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**SAMPLING METHODS FOR GEO-
THERMAL FLUIDS AND GASES**

Magnús Ólafsson

OS-88041/JHD-06

October 1988



ORKUSTOFNUN - National Energy Authority
Geothermal Division

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RESULT OF CHEMICAL
ANALYSIS OF
GEOHERMAL SAMPLE

Sample No.	County	Locality	Area No.	Location	Year	Month	Date	No.	Batch No.	Sampled by
Location (well, spring)										
County, City					Locality					
P ₀ (bar)	P _s (bar)	H ₂ (MJ/kg) / Date		Flow (kg/s)	Quartz temp (°C)	Chalcedony temp (°C)		Na/K temp (°C)		
Chemical composition of water phase (mg/kg)					Gas (Vol - %)			Chem. comp. condensate (mg/kg)		
Temp °C		H ₂ S			CO ₂			pH/°C		
pH/°C	/	Cl			H ₂ S			CO ₂		
Ωm/°C	/	F			H ₂			H ₂ S		
SiO ₂		TDS			O ₂			Na		
Na					CH ₄					
K					N ₂					
Ca										
Mg								Chem. comp. steam (mg/kg)		
CO ₂		Ionic balance						CO ₂		
SO ₄		Mass balance						H ₂ S		
					Ig:kgC °C	/				
Notes										

Figure 2: A laboratory record card for chemical analyses.

2 COLLECTION OF HOT WATER

The collection of samples of non-boiling water can be divided into two categories. First, samples from natural hot springs, and second samples from geothermal drillholes. For such sampling some or all of the following apparatus is necessary:

Funnel, rubber hoses and connectors

Cooling device

Water sampling bulbs

Polyethylene bottles for samples (100 ml and 500 ml)

Pump

Filtering apparatus

Thermometer

Pipettes

Distilled water

pH-meter

500 ml volumetric flask

Hydrochloric acid (6N HCl)

Zinc acetate 0.2M $Zn(CH_3COO)_2$

Field record card and a permanent marker.

When collecting water from hot springs it is desirable that the water be free-flowing from the sample spot. Sometimes, however, it is necessary to pump the water. When the sampling apparatus has been set up and the water cooled to room temperature, collection can begin. Figure 3 shows a general setup for the collection of hot water.

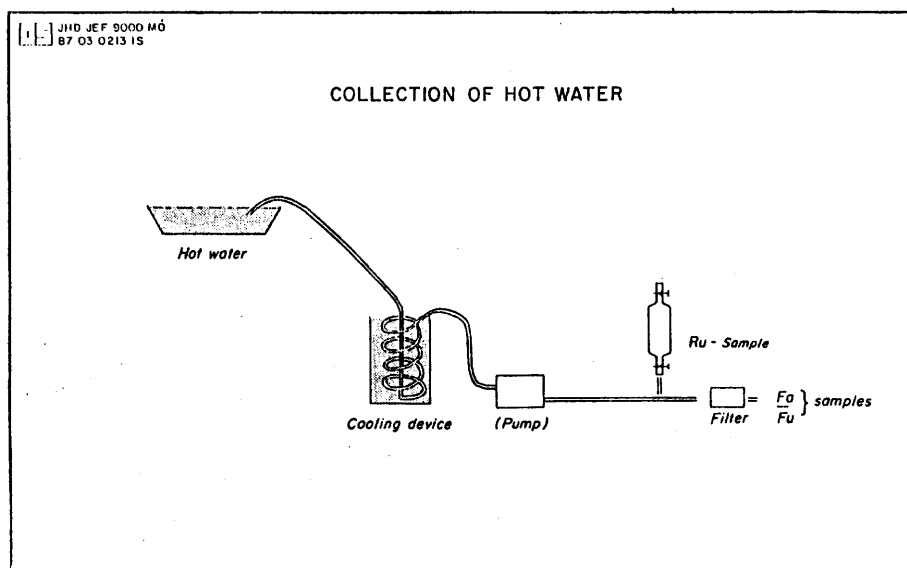


Figure 3: Collection of hot water.

First a gas-sampling bulb, which has been rinsed thoroughly, is filled with water. Next, an untreated sample is collected for SiO_2 analysis. If the SiO_2 concentration is expected to be more than 100 mg/kg, it is necessary to dilute the sample with distilled water. Ideally, the concentration of silica in the diluted sample should be in the range 30 to 100 mg/kg. If dilution is necessary, three such samples are collected into 100 ml polyethylene bottles and labelled Ru f. SiO_2 or Rd f. SiO_2 and the dilution factor is marked on the bottle. The next step is to collect samples into four 500 ml polyethylene bottles by the following procedure: First a filtered and untreated sample is sampled into one bottle and labelled Fu. Next one ml of 6N HCl is added to a 500 ml volumetric flask and filled to the mark with filtered sample. Two such bottles may be needed for a whole chemical analysis. The samples are transferred to 500 ml sampling bottles and labelled Fa. In order to precipitate sulfide 10 ml of 0.2M $\text{Zn}(\text{CH}_3\text{COO})_2$ solution are added to a 500 ml volumetric flask and filled to the mark with filtered sample. The sample is transferred to a 500 ml sampling bottle and labelled Fp. If no sulfide is present in the water replace the Fp sample with a Fu sample. Always remember to record the temperature of the water and try to measure or estimate the discharge.

The collection of cold water is basically done in the same way as the collection of hot water except that no cooling is needed.

3 COLLECTION OF GASES AND CONDENSATE FROM HOT SPRINGS AND FUMARoles

Natural steam discharge may occur in many different forms, such as a gentle discharge from a large area of hot ground, as a major discharge from large fumaroles or hydrothermal explosion craters. The most useful information is often obtained from steam discharged from powerful fumaroles. The following apparatus is needed for collection.

Polyethylene funnel

Tubing, connectors, clamps and a three-way connector

Gas sampling bulbs of known volume

Gas-washing bottle (125-250 ml) with 40% NaOH

Plastic bottles for samples (100 ml and 500 ml)

0.2M $Zn(CH_3COO)_2$ solution

Cooling device

Thermometer

Vacuum pump

Pipettes and measuring cylinder

pH-meter

Shovel and rod

Field record card and a permanent marker.

Prior to sampling it is necessary to measure the temperature in a number of locations in order to find the hottest fumarole or spring, which is chosen as a sampling spot. In a large spring the temperature variation across the surface area may be considerable, perhaps 10°C or more. Figure 4 shows a schematic setup for the collection of steam and condensate.

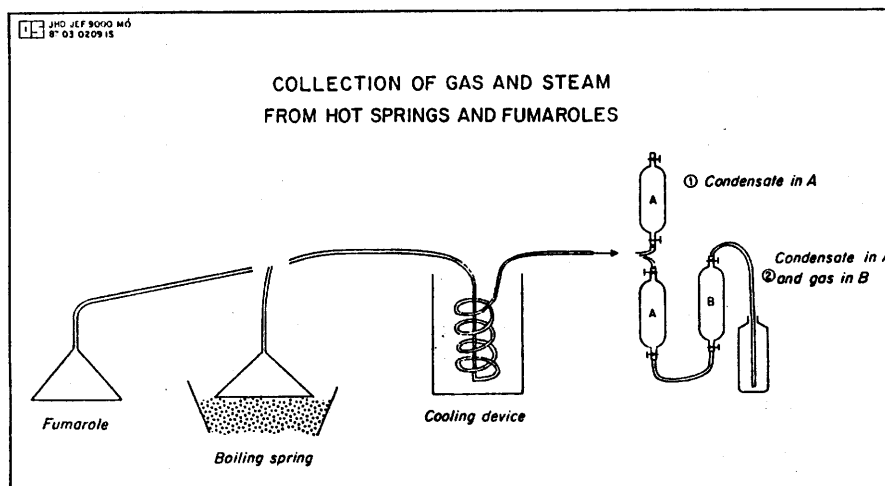


Figure 4: Collection of steam and condensate.

The funnel is placed over the sampling spot upside down and half submerged in the water in order to keep the sample as free from atmospheric contamination as possible. The funnel can be fasten to the springbank with a rod. When collecting gas and condensate from fumaroles the funnel is placed upside down over the major upflow and tightly packed with mud and clay in order to prevent atmospheric contamination.

If possible, it is convenient to have a free flow of water from the sampling spot and through the cooling device. Otherwise a vacuum pump is needed. The geothermal fluid should be cooled to 20 - 25°C prior to sampling.

When collection begins, two gas sampling bulbs should be rinsed thoroughly with the fluid to be collected. The smaller gas sampling bulb, which will be used to sample gas, is filled completely with condensate. Then the two bulbs are connected with a short piece of rubber tubing, which has also been cleaned. To the other end of the condensate-sampling bulb one connects a piece of rubber tubing and puts the loose end into a measuring cylinder. The gas sampling bulb, which has been filled with condensate, is now turned upside down, and the gas expels the condensate into the second gas bulb and finally into the measuring cylinder. When the gas sampling bulb has been filled with gas, the lower end of it is closed first in order to over-pressurize the gas a little bit. The upper end is now closed and both gas sampling bulbs labelled. The amount of condensate sampled with the gas is measured in the following way:

$$\frac{(\text{vol. of cond. in bulb}) + (\text{vol. cond. in cylind.}) - (\text{vol. of gas bulb})}{(\text{vol. cond. sampled with gas})} =$$

The next step in this sampling procedure is to collect condensate into a polyethylene bottle. In order to precipitate sulfide from the water, 200 - 300 ml of condensate is collected into a known amount of $\text{Zn}(\text{CH}_3\text{COO})_2$ solution. Usually the ratio 50:1 can be used. The bottle is labeled Fp and the amount of zinc acetate marked.

Finally steam is collected into a concentrated (40%) NaOH solution, as is shown schematically in Figure 5.

Prior to sampling approximately 50 ml of 40% NaOH solution are measured into a gas-washing bottle. The bottle is stoppered with a rubber stopper with two pipes connected to a rubber tubing and clamps. One pipe runs down to the bottom of the flask while the other one ends just below the stopper. The flask is evacuated with a pump and/or by boiling, dried and weighed (V_1). The flask is now ready for steam collection. Connect the longer nylon pipe of the flask to the cooling device and admit the steam. Shake the flask intermittently and collect the steam through the NaOH solution until bubbling stops. Close the nylon pipe and the collection is finished. Then the flask is weighed again (V_s) and the total volume of sample and NaOH solution (R_s) measured. Finally one can calculate D, which is used when analyzing for CO_2 and H_2S .

$$D = \frac{(V_s - V_1)}{R_s}$$

If the amount of other gases is insignificant, one can calculate the mass-percentage of gas based on the CO_2 and H_2S analyses in the following way:

$$\% \text{GAS} = \frac{(\text{CO}_2(\text{ppm}) + \text{H}_2\text{S}(\text{ppm}))}{10000}$$

If, on the other hand, there is a significant amount of other gases present, it is necessary to collect gas into a special gas sampling bulb and have it analyzed.

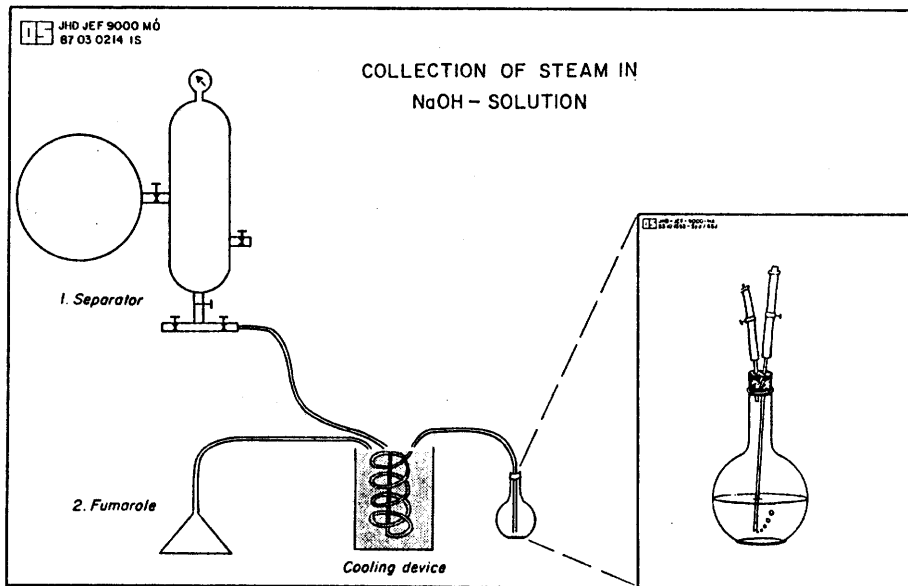


Figure 5: Collection of steam into NaOH solution

4 COLLECTION OF GEOTHERMAL FLUID FROM HIGH TEMPERATURE WELLS

The collection of representative samples from high temperature drillholes is a complex procedure. It is done either by using the separator on the wellhead separating the whole discharge, or a small Webre separator as shown in Figure 6.

If representative samples are to be obtained, great care has to be taken that the sampling valve, to which the separator is connected, is properly located. Tests have shown that the optimum location is about 1.5 m from the T-joint at the well top. At this point the flow is free from interference from the T-joint, but the water and steam phases are still in thermodynamic equilibrium. This configuration is shown in Figure 7. The hole through which the fluid sample flows should be large enough not to become regularly blocked by deposition, yet small enough for a faulty valve to be replaceable without turning the flow off the pipeline. In our experience the optimum diameter is about 5 mm.

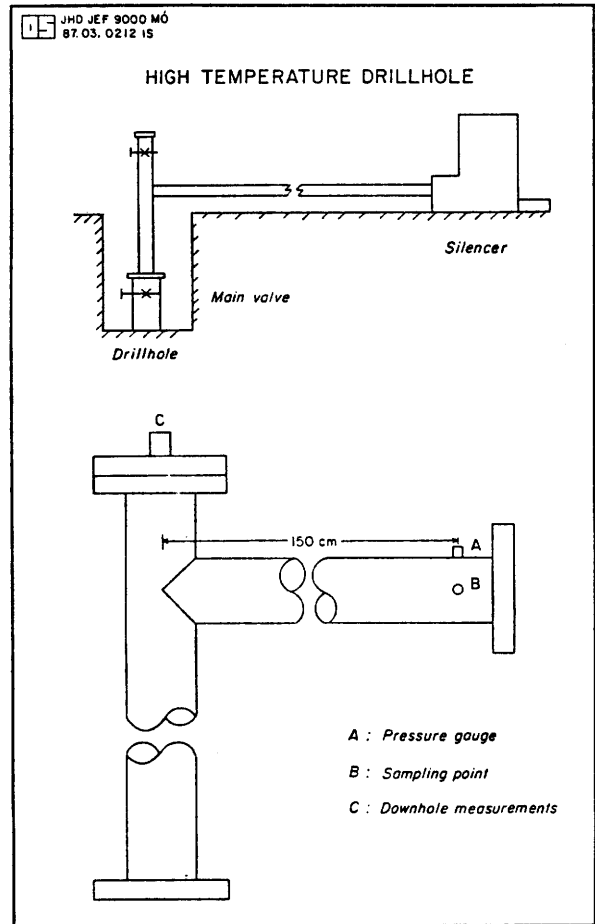
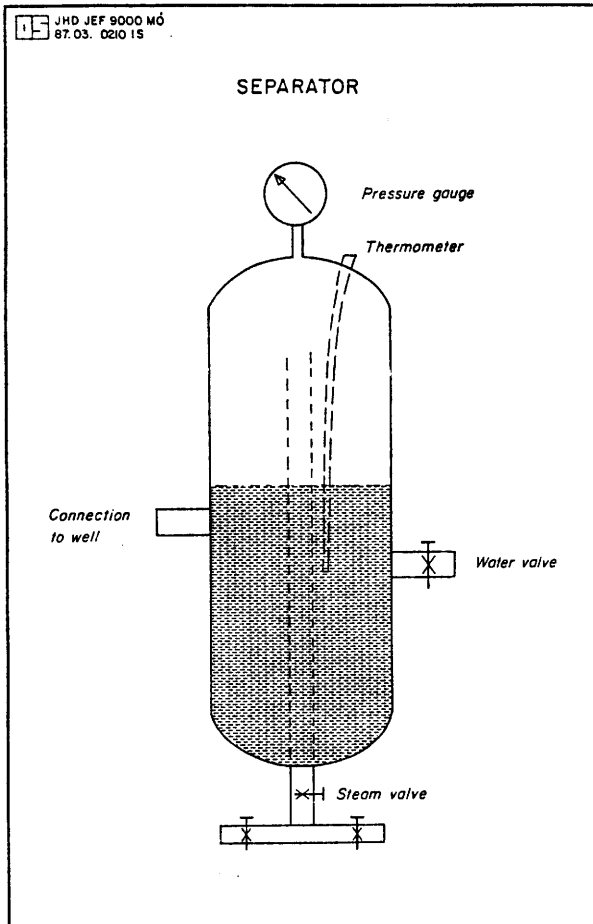


Figure 6: A schematic drawing of a Webre separator.

Figure 7: The top of a high-temperature drillhole.

The following apparatus is required for the collection of water and gas from wet steam wells:

- Separator and sampling hoses
- Tools, fittings and teflon-tape
- Cooling device
- Pressure gauge
- Thermometer
- Filtering apparatus
- Gas sampling bulbs
- Round flat-bottom flasks with 40% NaOH
- Plastic bottles for samples (100 ml and 500 ml)
- Two volumetric flasks (500 ml)
- 500 ml measuring cylinder
- Automatic pipettes
- Hydrochloric acid (6N HCl)
- Zinc acetate (0.2M $\text{Zn}(\text{CH}_3\text{COO})_2$)
- pH-meter
- Field record card and a permanent marker.

The separator is connected to the steam line and kept open for 10 to 15 minutes to rinse it out and warm it up. Then the separator is closed and the pressure on the separator pressure gauge (P_s) recorded. In order to obtain a representative sample, P_s should be comparable to a pressure reading on the steam line itself (P_o). The setup of a small Webre separator for collecting water, gas and steam from a high-temperature well is illustrated in Figure 8.

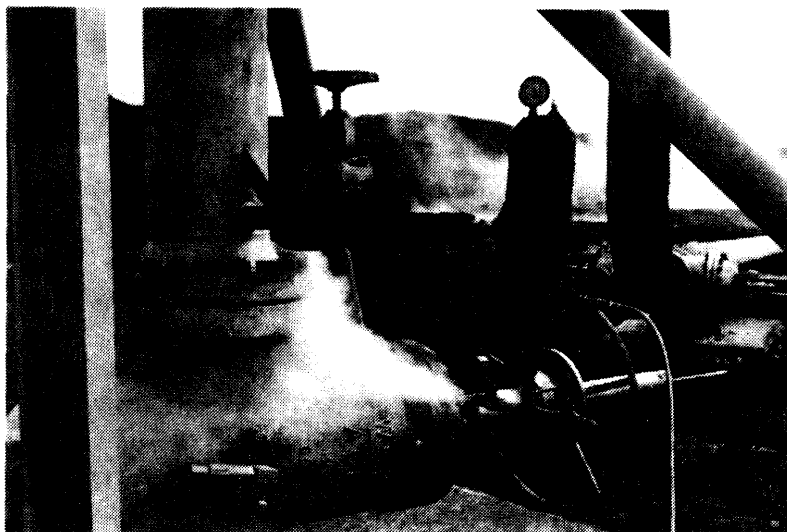


Figure 8: A Webre separator at well-head.

After opening the separator, take care that the pressure in it does not fall significantly (preferably less than 0.1 bar), because a pressure drop will cause boiling at lower temperatures in the separator and upset the separation of the two phases. One should keep an eye on the pressure gauge while sampling.

The cooling coil is connected to one of the steam outlet valves on the separator. The valve is kept closed. The other steam outlet is opened and the water and steam taps closed. The water tap is then partly opened and the gas tap opened slightly so that a mixture of steam and water will discharge through the water tap and dry steam through the steam tap. The dry steam is barely visible close to the steam outlet and is conical in shape. Now the steam outlet connected to the cooling coil is opened but the other one closed. Keep it open for a while to rinse the cooling coil. During sampling the steam will condense, but not gases such as CO₂, H₂S and H₂. Two phases need therefore be collected, condensate and gas.

Gas and condensate are collected into two gas sampling bulbs, and condensate into a 100 ml polyethylene bottle as well. All containers are first cleaned thoroughly with the cooled steam.

The two gas bulbs are connected by rubber tubing and a short piece of rubber tubing is connected to the second gas bulb and into a measuring cylinder. When sampling, one gas bulb is first filled with condensate, then it is turned upside down and the gas expels the condensate into the second gas bulb and finally into the measuring cylinder. During the sampling procedure the fluid temperature should be kept as constant as possible and recorded. Having sampled the gas, measure the volume of the condensate in the following way and record it:

$$\frac{(\text{vol. of cond. in bulb}) + (\text{vol. cond. in cylind.}) - (\text{vol. of gas bulb})}{(\text{vol. cond. sampled with gas})} =$$

In order to estimate how effective the separation is, it is necessary to analyze a non-volatile element in the condensate (e.g. Na). One can then calculate the fraction of water phase carry-over in the condensate. In order to do so, sample condensate into one 100 ml polyethylene bottle and label it Ru.

Finally steam is collected into a concentrated (40%) NaOH solution (Figure 5). This method has the advantage that the amount of steam accompanying the gases can be determined. During sampling the condensate is added to the sodium hydroxide solution and the gaseous carbon dioxide and hydrogen sulfide are dissolved. Before sampling can take place approximately 50 ml of 40% NaOH solution have to be measured into a round-bottom flask. Stopper the flask with a rubber stopper containing two nylon pipes connected to rubber tubing with clamps on. One of the pipes runs down to the bottom of the flask while the other ends just below the rubber stopper. Now the flask is evacuated using the shorter pipe, with a pump and/or by boiling. Dry the outside of the evacuated flask and weigh it (V_1). The flask is now ready for collection of steam. Connect the longer plastic pipe of the flask to the cooling device and admit the steam. Shake the flask intermittently and sample the steam through the NaOH solution until bubbling stops. While sampling it is recommended to wear vinyl gloves and a face mask. Weigh the flask again (V_s) and

measure the total volume of sample and NaOH solution (R_s). Now one can calculate D, which is used when analyzing for CO_2 and H_2S .

$$D = \frac{(V_s - V_1)}{R_s}$$

If the amount of other gases is insignificant, one can calculate the mass-percentage of gas based on the CO_2 and H_2S analyses in the following way:

$$\%GAS = \frac{(CO_2(\text{ppm}) + H_2S(\text{ppm}))}{10000}$$

If, on the other hand, there is a significant amount of other gases present, it is necessary to collect gas into a special gas sampling bulb and have it analyzed.

The next step in this sampling procedure is to collect the water phase. The two steam outlets on the separator are kept open while the water tap is opened slightly. Open the steam tap until the steam is obviously wet. This can be tested for by inserting a vinyl gloved hand into the stream. After adjusting the separator connect the the cooling coil to the water tap and let the water flow through it to rinse it out. Collect water into one sampling bulb for analysis of volatiles. Collect three unfiltered and untreated samples for the analysis of silica into 100 ml polyethylene bottles. Often the sample has to be diluted with distilled water 2 to 50 times. Ideally, the concentration of silica in the diluted sample should be in the range of 30 to 100 mg/kg. Label the samples with Rd and the dilution factor. Into one 500 ml polyethylene bottle collect a filtered, untreated sample and label it Fu. To a 500 ml volumetric flask add 1 ml of 6N HCl and fill it to the mark with filtered sample. Transfer the sample to a 500 ml polyethylene bottle and label it Fa. Two such samples should be collected. Next add 10 ml of 0.2M $Zn(CH_3COO)_2$ solution to a 500 ml volumetric flask and fill it to the mark with filtered sample. Transfer the sample to a 500 ml polyethylene bottle and label it Fp.

5 SUMMARY OF SAMPLES AND DATA GATHERED

The following abbreviations are employed to describe various treatments of the samples. The sample containers are labeled accordingly:

Ru: raw, untreated

Rb: raw, base added (note amount of base)

Rd: raw, diluted (note dilution)

Fu: filtered, untreated

Fp: filtered and precipitated (note amount of 0.2M $\text{Zn}(\text{CH}_3\text{COO})_2$)

Fa: filtered and acidified (note amount of 6N HCl)

Notice: Before sampling, always rinse the sample containers three times with the fluid to be sampled.

Water:

One sampling bulb, cooled to approx. 20°C

One 100 ml sample raw or three diluted (Ru)

One 500 ml sample filtered but untreated in polyethylene bottle (Fu)

Two 499 ml filtered samples + 1 ml 6N HCl in each (Fa)

One 490 ml filtered sample + 10 ml $\text{Zn}(\text{CH}_3\text{COO})_2$ (Fp)

Condensate:

One gas sampling bulb, cooled to 20-30°C

100 ml sample, untreated, in polyethylene bottle (Ru)

Gas:

One gas sampling bulb

Steam:

Sample collected into 50 ml 40% NaOH solution in an evacuated 1000 ml flask

Measurements:

Pressure during sample collection

Volume of condensate with gas and its temperature

Weight of evacuated 1000 ml flask before and after collection

The volume of sample + NaOH solution

Temperature of water and discharge.

6 ANALYTICAL PROCEDURES FOR VOLATILE CONSTITUENTS

Volatile constituents such as CO₂ and H₂S as well as pH must be measured soon after sample collection. Therefore a description of analytical procedures for these elements is included.

6.1 Determination of pH and carbonate

Total carbonate is determined by titration with 0.1N HCl solution from pH=8.2 to pH=3.8 at about 20°C but pH is measured using a pH meter.

The following equipments and reagents are needed:

- 1) Portable pH meter
- 2) pH electrode
- 3) Saturated KCl solution
- 4) Three small beakers for pH buffers
- 5) 150 ml beaker for sample
- 6) 50 ml and 100 ml volumetric flasks
- 7) Thermometer
- 8) 25 ml or 50 ml burette calibrated at 0.1 ml intervals
- 9) Burette stand and clamp
- 10) 1 ml and 5 ml automatic pipettes
- 11) 0.1N HCl solution
- 12) Approximately 0.1N NaOH solution
- 13) pH buffers (pH=4, pH=7 and pH=9)
- 14) Distilled water

The analytical procedures for water, condensate and steam are as follows.

Water:

- 1) Adjust the pH meter using the pH 7 and pH 4 buffers
- 2) Measure the pH 9 buffer
- 3) Measure 50 ml of sample using the volumetric flask and put into the 150 ml beaker
- 4) Determine the pH and temperature of the sample
- 5) Adjust the pH carefully to pH=8.2:
using 0.1N HCl if the pH is higher than 8.2 or
using 0.1 N NaOH if the pH is lower than 8.2

- 6) Titrate the sample from pH=8.2 to pH=3.8 using 0.1N HCl
- 7) Record the amount of 0.1N HCl
- 8) $\text{ppmCO}_2 = (88 * \text{ml HCl}) - 7.92 - (1.182 * \text{ppmH}_2\text{S}) - (0.0088 * \text{ppmSiO}_2)$

Condensate:

The same procedure as for water except that 50 ml of sample is combined with 0.4 ml of 5N NaOH solution at stage 3, and a small sample is immediately put separately into a small beaker for stage 4. The total amount of carbonate is calculated in the following way:

$$\text{ppmCO}_2 = \left(\frac{50.4}{50}\right) * (88 * \text{ml HCl}) - 7.92 - (1.182 * \text{ppmH}_2\text{S})$$

C) Steam:

The procedure is essentially the same as for water except that at stage 3, 2 ml of sample is added to distilled water in the 50 ml flask, which is then filled to the mark, stage 4 is omitted, and additional solutions containing 6N HCl and 1N HCl are needed for the pH adjustment in stage 6. The total amount of carbonate is calculated in the following way:

$$\text{ppmCO}_2 = \left\{ \frac{(2200 * \text{ml HCl}) - 2700 + (1663 * D)}{D} \right\} - (1.182 * \text{ppmH}_2\text{S})$$

The calculation of D is described with the collection of steam into the NaOH solution.

6.2 Determination of hydrogen sulfide by dithizone

Hydrogen sulfide is determined by titration with $\alpha\text{Hg}(\text{CH}_3\text{COO})_2$ solution. The following equipment and reagents are needed.

- 1) 10 ml burette calibrated at 0.05 ml intervals, burette stand and clamp or a 1 ml micro syringe
- 2) 50 ml Erlenmeyer flask
- 3) Finnpiettes (0-200 μl , 0-1000 μl and 0-5000 μl)
- 4) 10 ml measuring cylinder
- 5) Acetone
- 6) 5N NaOH solution
- 7) Solid dithizone
- 8) 0.001M $\alpha\text{Hg}(\text{CH}_3\text{COO})_2$ solution freshly prepared

The analytical procedures for water, condensate and steam are as follows.

Water:

- 1) 50 ml of sample is combined with 0.4 ml of 5N NaOH solution in a volumetric flask.
- 2) Measure 5 ml 5N NaOH and 5 ml acetone into a 50 ml Erlenmeyer flask.
- 3) Add 0.1 - 10 ml of sample, from step 1, plus distilled water to the flask. The amount of sample depends on the H₂S concentration. The total amount of sample and distilled water should be 10 ml.
- 4) Add a small grain of solid dithizone
- 5) Titrate with 0.001M $\alpha\text{Hg}(\text{CH}_3\text{COO})_2$ to red endpoint
- 6) Record volume of sample and amount of $\alpha\text{Hg}(\text{CH}_3\text{COO})_2$ needed
- 7)
$$\text{ppmH}_2\text{S} = \left(\frac{50.4}{50}\right) * \frac{(\text{ml } \alpha\text{Hg}(\text{CH}_3\text{COO})_2 * 34)}{(\text{ml} * \text{sample})}$$

During the titration, a black precipitate of HgS forms. The endpoint is recorded when the color changes from the yellow color of the dithizone in alkaline solution to the red color of the Hg-dithizonate. If the concentration of H₂S is high the sample becomes yellowish brown and even black during titration. This is caused by the HgS precipitate and makes the endpoint uncertain. In the case of high concentrations of H₂S it is better to reduce the volume of the sample.

Condensate:

The procedure is essentially the same as that for water, except usually a smaller sample is used for titration. Measure 0.1 - 1.0 ml of sample from the volumetric flask and combine with 5 ml of 5N NaOH solution, 10 ml of distilled water and 5 ml of acetone.

Steam:

For the steam fraction collected into the NaOH solution take 0.1 - 0.2 ml of the sample itself and combine it with 5 ml of 5N NaOH solution, 10 ml of distilled water and 5 ml of acetone and stage 7 becomes;

$$\text{ppmH}_2\text{S} = \frac{\text{ml Hg}(\text{CH}_3\text{COO})_2 * 34}{\text{ml sample} * D}$$

The calculation of D is described with the collection of steam into a concentrated NaOH solution.