PUBLIC POWER CORPORATION

ATHENS, GREECE

A FIELD GUIDE TO SAMPLING OF

HIGH TEMPERATURE GEOTHERMAL WELLS,

SELECTED ANALYTICAL PROCEDURES AND

PRELIMINARY COMPOSITIONAL CALCULATIONS

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NATIONAL ENERGY AUTHORITY

VIRKIR CONSULTING GROUP LTD.

REYKJAVÍK, ICELAND

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1   INTRODUCTION

Geothermal samples may consist of water, a mixture of water and steam, or steam only (Steam: water vapour and non-condensable gases). Sample sources may be geothermal wells, hot springs or fumaroles. The main emphasis here is on the sampling of water-steam mixtures from high temperature wells, which is the most accomplished of sampling opera-tions. A description of a few analytical procedures for the field, and a short guide to elementary deep-water and deep-steam calculations follow.

2   GENERAL CONDITIONS

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 still in a thermodynamic equilibrium as regards water and steam phases. This is shown in Fig. 1, which portrays sampling locations on a well head. The hole through which the fluid sample flows should be large enough not to become regularly blocked by deposition and small enough for a faulty valve to be replacable without turning the flow off the pipeline. In our experience the optimum diameter is about 5 mm.

For proper evaluation and interpretation of analytical resutls it is necessary to know the sampling pressure and the enthalpy of the flow, from which the steam fraction can be calculated. There are several parameters which can be measured but a set of two is sufficient to calculate the desired properties. We have had most success with: Critical lip pressure and water flow (James, 1962). This method can only be used if water is separated from steam. Generally silencers at the well head act as separators. With superheated wells the measurement of differential pressure over an orifice (American Society of Mechanical Engineers, 1971) has proved more successful than the measurement of critical lip pressure. Fig. 2 shows a design for the measurement of differential pressure over an orifice and of critical lip pressure. If the water flow is small, it is generally measured directly by timing the flow into a container of a known volume. A V-shaped notch is used in case of larger flows. The water flow is then calculated from the following formula:

$$H = (B + 0.85)/1000 \tag{1}$$
$$Q = 1.365 \, H^{2.5}$$
$$W = Q \times \rho_{100°}$$

Where Q = Water flow (m^3/s)

ρ = Density of water at 100°C, 958 kg/m^3

W = Water flow (kg/s) at 100°C

B = Height of water surface, from bottom of notch, mm

When critical lip pressure and water flow are known the following relation can be used to obtain the desired properties.

$$\frac{W}{799 \cdot A \, P_c^{0.96}} = \frac{2673-h}{h^{1.102}} \tag{2}$$

where W = water flow (kg/s) at 100°C
      A = Section area of pipe (m^2)
      P = Critical lip pressure (bar abs)
      h = enthalpy (kJ/kg) of fluid

If the enthalpy and the water flow are known, total flow (T: kg/s) can
be obtained

$$t = \frac{2258 \ W}{2673-h} \qquad (3)$$

Steam fraction and thus steam flow at different pressures can be
obtained from the relation

$$h = h_1 + X_1 L_1 \qquad (4)$$

where h = enthalpy (kJ/kg) of fluid
      h_1 = enthalpy (kJ/kg) of water phase at pressure P_1 (bar a)
      L_1 = heat of evaporation (kJ/kg) at pressure P_1 (bar a)
      X_1 = steam fraction at P_1

Heat of evaporation and enthalpy of water phase is obtained from steam
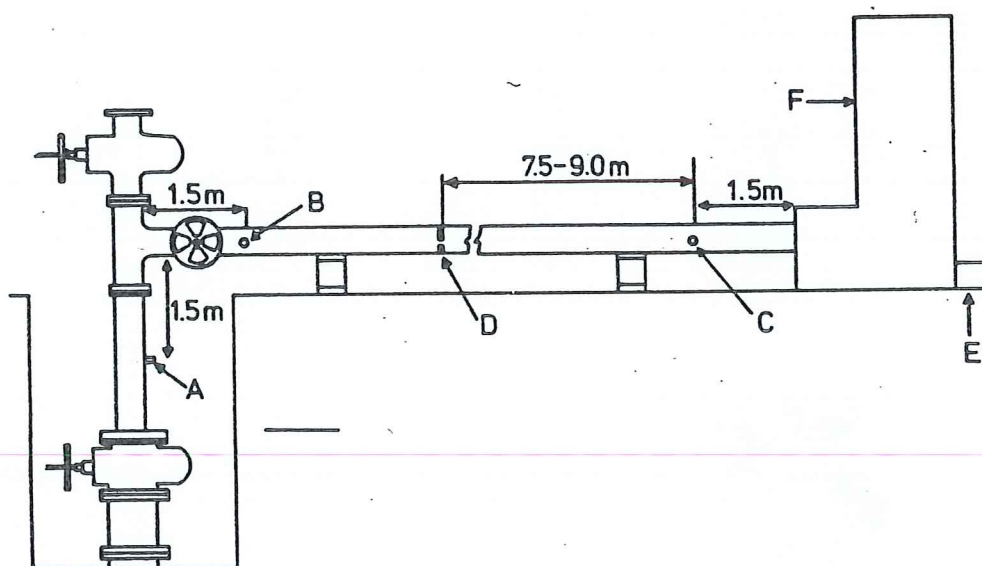tables.

Fig. 1 The positions of sampling points on the surface piping of a geothermal well from which representative steam and water samples are collected. A, B, and C, sample points; D, constriction such as back pressure plate or valve; F, silencer; E, weir box of silencer. (Ellis and Mahon 1977)
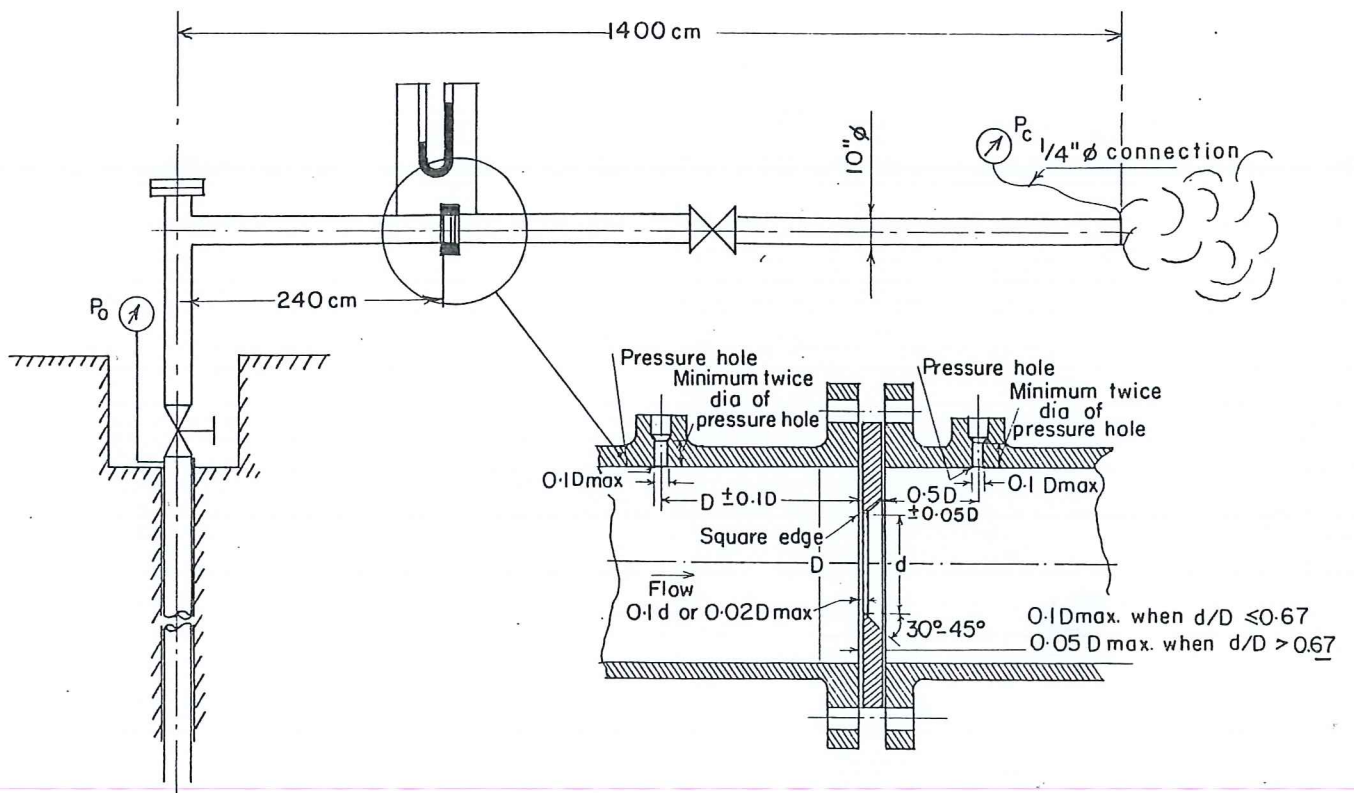
Fig. 2 Design for the measurement of differential pressure across an orifice, and the measurement of critical lip pressure.

3   COLLECTION OF GEOTHERMAL FLUID FROM HIGH TEMPERATURE WELLS

3.1 Introduction

The collection of representative samples of water and gas from wet steam drillholes is a complex procedure. It is necessary to sample each phase separately. This may be done by using the separator on the well head separating the whole discharge or a small Webre separator (Figure 3).

3.2 Apparatus

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

1) separator
2) stainless steel cooling coil
3) bucket
4) tubing 1/4"
5) thermometer
6) pressure gauge
7) filtering apparatus
8) two retort stands with 4 sets clamps and bosses
9) gas sampling bulbs, one 1000 ml evacuated flask with 50ml 40% NaOl
10) polyethylene bottles for the samples (3x500 ml and 4x100 ml)
11) 2 x 500 ml volumetric flasks, plastic
12) 500 ml measuring cylinder, plastic
13) pipettes (1,2,5,10 ml) or Finnpipettes (200-1000 μl, and 1000-5000 μl)
14) hydrochloric acid (HCl) concentrated
15) zinc acetate ($Zn(CH_3COO)_2$). Dissolve 20.88 g of the reagent in 1000 ml of distilled water
16) tools and fittings.

3.3 Procedure

3.3.1 Separator set-up

The Separator is connected to the by-pass and kept open for 10 minutes to rinse it out. Then the separator is closed and a pressure reading taken on the separator pressure gauge (P_s). The set up of the apparatus for collecting water, gas and steam is illustrated in Figure 4.

After opening the separator take care that the pressure in it does not fall significantly because a pressure drop will cause boiling in the separator and upset the separation of the two phases.

3.3.2 Collection of condensate and non-condensable gas

Connect the cooling coil to one of the steam outlet taps and keep it closed. The other steam outlet is kept open and the water and steam taps closed. The water tap is partly and the steam tap slightly opened so that a mixture of water and steam will discharge through the water tap but dry steam through the steam tap. Open the steam outlet connected to the cooling coil and close the other one. Keep open for a while before cooling to rinse out the cooling coil. Then place the cooling coil in the bucket with cold water. During cooling the steam will condense, but not gases such as CO_2, H_2S and H_2. Two phases need therefore be collected, condensate and gas.

Condensate Collect condensate into one gas sampling bulb and a 100 ml polyethylene bottle.

Gas When collecting gas, the gas sampling bulb (250 ml) is first filled with condensate, and short rubber tubing connected to the other end. Then the bulb is turned up side down. The gas expels the condensate which is collected into a bottle. Having collected the gas, measure the volume of the condensate and its temperature. The volume of the condensate corresponds to the volume of gas collected plus the volume of gas sampling bulb.

3.3.3 Collection of steam (gas and condensate) into NaOH

The sampling method described below has the advantage that the amount of steam accompanying the gases can be determined. The steam is collected into a strong hydroxide solution. Figure 5 is a schematic view of the apparatus for this method of collection. One liter evacuated flasks are used. During sampling the condensate is added to the hydroxide solution and the gaseous carbon dioxide and hydrogen sulphide are dissolved.

Method Measure approximately 50 ml of 40% NaOH solution into the round bottom flask. Stop it with rubber stopper containing two nylon pipes connected with latex tubing with clamps on. Evacuate the flask using the shorter pipe with pump and/or by boiling. Dry the evacuated flask and weigh. Connect the flask to the steam vent. Open for the steam and shake intermittently. Weigh the contents of the flask

and record the total volume collected.

3.3.4 Collection of water

The two steam outlet taps are kept open and the water tap opened a little. Open the steam tap until the steam is obviously wet. This can easily be tested by inserting some object into the discharge and observe it become wet. Having adjusted the separator connect the cooling coil to the water tap. Let the water flow through the cooling coil for a while before placing it in the bucket, to rinse it out. Place the cooling coil in the bucket. Collect water into one gas sampling bulb, for analysis of pH, CO_2 and H_2S. Into one 500 ml polyethylene bottle collect filtered, untreated sample. To 500 ml volumetric flask add 5 ml conc. HCl and then fill to the mark with filtered sample. Transfer to 500 ml polyethylene bottle. Add 10 ml of the $Zn(CH_3COO)_2$ solution to 500 ml volumetric flask and fill to the mark with filtered sample. Transfer to 500 ml polyethylene bottle. This part of the sample is later used for the determination of sulphate and chloride. Dilute unfiltered sample 10-50 times into three 100 ml graduated flasks and transfer to 100 ml polyethylene bottles for silica determination.

3.3.5 Summary of samples and data gathered during collection

Water:	one gas sampling bulb, cooled to approx. 20°C
	500 ml sample filtered, untreated, in polyethylene bottle (Fw)
	495 ml sample + 5 ml conc. HCl (Fa)
	490 ml sample + 10 ml $Zn(CH_3COO)_2$ solution (Fp)
	3x100 ml samples, diluted for SiO_2 determination (Rd)
Condensate:	one gas sampling bulb, cooled to 20-30°C (Ru)
	100 ml sample, untreated, in polyethylene bottle (Ru)
Gas:	One gas sampling bulb
Steam:	Sample collected into 50 ml 40% NaOH solution in an eavacuated 1000 ml flask (Rb)
Measurements:	pressure during collection, volume of condensate with gas sampling bulb gas and its temperature, weighing of evacuated 1000 ml flask before and after collection, and the volume of sample + NaOH solution.

The following abbreviations are employed to describe various treat-

ments and the sample containers labelled accordingly.

Ru: raw, untreated
Rb: raw, base added
Rd: raw, diluted
Fu: filtered, untreated
Fp: filtered, precipitaded
Fa: filtered, acidified

Every container is labelled as shown: 82   07   23   1093
                                      year month day sample number

Notice: Before sampling always rinse the sample container three times
with the fluid to be sampled. Fill the gas sample tubes, close the
bottom tap and carry on the collection until they are slightly over-
pressurized. Leave a little air space for expansion in the water-
bottles and tightly stopper them. Always write down the sampling
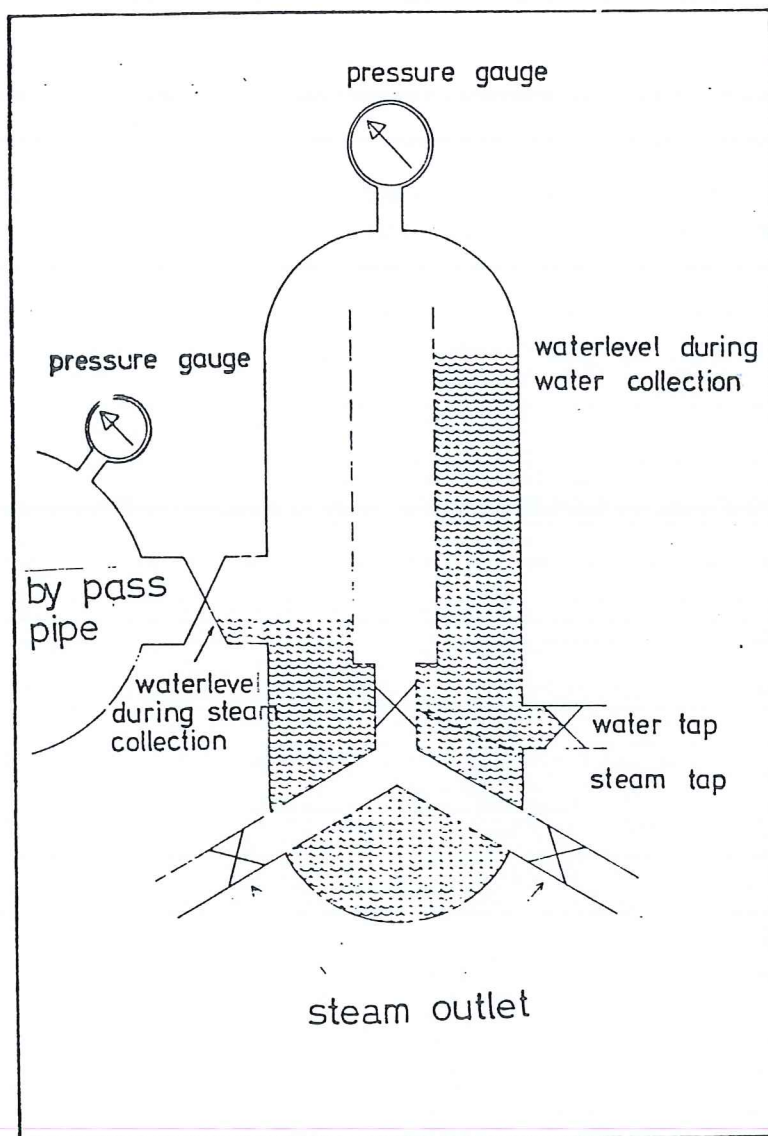temperature and pressure.

Fig. 3   Cross section of separator used for collecting water and
steam from geothermal wells.
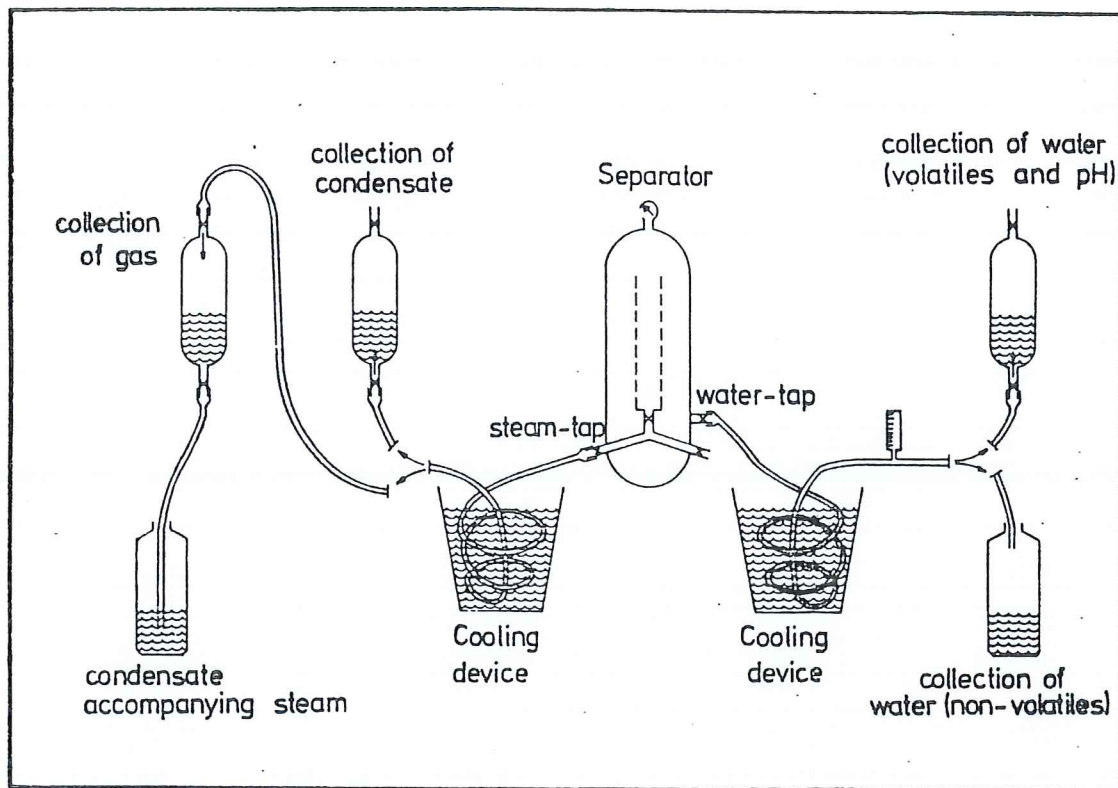
Fig. 4   Schematic drawing of apparatus used to collect water and gas
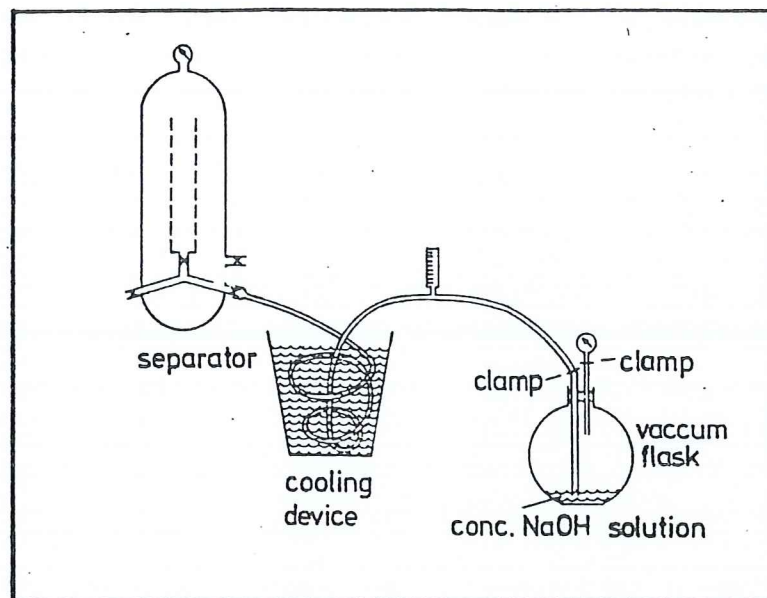   from geothermal wells.

Fig. 5   Schematic   drawing   of   apparatus   used for collecting gas by
          dissolution.

4 SELECTED FIELD DETERMINATIONS

4.1 Determination of pH and carbonate

4.1.1 General description

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

4.1.2 Equipment and reagents

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 or 50 ml burette calibrated at 0.1 ml interval, burette stand and clamp or 2.5 ml micro syringe
9) 1 ml and 5 ml pipettes
10) 0.1 N HCl solution (e.g.titrisol 0.1 N HCl, Merck 9973)
11) Approx. 0.1 N NaOH solution. Dissolve 4 g NaOH in 1 liter of distilled water
12) pH buffers. For pH = 4.0, 7.0 and 9.0
13) distilled water

4.1.3 Procedure

A) Water
1) Fill the electrode with KCl solution if necessary
2) Adjust the pH-meter using the 7.0 and 4.0 pH buffers
3) Measure the 9.0 buffer
4) Measure 50 ml of sample using the volumetric flask and put into the 150 ml beaker
5) Determine the pH and the temperature
6) Adjust the pH carefully to 8.2 using 0.1 N HCl if the pH is higher than 8.2 but using 0.1 N NaOH if the pH is lower than 8.2
7) Titrate from pH 8.2 to pH 3.8 using 0.1 N HCl stirring continuously.
8) Record the amount of HCl used
9) C_{CO_2} = 88 x ml HCl - (7.92 + 1.182 C_{H_2S} + 0.0088 C_{SiO_2})

B) Condensate

The same procedure is followed except that 50 mls of sample are run into 0.4 ml of 5 N NaOH in stage 4, and a small sample is immediately run separately into a small beaker for stage 5

Stage 9) C_{CO_2} = 88 x ml HCl - (7.92 + $1.182 \times C_{H_2S}$)

C) Steam sample in NaOH solution

The procedure is essentially the same except that in stage 4, 2 mls of sample are added to distilled water in the 50 ml flask which then is filled to the mark, stage 5 is omitted, and additional solutions containng 6 N HCl and 1 N HCl are needed for the pH adjustment in stage 6.

Stage 9) C_{CO_2} = (2200 x ml HCl - 2700 + 1663xd)/d - 1.182 x C_{H_2S}

where d = weight of sample/volume of sample + NaOH solution.

Note: Always rinse electrode with distilled water between determina-
tions.

4.2 Determination of H_2S by dithizone

4.2.1 General description   check 0.4 ml 5 N NaOH

Hydrogen sulphide is determined by titration with $Hg(CH_3COO)_2$ solution using dithizone as an indicator.

4.2.2 Equipment and reagents

   1) 10 ml burette calibrated at 0.05 ml intervals,
       burette stand and clamp or 1 ml micro syringe.
   2) 50 ml Erlenmayer flask
   3) Finnpipettes (0-200 µl, 0-1000 µl, 0-5000 µl)
   4) 10 ml measuring cylinder
   5) Acetone
   6) 5 N NaOH solution. Dissolve 200 g NaOH in 1 liter
       distilled water
   7) Solid dithizone.
   8) 0.001 M $Hg(CH_3COO)_2$ solution freshly prepared.
       Dissolve 0.3187 g $Hg(CH_3COO)_2$ in 1 liter distilled water

Procedure:

   1) Measure 5 ml 5N NaOH and 5 ml acetone into 50 ml
       Erlenmayer flask.
   2) Add 0.1 - 10 ml of sample plus distilled water to the flask.

The amount of sample depends on the H_2S concentration.

The total amount sample + distilled water should be 10 ml.

3) Add small grain of solid dithizone.

4) Titrate with 0.001 M $Hg(CH_3COO)_2$ to red end point.

5) Record volume of sample and amount of $Hg(CH_3COO)_2$ needed.

6) $$C_{H_2S} \text{ (mg/kg)} = \frac{\text{ml } Hg(CH_3COO)_2 \quad 34}{\text{ml sample}}$$

During the titration, a black precipitate of HgS forms. The end point is decided when the colour changes from the yellow colour of the dithizone in alkaline solution to the red colour of the Hg-dithizonate. If the concentration of H_2S 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 H_2S it is better to reduce the volume of the sample. For steam fraction collected into NaOH stage 6 becomes

$$C_{H_2S} = \frac{\text{ml } Hg(CH_3COO)_2 \quad 34}{\text{ml sample} \quad d}$$

where d = weight of sample/volume of sample + NaOH solution.

4.3 Spectrophotometric determination of silica

4.3.1 General description

This method is based on the reaction of silica with molybdate ions at pH of 1.2 - 1.5. A yellow silicomolybdate complex is formed which is determined by spectrophotometry.

If the concentration of silica in thermal water is higher than 100 ppm, the silica polymerizes and the polymerized silica will not react with molybdate in the cold. Treatment with alkali converts it all to the monomeric state.

As described under sample collection it is desirable to dilute samples containing more than 100 ppm SiO_2 sufficiently to bring the final silica concentration below 100 ppm. When this is done, later analysis should follow the procedure described for samples containing less than 100 ppm SiO_2. Dilution below 100 ppm is necessary for saline waters. The silica in excess of this concentration will precipitate upon storage for one week or less.

The adopted procedure covers the concentration range of 20 - 500 ppm. Higher concentrations can be determined by taking smaller aliquots. No interference will occur from elements present in the thermal waters. Only colour or turbidity of the sample will interfere. High concentrations of hydrogen sulphide may reduce the silicomolybdate complex to molybdenum blue. This can be prevented by oxidizing the sulphide with iodine.

The main disadvantage of this method is the instability of colour of the solution. This necessitates that samples and standards need to be prepared at the same time and that absorbance must be read between 10 and 60 minutes after developing the colour.

Average difference between duplicate samples should be 3% or less over the whole concentration range.

4.3.2 Reagents

1) 1 N sodium hydroxide (NaOH). Dissolve 40 g of analytical grade sodium hydroxide in distilled water and dilute to 1 litre. This solution is required only for digesting samples containing more than 100 ppm SiO_2.

2) Hydrochloric acid, sp. gr. 1. 18, analytical reagent grade.

3) 1 N hydrochloric acid (HCl) solution. Mix 40 ml of the concen-
trated acid with 400 ml of distilled water. This solution is
needed to neutralize samples after digestion with NaOH-solution.

4) 6 N hydrochloric acid (HCl) solution. Mix 240 ml of the concen-
trated acid with 200 ml of distilled water.

5) Ammonium molybdate solution, 10%. Dissolve 20 g of the reagent in
water and dilute to 200 ml.

6) Iodine solution approx. 0.05 N. Dissolve 0.634 g iodine in 100 ml
distilled water.

7) Sodium thiosulphate approx 0.05 N. Dissolve 1.2409 g of reagent
grade sodium thiosulphate in 100 ml distilled water.

8) Standard silica solution 100 ppm. The solution can be obtained
from manufacturers of chemicals. If not available, solution of
this strength can be prepared as follows: Fuse 0.2 g of pure
silica with 3 g of sodium carbonate in a platinum crucible.
Dissolve in water and make to 200 ml. Store in polyethylene
bottle. It is convenient to standardise the solution by
gravimetric analysis. Or use analysed geoth. spring water,

9) Oxalic acid solution ca 0.6 M. Dissolve 7.5 g analytical grade
oxalicacid in distilled water and dilute to 100 ml.

4.3.3 Standards

Stock

From the 1000 mg/l SiO_2 solution prepare standard solutions containing
20, 50, 100, 150, 200 ppm SiO_2. Proceed as described in stage 5-7 of
the procedure. Alternatively natural water whose SiO_2 concentration
has been determined gravimetrically, and is not in excess of 100 mg/kg
can be used and diluted.

4.3.4 Procedure

Sample containing more than 100 ppm SiO_2	Samples containing less than 100 ppm SiO_2
1) Pipette 5 ml sample into platinum crucible or PTFE beaker	1) Pipette 5 ml sample into 50 ml volumetric flask
1a) Add 0.5 ml of 1 N NaOH solution	
1b) Add 5 ml distilled water and heat on a steam bath for 10 minutes. Take care that there is no significant loss of	

volume by evaporation

ld) Add 0.5 ml of 1N HCl

If the sample's hydrogen sulphide concentration is high follow step 2-3 otherwise go to step 4.

2) Add iodine solution dropwise until the solution in the volumetric flask becomes yellow or yellow brown

3) Destroy the yellow or yellow brown colour by adding sodium thiosulphate dropwise

4) Add 2 ml of ammonium molybdate solution. *Mix and leave for 10 minute.*

5) Add 1 ml of 6 N hydrochloric acid and fill with distilled water to about 40 ml. Mix ~~and leave for 10 minut~~es.

6) Add 2 ml oxalic acid solution, fill to mark with distilled water and leave for 5 minutes.

7) Read the absorbance at 410 millimicron.

8) Calculate SiO_2 concentration by referring to the absorbance of the standards.

4.4 Mohr titration for the determination of chloride

4.4.1 General description

This method which is described here has been modified in order to reduce the size of aliquot required. The usual Mohr titration requires 10 to 100 ml of the sample for each titration, but this modification only requires up to 10 ml of sample. The chloride is titrated with silver nitrate solution using potassium chromate as an indicator. Insoluble silver halides other than AgCl are precipitated, but their concentrations in thermal waters are negligible compared with those of chloride. The end point is not sharp. It is marked by gradual change of colour from yellow to brown. The precision of the titration depents on the skill of the analyst.

4.4.2 Reagents

1) Silver nitrate solution, 0.0141 M. Dissolve 2.395 g of analytical grade silver nitrate in water and dilute to 1 liter in a volumetric flask.
2) Potassium chromate indicator, 5%. Dissolve 5 g of analytical grade potassium chromate in 100 ml of water.
3) Sodium hydroxide solution, 1 N. Dissolve 20 g of analytical grade sodium hydroxide in 500 ml of water.

4.4.3 Apparatus

1) 50 ml beakers
2) microburette (if usual burette is used a larger amount of sample is needed)
3) pipettes (0.5 ml, 1 ml, 2 ml, 5 ml).
4) glas rod

4.4.4 Procedure

1) Transfer 10 ml of distilled water to each of two 50 ml beakers (blanks) and add 3 drops of potassium chromate. Titrate one of the blanks with the 0.0141 silver nitrate solution to a brown endpoint, stirring the solution with the glas rod while titrating. These blanks, one untitrated and one titrated are used as references during titration of samples. They should be prepared

for each working day.

2) Transfer an aliquot of sample (0.5 to 10 ml depending on the chloride concentration to 50 ml beaker, and make the volume to approximately 10 ml with water.

3) Ensure that the pH is above 8.2. If not add sufficient amount of 1 N NaOH solution. The pH should not exceed 8.2 greatly.

4) Add 3 drops of potassium chromate indicator.

5) Titrate the sample with 0.0141 M silver nitrate solution to brown end point (the colour should match with that of the titrated blank).

6) $Cl \ (mg/kg) = \dfrac{ml \ AgNO_3 \ (sample - blank) \quad M \ (AgNO_3)}{ml \ sample} \quad 35457$

4.5 Determination of ammonia

(Adapted from Koroleff 1983)

4.5.1 General description

Ammonia reacts in moderately alkaline solution with hypochlorite to monochloramine which, in the presence of phenol, catalytic amounts of nitroprusside ions and excess hypochlorite, gives indophenol blue.

At a pH higher than 9.6, some precipitation of Mg and Ca ions as hydroxides and carbonates may occur but these ions can be held in solution by complexing them with citrate. The formation of monochloramine requires a pH between 8 and 11.5. The formation of indophenol blue takes several hours at room temperature. The reaction can be speeded up (i) by increasing the concentration of the reagents, (ii) by increasing the reaction pH to more than 12 and (iii) by increasing the reactiontemperature.

A reaction pH higher than 11.0 must be avoided, otherwise erratic blank values with greenish shades are obtained. A reaction temperature of 37-40°C causes complete colour formation within 30 min. Samples containing more than 2 mg/l sulphide should be diluted.

4.5.2 Equipment

The main procedure is performed in stoppered 50 ml flasks (reserved solely for this determination). Flasks should be cleaned with acid, rinsed well with water free from NH_3 and kept closed between analyses. Heating the bottles does not always remove traces of ammonia from the walls

4.5.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

1. "Ammonia-free" water (to be used throughout this method). Pass distilled or de-ionised water through a column containing a strong cation exchange resin in the hydrogen form. A commercial column may be used and appropriate flow rates and regeneration procedures obtained from the supplier. The water should be stored in a

sealed container and used the day of preparation.

2. Natural seawater. Surface seawater collected shortly after a plankton bloom usually contains only traces of ammonia. Filter this water and store in a tightly stoppered container.

3. Sodium hydroxide, 1.0 mol/l. Dissolve 40 g sodium hydroxide (NaOH) in water and dilute to 1 l. Store in a well-stoppered polyethylene bottle.

4. Sodium hydroxide, working solution. Add 2 ml phenol reagent (reagent 5) and 1 ml citrate solution (reagent 9) to 50 ml water. Titrate with the NaOH (reagent 3) to a pH of 11.0 using a pH-meter. Dilute the 1 mol/ml NaOH so that the pH is 11.0 when 2 ml is added. The solution obtained in this way contains about 0.8 mol/ml and is used for preparing the hypochlorite reagent. Store in a tightly closed polyethylene bottle.

5. Phenol reagent. Dissolve 80 g of colourless phenol (C H OH) in 200 ml ethanol and add 600 ml water. Dissolve 600 mg disodium nitroprusside dihydrate (Na Fe(CN) NO 2H O) in 100 ml water. Add this solution to the phenol solution and store in a refrigerator in a tightly closed amber glass bottle. The reagent is stable for months.

6. Hypochlorite solutions. In early work, commercial bleaching solutions were in general use; however, according to several workers, they often give unstable dilute solutions.

    Hypochlorite solutions, usually containing 3.5% of available chlorine in ca 0.1 mol 1 NaOH, can be obtained from some manufacturers. Their available chlorine content may be determined as follows: Dissolve approximately 0.5 g potassium or sodium iodide in 50 ml of about 0.5 mol/ml sulphuric acid. Add 1.0 ml hypochlorite solution and titrate the iodine liberated with 0.1 mol/l thiosulphate in the usual way; 1 ml of this thiosuophate solution ie equal to 3.54 mg active chlorine. Always check the stock solution before use.

    Trione is an alternative hypochlorite donor. Trione is the abbreviation for dichloroisocyanuric acid, (dichloro-s-triazine-2,4,6(1H,3H,5H) trione). This reagent has the advantage of being a stable solid, and the formation of hypochlorite when hydrolysed is rapid. The acid form contains 60% of available chlorine.

7. Hypochlorite reagent. Dissolve 0.5 g Trione, equal to 300 mg of available chlorine in 100 ml of the working NaOH (reagent 5). Store cold in an amber lab glass bottle. The reagent is stable for at least 3 weeks.

8. Tri-sodium citrate solution. Dissolve 240 g tri-sodium citrate dihydrate ($C_6H_5Na_3O_7$ $2H_2O$) in about 500 ml distilled water. Make the solution alkaline with 10 ml NaOH (reagent 3). Add

anti-bumping granules and remove ammonia by boiling until the volume is below 0.5 l. Cool and dilute to 500 ml with water free of NH_3. Store in a well-stoppered polyethylene bottle. The solution is stable.

9. Standard stock solution. Drÿ ammonium chloride (NH_4Cl) at $100°C$. Dissolve 31.7 mg in NH_3-free water and dilute to 100.0 ml. Preserve with a drop of chloroform. Kept in a glass bottle in a refrigerator the solution is stable for months. The standard contains 100 g/ml NH_3.

10. Working standard solution. Dilute stock solution 20 times with ammonia-free water (reagent 1).

4.5.4 Sampling and storage

It is convenient to collect samples in stoppered glass or polyethylene bottles with a volume of 0.5-1 l directly from the water sampler. The analysis should be commenced without delay (within about 3 h). If the samples are not cooled, they must be analysed immediately after collection. Tubes.

The problem of storage has received much attention. Although quick deep-freezing is recommended by many authors, others have observed changes. Preservation with acid is effective, but the samples should be neutralized prior to determination and this step may introduce errors. Good results have been obtained using a phenol conservation method (0.4g / 100 ml). Sublimate was, and is perhaps still, a commonly used preserving agent. The use of mercuric salts should be limited for this purpose since they are toxic pollutants. Filtration of even turbid samples cannot be recommended since it is almost impossible to obtain filters free of ammonia.

4.5.5 Procedure

Samples containing more than 0.5 mg/l NH_3 have to be diluted. 50 ml is subsampled with a 50 ml graduated cylinder (smaller samples are taken with bulb pipettes and diluted in the cylinder to 50 ml with NH_3-free water). The sample is then poured into the reaction flask. Add 2 ml phenol reagent (reagent 5), 1 ml citrate solution (reagent 8) and 2 ml hypochlorite reagent (reagent 7). Mix well by swirling between additions. Close the bottle and put in a thermostat (37-40°C) for 30 min. After this time allow the sample to cool on the lab bench for a further 30 min. Once formed, the colour of the indophenol blue is stable for at least 30 h if the reaction flask is well sealed. Read standards and blank after about the same time. Measure the

absorbance in a suitable cell at 630 nm, and use as reference a cuvette of similar length filled with water. Add 1,3 and 5 ml portions of working standard solution (reagent 10) to 50 ml volumetric flanks and use as reference standards (containing 0.1, 0.3 and 0.5 mg/l NH_3).

5   DEEP-FLUID-STEAM CALCULATIONS

Samples from high temperature geothermal wells are usually collected at well head pressure. The sample may consist of water, gas, condensate and steam. Due to pressure drop and boiling in the well, water and gases are transferred into the steam phase. In the reservoir the fluid may consist of water or steam only or a mixture of both. In order to get knowledge of the composition of the deep water and/or deep steam from the well head sample, a series of calculations has to be made. Besides the results of the chemical analysis of the phases of the sample, several other types of information are necessary, i.e. the enthalpy of the discharge, the sampling pressure and the measured or calculated ratio between noncondensable gas and condensate.

The steam fraction at different pressures can be calculated from the known enthalpy of the discharge:

$$h_0 = h_1 + X_1' L_1 = h_2 + X_2' L_2 \tag{1}$$

where h is enthalpy, X is steam fraction, L is latent heat of evaporation and the subscript o means in the total discharge and 1 and 2 refer to different pressures. For a sample we have:

$$h_0 = h_s' + L_s' X_s' \tag{2}$$

where s refers to the sampling pressure. The values for h and L can be found from steam tables.

The enthalpy of the discharge can be found by several different methods. Three will be mentioned:
    1) From measured temperature
    2) From calculated quartz temperature
    3) Measured enthalpy at well head.

The first two methods can only be used if the inflow into the well is water phase only. The quartz temperature is found by "simulated boiling" from the sampling pressure to atmospheric pressure and calculating the concentration of the sample at 100°C

$$X_{100°} = \frac{h_s - 419.1}{2256.9} \tag{3}$$

[SiO]

$$[SiO_2]_{100} = \frac{[SiO_2]sw}{1 - X_{100}} \qquad (4)$$

X_{100} is steam fraction, h_s is the enthalpy at the sampling pressure, $[SiO_2]_{100}$ and $[SiO_2]_{sw}$ are the concentration of SiO_2 at 100°C and the measured sample concentration respectively. The quartz temperature can now be found from equation (5) or Fig. 6 and the enthalpy from steam tables.

$$t° = 4.2198 + 2.8831 \times 10^{-1} [SiO_2] + 3.6686 \times 10^{-4} [SiO_2]^2$$
$$+ 3.1665 \times 10^{-7} [SiO_2]^3 + 7.8304 \log [SiO_2] \qquad (5)$$

Now the concentration of various chemical components can be calculated in the total discharge. The following equation is valid for the non-volatile components which are found in the water phase

$$[A]_0 = [A]_{sw} (1-X_s) \qquad (6)$$

[A] indicates the concentration of the component A, the subscript o means in the total discharge and sw in the water phase of the sample.

The volatile components like CO_2 and H_2S are found both in the water and the steam. The concentration is then:

$$[A]_0 = [A]_{sw} (1-X_s') + [A]_{ss} X_s \qquad (7)$$

$[A]_{ss}$ means concentration of component A in the steam phase of the sample. The following relation is valid for volatile components like H_2 which are only found in the steam

$$[A]_0 = [A]_{ss} X_s \qquad (8)$$

The steam phase is often collected in two parts, i.e. condensate and non-condensable gas. The concentration of a component in the steam phase can be calculated:

$$[A]_{ss} = [A]_{sc} + 10 \ Ag \ \frac{MW_A}{(22.4 + 0.08t)} \ R \qquad (9)$$

where $[A]_{sc}$ is the concentration of A in the condensate, Ag is % volume of the component in the non-condensable gas, MW_A is the molecular weight of the component gas, t is the collection temperature in °C and R is the ratio of liters noncondensable gas to kg condensed water.

If the inflow into the well is water phase only and boiling is confined to the well itself the calculated concentrations are the same as the concentrations of the deep water. If the inflow is a mixture of steam and water and the reservoir temperature is known, then it is possible to calculate the chemical composition of the deep steam and deep water, from following equations
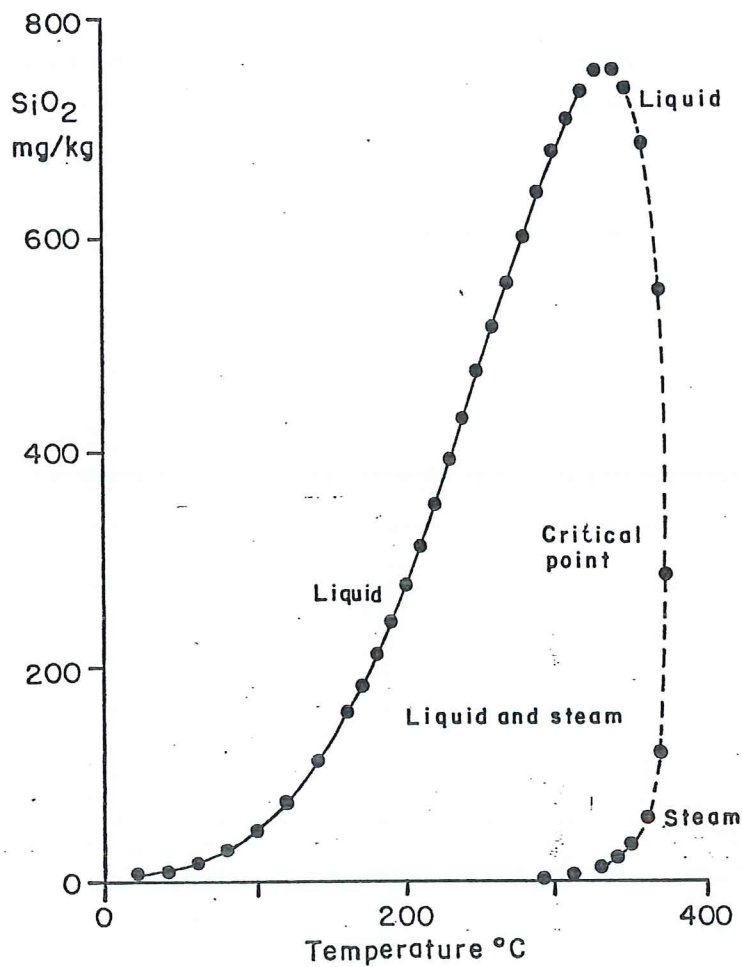
$$X = \frac{h_o - h_r}{L_r} \tag{10}$$

$$[A]_{rw} = \frac{[A]_o}{1 - X_r} \tag{11}$$

for nonvolatile components.

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Fig. 6

The solubility of quartz in water at the vapor pressure
of the solution. The dots are points calculated using
the equation of Fournier and Potter. The solid line is
from equation 5 and the dashed line shows dissolved silica
in liquid and steam outside the range of conditions for application
of equation 5

Fig. 6   The solubility of quartz at the vapor pressure of the solution
(Fournier and Potter 1982)

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APPENDIX

SAMPLING AND ANALYTICAL METHODS

Orkustofnun - National Energy Authority
Geothermal Division. 1984 10.12 HA/TH

1.   SAMPLING - GENERAL

1.1   SAMPLING POINT

shall be a horizontal outlet (>1/2") on the line, ideally about
1.5 m from T-joint on well-head.

1.2   SEPARATION

of liquid and vapor phase should be carried out under pressure
with minimal pressure drop between pipeline and separator (Valve
fully open). The separator should be insulated to prevent
condensation.

1.3   COOLING

The separated steam and liquid phase shall be cooled down to
ambient temperature in small diameter stainless steel spiral
tubes.

1.4   SEPARATION EFFICIENCY

To check for separation efficiency during sampling no bubbles
should be observed in the liquid phase flow and the steam cone
should be checked for dryness.
The sodium or chloride concentration of the condensate fraction is
determined and compared with that of the water fraction as a
further sampling efficiency test (see below).

1.5   SAMPLE FRACTIONS

Steam can be collected by one of two methods (2.1 and 2.2-2.3
respectively). The first method involves sampling into NaOH
solution in an evacuated flask. The second method involves
separate collection of condensed steam and non-condensable gases.
Sampling of the liquid phase is described under 2.4.

1.6 PRECAUTIONS

Before sampling always rinse the sample container three times with the fluid to be sampled. Fill the gas sample tubes completely and leave no space for air. Always write down the sampling temperature and pressure. Well head pressure, enthalpy and flow at the time of sampling have to be known.

2. SAMPLING OF DIFFERENT FRACTIONS

2.1 STEAM

Add 50 ml 40% sodium hydroxide solution to a round bottomed flask and evacuate. Collect gas and condensate until the pressure inside the flask is slightly below atmospheric pressure. Shake vigorously.

2.2 NON-CONDENSABLE GASES

Fill gas sampling tube with condensate, reverse the tube (or flow) and drive the condensate out with the gas.

2.3 CONDENSATE

Collect samples for the determination of pH and volatile constituents into a gas sampling tube. Collect a separate 100 ml sample into a plastic bottle for the determination of sodium, as a check on sampling efficiency.

2.4 LIQUID PHASE

Collect samples (Ru = Raw, untreated) for the determination of pH and volatile constituents into gas sampling tubes, but the rest into four plastic bottles marked as follows.

Rd: raw, diluted 1/10 with distilled water for SiO_2 determination

Fu: filtered, through 0,45 um membrane filter, untreated.

Fp: filtered, precipitated by adding 10 ml 0,2 M $ZnAc_2$ to a 500 ml volumetric flask and filling to the mark with the sample (for sulphate analysis)

Fa: filtered, acidified by adding 1 ml 6N HCl to a 500 ml volumetric flask and filling to the mark with the sample

Thus the following determinations are done on the different samples.

Ru: pH, CO_2, H_2S
Rd: SiO_2
Fu: F, conductivity, total dissolved solids
Fp: Cl^-, SO_4
Fa: Na, K, Ca, Mg

3.   ANALYTICAL METHODS FOR STEAM FRACTION

3.1   CARBON DIOXIDE

To 2 ml of the sample and 2 drops of 30% H_2O_2 (to destroy H_2S). Allow to stand for 1 min. then dilute to 50 ml. Adjust the pH to 8,2 with hydrochloric acid, and titrate from pH 8,2 to pH 3,8 with 0.1 N HCl using a glass electrode. Subtract blank contribution.

3.2   HYDROGEN SULPHIDE

Add 0.1 - 0.5 ml of the sample solution (2.1) to 10 ml distilled water. Add 5 ml 5N sodium hydroxide solution, 5 ml acetone and a few dithizone crystals. Titrate with 0,001 M mercuric acetate.

4.   ANALYTICAL METHODS FOR NON-CONDENSABLE GASES

Gas chromatography employing a Poropak column for acid gases (CO_2, H_2S), and a Molecular Sieve column for other gases (H_2, N_2, O_2, CH4). Hydrogen is extracted from the helium carrier gas stream through a palladium tube and detected in a nitrogen gas stream with thermal conductivity detectors.

5.   ANALYTICAL METHODS FOR CONDENSATE FRACTION

5.1   pH

Use glass electrode, calibrate with buffers (pH = 4,7 and 9)

5.2   CARBON DIOXIDE

Run 50 ml of sample into a volumetric flask, containing 0,4 ml 5N NaOH, immediately upon opening the sampling tube. Titrate from pH 8,2 to pH 3,8 with 0,1 N HCl using a glass electrode. Subtract blank and hydrogen sulphide contributions.

5.3 HYDROGEN SULPHIDE

Run 50 ml of sample into a volumetric flask, containing 0,4 ml 5N NaOH, immediately upon opening the sampling tube. Add 0.1 - 1 ml to ca 10 ml water. Add 5 ml 5N sodium hydroxide solution, 5 ml acetone and a few dithizone crystals. Titrate with 0,001 M mercuric acetate as soon as possible.

5.4 SODIUM

Either determine directly flame - photometrically or at 589 nm by AAS adding a large excess of a lithium salt.

6. ANALYTICAL METHODS FOR LIQUID PHASE

6.1 pH

Use glass electrode, calibrate with buffers (pH = 4,7 and 9).

6.2 CARBON DIOXIDE

Titrate 50 ml of sample from pH 8,2 to pH 3,8 with 0,1 N HCl. Subtract on a theoretical basis interferences from water, hydrogen sulphide, silica and boron.

6.3 HYDROGEN SULPHIDE

Run 50 ml of sample into a volumetric flask, containing 0,4 ml 5N NaOH, immediately upon opening the sampling tube. To 1-50 ml add 5 ml 5N NaOH solution, 5 ml acetone and a few dithizone crystals. Titrate with 0,001 M mercuric acetate.

6.4 SILICA

Dilute sample 10 times upon collection (giving < 100 ppm SiO_2) to avoid polymerization (Rd). If H_2S is present in significatn amounts (1 ppm) add 0.1 N iodine to 10 ml of diluted sample to oxidize sulphide (till iodine colour is persistent) and then 0,05N sodium thiosulphate solution to destroy excess iodine. Add 2 ml 10% ammonium molybdate solution and 1 ml 6 N hydrochloric acid, dilute to 50 ml and determine spectrophotometrically at 410 nm. For control purposes boil a few samples with NaOH before determination (total silica). If results are higher this way, all samples will have to be treated thus.

6.5 SULPHATE

Filter sample (Fp) and pass filtrate through a cation exchange resin. Add 20 ml propanol-2 and 1-2 drops 0,2% thorin solution to 5 ml sample. Titrate with 0.005 N barium perchlorate solution. In saline waters sulphate must be determined gravimetrically as barium sulphate.

6.6 CHLORIDE

Filter sample (Fp). If H_2S is present significant amounts add 1N H_2SO_4 to filtrate and heat on a water bath to remove sulphide. Take care that pH is not higher than 8.2. Employ Mohr titration with $AgNO_3$ and potassium chromate indicator.

or

Filter sample (Fp), acidify the filtrate with nitric acid and blow free of H_2S with air, add 30% hydrogen peroxide to remove all traces of sulphide . Add a measured excess of silver nitrate. Remove the silver chloride precipitate by centrifugation (must be white; brownish color indicates sulphide), and determine silver in the remaining solution by AAS at 328,1 nm. Calculate the chloride concentration from the difference in silver concentrations between blank and solutions.

6.7 SODIUM

Determine a suitably diluted sample at 589 nm by AAS adding a large excess of a lithium salt. Flame photometry may also be employed.

6.8 POTASSIUM

Determine a suitably diluted sample (Fa) at 766,5 nm by AAS. Flame photometry may also be employed.

6.9 CALCIUM

Determine a suitably diluted sample (Fa) at 422,7 nm by ASS, adding 2 ml 5% lanthanum oxide solution to 10 ml of diluted sample to overcome interferences.

6.10 MAGNESIUM

Similarly add to diluted sample (Fa) lanthanum oxide solution and determine at 284,2 nm by AAS.

6.11 FLUORIDE

Add TISAB buffer to sample (Fu) and standards and determine concentrations by means of fluoride selectrode.

6.12 CONDUCTIVITY

Use conductivity bridge or suitable electronic equipment on samples (Fu).

6.13 DISSOLVED SOLIDS

Evaporate sample (Fu) to dryness at 105°C and determine gravimetrically.

7. ANALYTICAL METHODS FOR SOME MINOR CONSTITUENTS

7.1 BORON

Determined spectrophotometrically in condensate and liquid (Fu) fractions with either curcumin or methylene blue.

7.2 AMMONIA

Determined in condensate and liquid (Ru) fractions, spectrophotometrically as indophenol blue, preferably in a closed circuit set up, such as an Auto-Analyser, as soon as possible after collection. If any storage is necessary, samples will have to be frozen.

Alternatively ammonia can be determined in the field with a specific ion electrode after the addition of sodium hydroxide to the sample.

7.3 ARSENIC

Determined spectrophotometrically with silver diethyldithio-carbonate after generation of arsine with sodium borohydride in condensate and liquid fractions to which potassium permanganate and nitric acid are added upon collection.

7.4 ALUMINIUM

Determined fluorometrically in liquid fraction sample (Fa) with lumogallion.

7.5 MERCURY

Determined by flameless AAS after amalgamation on gold in steam and water (filtered) fractions which are specifically collected into a permanganate solution acidified with nitric acid.

7.6 IRON

Determined by AAS or spectrophotometrically with phenanthroline on liquid sample (Fa).

7.7 MANGANESE

Determined by AAS or spectrophotometrically by periodate oxidation of malachite green leuco base to malachite green.

7.8 CADMIUM, ZINC, COPPER, LEAD, COBALT, NICKEL AND SILVER

By AAS on liquid fraction, preferably after on site extraction with dithizone/chloroform or APDC/MIBK, or after a similar extraction of stored sample (Fa).

7.9 NITRITE AND NITRATE

Spectrophotometrically on liquid sample (Fu) after diazotization and coupling with sulphanilamide and N-(1-napthyl) ethylenediamine directly for nitrite, but after reduction with a cadmium-copper column for nitrate.

7.10 PHOSPHATE

Spectrophotometrically with ammonium molydate, ascorbic acid and potassium antimonyltartrate on liquid sample (Fa).

7.11 OTHER METALS

The possibility of analysis for antimony, chromium and vanadium has arisen, but no simple method can be recommended for the relatively low concentrations which could be expected in geothermal waters.

7.12 ION CHROMATOGRAPHY

NEA has available an ion chromatograph. Where such an instrument is available, it can be recommended for the analysis of most common anions, e.g. Cl^-, Br^-, I^-, F^-, NO_2^-, NO_3^- (Fu) and SO_4^{-2} (Fp).