colorimetric determination of a silica-molybdate complex, but some laboratories used AAS and ICP. There is a marked difference between the methods in that the spectrophotometric method only detects monomeric silica and therefore samples with high silica content ($> 120 \text{ mg/L}$) must either be diluted to suitable concentration in the field or digested with NaOH before analysis, whereas the AAS and ICP methods determine total silica and demand that samples be acidified in the field.

5.5 Cation analysis

AAS (flame for major, carbon furnace for minor cations), flame emission spectrometry (FES) (major cations), ion chromatography (major cations) and inductively coupled plasma with atomic emission spectrometry (ICP/AES) or mass spectrometry (ICP/MS) (major and minor cations) are all widely used techniques for cation analysis. Specific applications include fluorimetry for Al^{3+} , spectrophotometry for field determinations of Fe^{2+} and the determination of ammonia in saline water, and ion selective electrode for the determination of ammonia in dilute water.

5.6 Anion analysis

Ion chromatography (IC) is the most convenient technique for fluoride, chloride, bromide, nitrate and sulphate. Sulphide has to be removed from the sample upon collection by precipitation with zinc acetate before the sulphate determination. It may prove difficult to separate the fluoride and chloride peaks in saline fluids using IC, in which case fluoride can may be determined using an ion selective electrode. Boron and silica can both be determined easily either by spectrophotometry and ICP. It is also fairly common to determine sulphate by colourimetry and turbidometry. In Table 3 the results for the three methods for sulphate determination used by laboratories taking part in a comparative exercise are compared and for the two samples the best results are obtained by ion chromatography (Alvis-Isidro et al. 2002).

TABLE 3: Comparison of results for different methods of sulphate determination in the IAEA laboratory comparison 2001 (after Alvis-Isidro et al. 2002)

Sample No.	Method	Number of labs	Mean mg/l	RSD %
1	IC	8	22.3	10.0
	CO	16	24.2	27.0
	TU	11	26.9	38.2
	Reference		23.2	
3	IC	8	31.5	6.4
	CO	17	32.5	8.8
	TU	11	30.4	24.2
	Reference		31.8	

5.7 Gas analysis

The most important techniques for gas analysis are titrimetry, gas chromatography, mass spectrometry and radiometry. CO_2 and H_2S are determined titrimetrically in a solution of a strong alkali (NaOH or KOH), by an alkalinity titration with HCl, but by either iodometry or with mercuric acetate using

dithizone as an indicator. Gases that are not absorbed by the strong alkali (N₂, H₂, CH₄ (higher hydrocarbons if present), O₂, Ar, He) are determined by gas chromatography. Gas chromatographs are usually designed for their specific function. The instrument employed at Iceland GeoSurvey is a Perkin-Elmer Arnel 4019 Analyser designed for the analysis of geothermal gases. It combines into three analytical channels and employs N₂ and He as carrier gases. Its special capability are the separations of H₂ and He and of O₂ and Ar. Trace noble gases (Ne, Kr, Xe) are determined by mass spectrometry and radioactive gases (e.g. Rn) by radiometry.

5.8 Isotope analysis

Stable isotope ratios are determined by mass spectrometry (MS) by comparison with a standard, but radioactive isotopes by radiometry. The most common stable isotopes determined during geothermal work are ²H, ¹⁸O, ¹³C and ³⁴S but the most common radioactive isotopes ³H and ¹⁴C which are used for dating, and ²²²Rn which is taken to indicate permeability. As mass spectrometers are expensive and complex instruments, the analysis of stable isotopes are typically done at specialised isotope laboratories, but radioactive isotopes may often be determined in the field using handheld instruments. Due to interferences such as that of water vapour in MS the compounds containing the isotopes are converted to constituents that do not interfere. Thus H₂O is converted to H₂ for ²H analysis and CO₂ for ¹⁸O analysis. H₂S and SO₄ are converted to SO₂ for ³⁴S analysis and SO₄ to CO₂ for ¹⁸O determination. The radioactive isotopes are determined by liquid scintillation counting or by α -particle detection.

5.9 Quality control

The precision of methods can be checked by repeated analysis of the same sample or by duplicates or triplicates of several samples. To obtain an idea of the accuracy of the determinations several approaches are possible, i.e. the use of standard additions to sample to obtain % recovery, carrying out determinations of the same constituent by different methods, using standards or reference samples that are run with each batch of samples determined, checks on ionic balance, i.e. whether the sum of anions determined is close to the sum of cations determined, or a check on mass balance, i.e. whether the sum of constituent concentrations (as determined by dry-evaporation of a sample and gravimetry) matches that of the result of the determination of total dissolved solids.

One of the most useful checks is an inter-laboratory comparison in which samples whose composition is known is sent to a number of laboratories who use different methods for the determination of each sample. Thus each laboratory can measure itself against others in the same field. Examples are the inter-laboratory comparisons for the determination of major constituents of geothermal fluids organized by the International Atomic Energy Agency (Alvis-Isidro et al. 2002, Urbino and Pang 2004) from which the results presented in Table 3 are obtained. The methods used by the various laboratories that took part in the 2003 exercise (Urbino and Pang 2004) are presented in Table 4.

TABLE 4: Methods used for selected constituents by laboratories in IAEA Interlaboratory Comparison 2003 (After Urbino and Pang 2004)

Method	Cl	SO ₄	SiO ₂	K	Mg
Co	2	16	14		
Tm	23				1
IC	5	5		2	2
Tu		9			
AAS			9	24	21
ICP/MS			1		
ICP/AES			3		3
FES				1	

Co: Colorimetric; Tm: Titrimetry; IC: Ion Chromatography; Tu: Turbidometry; AAS: Atomic Absorption Spectrometry; ICP/MS: Inductively Coupled Plasma/Mass Spectrometry; ICP/AES: ICP/Atomic Emission Spectrometry; FES: Flame Emission Spectrophotometry

6. CONCLUSIONS

For proper sampling clean containers of appropriate material are needed. Care has to be taken that appropriate preservation techniques for particular constituents are applied. Thus each sample will be composed of several sample fractions ready for analysis. Volatile and urgent constituents are analysed for in a field laboratory or upon sampling. Analysis for most anions is usually best performed in the home laboratory but cations and most trace constituents may be advantageously analysed for in a commercial laboratory applying ICP techniques. A survey of 31 laboratories taking part in an IAEA laboratory comparison exercise showed that atomic absorption spectrophotometry, UV-Vis spectrophotometry and titrimetry were the techniques most widely employed.

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