Presented at Short Course VII on Exploration for Geothermal Resources,
organized by UNU-GTP, GDC and KenGen, at Lake Bogoria and Lake Naivasha, Kenya, Oct. 27 – Nov. 18, 2012.

GEOTHERMAL SAMPLING AND ANALYSIS

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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 (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 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 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, polymerization 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.

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 in double-port bottles may by-pass the cooling device and the bottle itself is cooled in cold 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.

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_2S in steam, $\delta^{34}S$ in H_2S 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	$\delta^{34}S$ and $\delta^{18}O$ 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

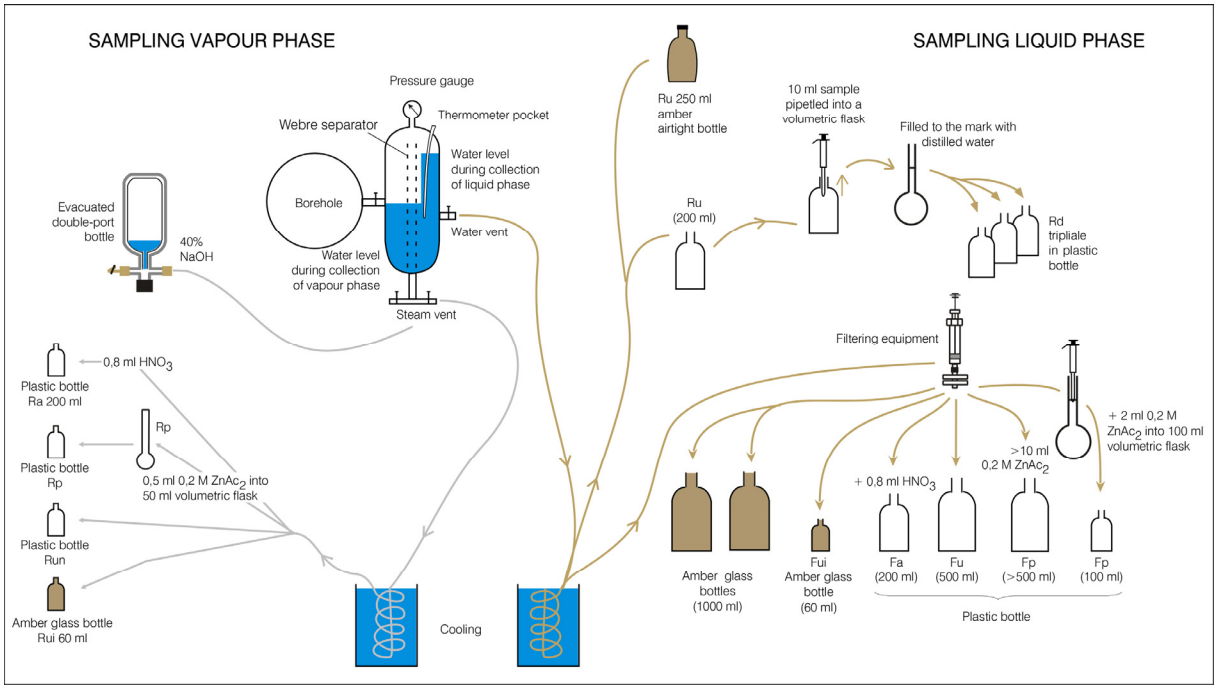

FIGURE 1: Overview of collection of a sample from a two-phase geothermal well for chemical analysis.

TABLE 2: Treatment and sub-samples from geothermal sampling

Phase	Treatment	Specification	To determine
Vapour	None; amber glass bottle	Ru	δ^2H, $\delta^{18}O$
	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, $\delta^{34}S$ 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)
	Filtration (0.45)	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, $\delta^{34}S$ and $\delta^{18}O$ in SO_4
	Filtration; 1 60 ml and 2 1000 ml amber glass bottle, with ground glass stoppers	Fui, Fuc, Fut	δ^2H, $\delta^{18}O$, ^{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°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 Ármannsson and Ólafsson (2006).

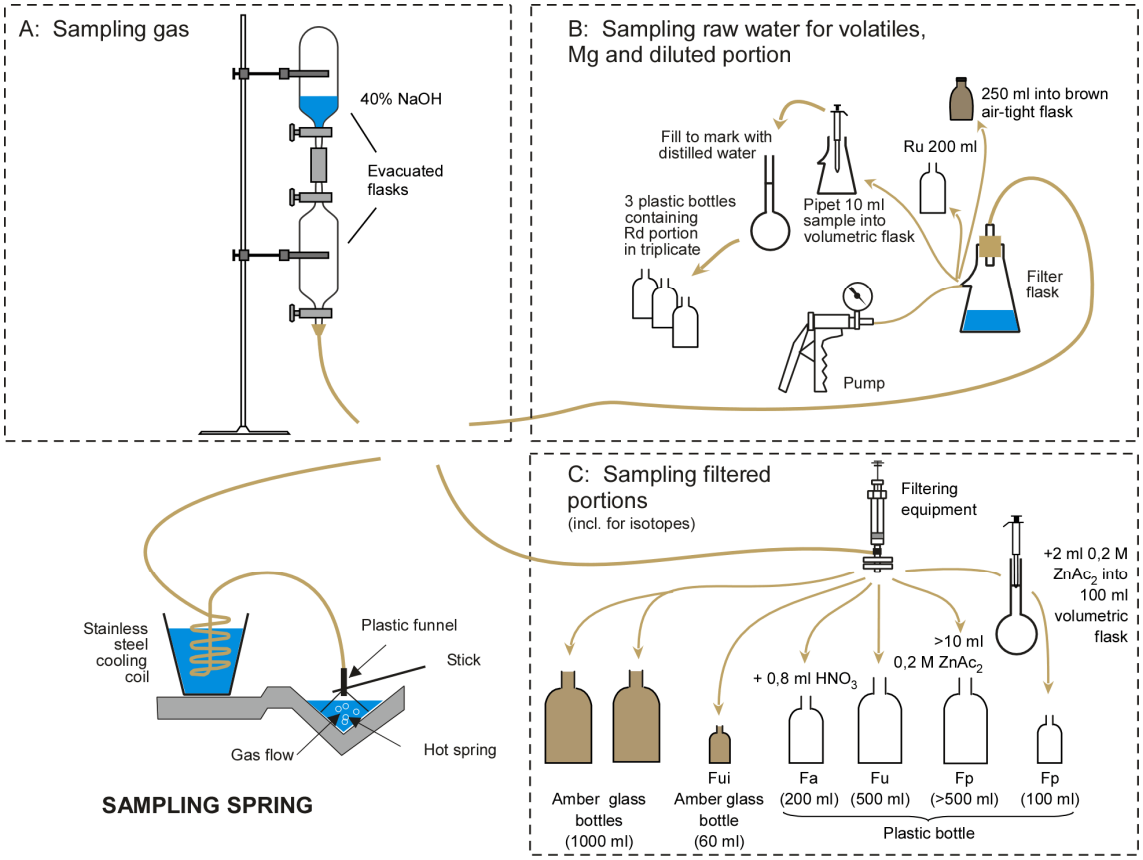

FIGURE 2: Collection of sample from a spring

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, CO_2, H_2S, NH_3, O_2), urgent constituents (e.g. SiO_2), 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 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 (N_2, H_2, CH_4 (higher hydrocarbons if present), O_2, Ar, He) are determined by gas chromatography. Gas chromatographs are usually designed for their specific function. The University of Iceland/Iceland GeoSurvey instrument is a Perkin-Elmer Arnel 4019 Analyser designed for the analysis of geothermal gases. It's most important features are three carrier flow sources, dual and single thermal conductivity detectors, four

valves, five analytical columns and three auxiliary carrier gas sources. It combines into three analytical channels and employs N_2 and He as carrier gases. Its special capability are the separations of H_2 and He and of O_2 and Ar. Trace noble gases (Ne, Kr, Xe) are determined by mass spectrometry and radioactive gases (e.g. Rn) by radiometry.

5.4 Determination of volatile constituents in water

It is recommended that analysis for oxygen and hydrogen sulphide be carried out in the field.

Oxygen is determined colourimetrically using ampoules from CHEMetrics, Inc., containing Rhodazine D for concentrations 0-100 ppb, but Indigo carmine for higher concentrations, but 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 which is carried out by reduction, gold amalgamation of elemental mercury, heating and flameless atomic absorption spectroscopy (AAS) (Ólafsson 1974).

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 is the most convenient technique for chloride, bromide and sulphate. Sulphide has to be removed from the sample upon collection by precipitation with zinc acetate before the sulphate determination. Fluoride can also be determined by ion chromatography if care is taken to separate its peak from the chloride peak but it is more conveniently determined using an ion selective electrode. Boron and silica can both be determined easily 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 used by laboratories taking part in a comparative exercise are compared and for the two samples the best results are obtained by ion chromatography.

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 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 ^{2}H, ^{18}O, ^{13}C and ^{34}S but the most common radioactive isotopes ^{3}H and ^{14}C which are used for dating, and ^{222}Rn. 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 H_2O is converted to H_2 for ^2H analysis and CO_2 for ^{18}O analysis. H_2S and SO_4 are converted to SO_2 for ^{34}S analysis and SO_4 to CO_2 for ^{18}O determination. The reduction of H_2O to H_2 has been problematic. Originally hot uranium was used (Friedman 1953) but that is too dangerous. Zn metal (Coleman et al. 1982) has been widely used but the general experience shows that for unexplained reasons the only reagent that seems to work is Zinc shot from BDH. Equilibration using a Pt catalyst (Horita 1988)) has given some useful results but only works for some samples. Those that give erroneous results generally contain H_2S. More recent developments involve the use of hot Cr for the reduction (Schoeller et al. 2000, Donnelly et al. 2001). Oxygen is generally equilibrated with carbon dioxide according to the method of Epstein and Mayeda (1954). Hydrogen sulphide is converted to SO_2 by precipitation as Ag_2S followed by oxidation with Cu_2O or V_2O_5 (Yanagisawa and Sakai 1983). $BaSO_4$ is precipitated either directly from high sulphate solutions or following ion exchange from low sulphate solutions, and then reduced with graphite to obtain CO which then is converted to CO_2 used for the ^{18}O determination (Nehring et al. 1977). The reduced sulphide is precipitated as Ag_2S and converted to SO_2 using the above procedure. The radioactive isotopes are determined by liquid scintillation counting.

5.8 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 matches that of the result of the determination of total dissolved solids.

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			
AA			9	24	21
ICP/MS			1		
ICP/AE			3		3
FE				1	

Co: Colorimetric; Tm: Titrimetry; IC: Ion Chromatography; Tu: Turbidometry; AA: Atomic Absorption; ICP/MS: Inductively Coupled Plasma/Mass Spectrometry; ICP /AE: ICP/Atomic Emission Spectrometry; FE: Flame Emission

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 2002, Urbino and Pang 2004) from which the results presented in Table 3 are obtained. It is interesting to find out which methods were used by the various laboratories that took part in the 2003 exercise (Urbino and Pang 2004) and are presented in Table 4.

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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