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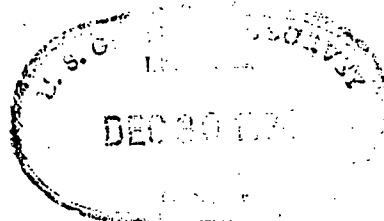
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Geothermal gas sampling methods

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by



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This report is preliminary and has
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The following method of geothermal gas collection meets our needs for chemical and isotopic gas analyses, requires a minimum of special equipment in the field, and provides field analytical data of assistance in a sampling program.

Geothermal gases (other than steam) generally consist mostly of CO_2 with lesser quantities of N_2 , CH_4 , H_2S , H_2 , O_2 , higher hydrocarbons, and inert gases in approximate order of decreasing abundance. H_2S is unstable in the presence of moisture, oxygen, and to a lesser extent ultraviolet light, and must be fixed at the time of collection if an analysis is to be made. In our method, H_2S is fixed by absorption in sodium hydroxide solution followed by precipitation of CdS . The sodium hydroxide also absorbs CO_2 , greatly reducing the bulk of the gas sample, and the reduction in volume of gas accurately indicates the ratio of $\text{CO}_2 + \text{H}_2\text{S}$ to other gases. The intensity of the yellow color of the CdS precipitate gives a rough indication of the relative quantity of H_2S .

Two 60 ml polypropylene syringes (Monoject) and an evacuated 50 ml pyrex gas sample bottle with an O-ring seal (constructed using Ace glass adapter 5027 modified by the addition of a second O-ring so that the exit tube can be evacuated) are connected by 1/8" ID Tygon tubing and four 3-way polypropylene stopcocks (Pharmaseal) with short pieces of tubing used to seal the joints (fig. 1). The entire assembly is clamped to a wooden board with broom clips.

At the start of each collection, 10 or 20 ml of 3 m NaOH (prepared from low carbonate reagent) is drawn into syringe B through stopcock 4. Dissolved air in the solution is reduced by closing the stopcock to the syringe (the stopcock handle indicates the closed direction; see detail of stopcock in fig. 1), pulling the plunger to produce a partial vacuum over the solution, shaking to join the air bubbles and releasing the accumulated air through the stopcock.

An inverted funnel connected to the apparatus with 1/8" Tygon tubing is dipped in the hot spring and filled with water. With stopcock 1 closed to the side tube, syringe A and stopcock 2 are used to pump water through the tubing and out of the sidearm of stopcock 4 which is closed toward the gas bottle. When this part of the tubing is water filled, the inverted funnel is moved over the gas vent and gas is allowed to accumulate. Further pumping with syringe A displaces the water in the tube with gas from the vent. When the tubing is flushed with gas, stopcock 4 is closed by moving it 45° to an intermediate position. Syringe A is then filled with 50 ml of gas which is allowed to cool to near air temperature. In collecting from high temperature springs, some condensate will accumulate in the syringe and this may be either discarded or collected through stopcock 1. The cooled gas, its volume noted, is then transferred into syringe B through stopcocks 2 and 3. With stopcock 2 closed to the sidearm the apparatus is shaken and the CO_2 and H_2S is rapidly absorbed into the NaOH solution. The volume of the non-absorbable or residual gas may be measured from the change in the position of the plunger of syringe B. It is not accurate to note the position of the meniscus because the

ends of the syringe and plunger are conical. The plunger is usually slightly sticky and an accurate volume measurement requires manipulation and bracketing by feel.

This procedure is repeated until approximately 25 ml of residual gas has accumulated in syringe B. The tubing from stopcock 2 to the glass sample bottle is then partially evacuated by closing stopcock 4 to the vent, stopcock 3 to the NaOH solution, and stopcock 2 to the funnel and pulling the plunger of syringe A out as far as possible without breaking the seal while the plunger is out. Stopcock 2 is then closed toward the gas bottle and the evacuated air and gas is released through stopcock 1. This procedure is repeated twice more. The evacuated glass sample bottle is then opened by unscrewing its threaded bushing slightly and pushing the closure tube into the bottle until the small hole in the tube is within the bottle. Now, with syringe B held upright, gentle opening of stopcock 3 to connect the glass bottle to syringe B allows the residual gas to flow into the bottle. When 4 ml residual gas remains in syringe B, stopcock 3 is closed, the gas bottle is closed by gently pulling its closure tube out of the bottle until its side hole is no longer connected to the bottle interior, and the bushing is tightened. The 4 ml of remaining gas is then pushed into the tubing to reduce the possibility of air contamination.

The pumping of gas and absorption of CO_2 and H_2S is repeated until a further 25 ml of residual gas is accumulated and it is also transferred into the glass sample bottle. It is important to keep track of the total amount of gas drawn into the system and of the amount of non-absorbable gas collected. If the total quantity of gas absorbed by the caustic exceeds 1200 ml the collection should be stopped even though the glass tube is not full because the absorptive capacity of 20 ml of 3M NaOH solution is limited to 1344 ml of CO_2 . The gas sample bottle is finally closed, tightened well, and labeled.

After the collection is finished half of the NaOH (now NaOH, Na_2CO_3 and NaHS) solution is sealed in a bottle containing 5 ml of a cadmium solution to preserve the H_2S and the other half in an empty bottle for eventual CO_2 analysis. This division is made roughly using the syringe calibrations and recalculated later from the weight gain of the bottles (both empty and with Cd solution) which are weighed before and after the collection. A solution of 5% Cd acetate in 1 normal Na acetate was found to be the most successful preservative of H_2S by Akeno (1973). Antioxydants may be necessary to preserve low levels of H_2S as described by Bamesberger and Adams (1969). CO_2 analysis is made by precipitation and weighing of BaCO_3 which is then preserved for carbon isotope analysis. An aliquot of the solution with suspended CdS can be analysed by thio-sulfate titration (Ellis, Mahon and Ritchie, 1968) and the rest preserved for sulfur isotope analysis. The pressure and volume of residual gas in the gas sample tube is measured and its composition analysed by gas chromatography. Atmospheric pressure and temperature at the time of collection are recorded for an independent check on the total/absorbed/residual gas ratios.

A fumarole is treated the same way if it discharges at boiling temperature through a shallow pool of water, except that steam is

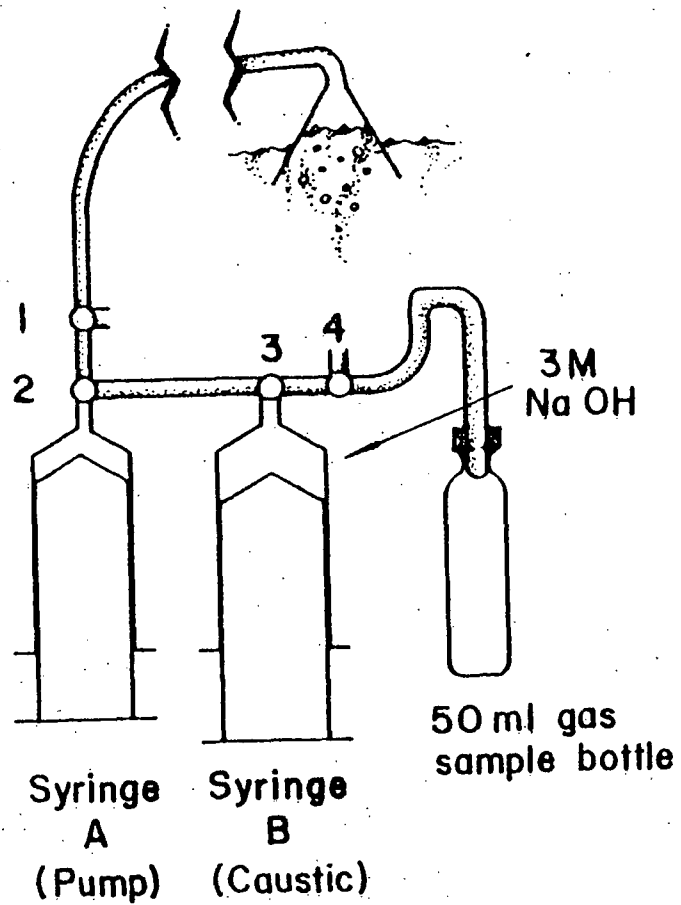
allowed to flush the funnel before the Tygon tube is attached and the tubing is flushed by repeated pumping. If the fumarole is superheated, an insulated funnel and air condenser (Wilson, 1955; Finlayson, 1970) allows the water/gas ratio to be measured.

Sampling of steam wells is done through an air or water condenser which is flushed with steam before sampling is started. As with superheated fumaroles, the water/gas ratio may be determined by noting the quantity of water expressed through stopcock 1. It is important that the condenser be efficient if accurate gas volume measurements are to be made.

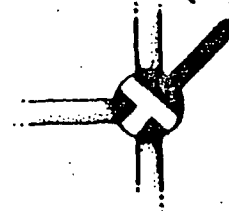
Sampling hot water wells requires a water-steam separator. This is discussed by Ellis and others (1968).

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Handle indicates
off direction



Detail of
Stopcock