GEOTHERMAL AND VOLCANIC GAS ANALYSES <u>CAPRAI A</u>. CALVI E. and MUSSI M.

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The chemical composition of geothermal and volcanic gases collected at their discharge near the surface is a key matter to understand process deep in the crust and to support geothermometry based on equilibrium temperatures among the various phases occurring at depth in thermal areas.

Samples can be analysed both for total and residual gases but residual gas sample method is preferable when the concentration of some components is below the detection limit of total gas method. Total gas samples can be collected "dry" or "wet" but with no chemical additive whereas NaOH 4N or H₃BO₃ solutions are preferred as residual gases are concerned. The two main problems in gas sampling are air contamination and physical or chemical reaction: in the last case the disproportional removal of one or more components can occur when passing from the source to the sample container. In this work we describe the gascromatographic methods routinely used for geothermal and volcanic fluids in the IIRG laboratory and a new analytical procedure to analyse H₂S and SO₂ from volcanic steam samples.

Gascromatographic analyses of multiple components fluids were checked to determine the limits of detection and of quantification for each component. This procedure involved three different devices using laboratory made mixtures of dry gases from commercial cylinders.

As wet analyses are concerned, we developed a new and quick procedure, aimed to determine SO_2 and H_2S as two separate components. In this case directly iodometric method cannot be applied because it adds the two components. According this procedure SO_2+H_2S (in the solution) can both be measured iodometrically. H_2S was separated by precipitating it as ZnS using a zinc acetate solution and then SO_2 (in the rest of solution) can be measured iodometrically. Accordingly, H_2S can be calculated.

In order to check the applied method, we measured gravimetrically the total sulphur by precipitating all the sulphur in the sample as BaSO4, after oxidation it by H_2O_2 . Moreover, precipitated H_2S as ZnS is dissolved in HCl and Zn determinated by atomic absorption standard methods. SO_4 from supernatant (oxided and precipitated as BaSO4) is finally weighted.

The described procedure was checked using three different samples from fumarolic activity in the Vulcano isle (Tyrrenian Sea). Differences between the new described method and the common reported gravimetric procedure spans from 1 to 10% for total sulphur, from 10 to 22 % for SO₂ and from 15 to 20% for H₂S. Atomic Absorption determination of Zn resulted as low as 5% with respect to iodometric determination.

In conclusion the proposed iodometric method appears to be faster and enough precise to analyse volcanic fluids, but standardisation of analytical methods among the various laboratories and/or, at least, intercalibration procedures are highly recommended to avoid misleading results.

References:

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