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Analysis of Sulphur Species in Volcanic Gases

Giordano Montegrossi (giordano@steno.geo.unifi.it)[1], **Franco Tassi** (francot@steno.geo.unifi.it)[2],
Orlando Vaselli (orlando@steno.geo.unifi.it)[2] & **Kristin Garofalo** (orlando@steno.geo.unifi.it)[2]

[1] CNR- CSMGA, Via G. La Pira, 4, 50121 Florence, Italy
[2] Dept. of Earth Sciences, University of Florence, Via G. La Pira, 4 Florence, 50121, Italy

Volcanoes that experienced recent or historical eruptive activity are generally characterised by a solfataric or fumarolic state. Volcanic fumaroles are usually located in the central part of the main crater and may release gases, in either diffuse way or localised vents, containing relatively high abundances of sulphur species such as SO_2, H_2S and S_8^0 at different proportions. Many efforts have been addressed to obtain representative chemical analyses, particularly with respect to those gas compounds that may be able to benchmark the status of a certain volcano as the sulphur species are. However, their determination can somehow be difficult to be obtained, especially when present at low concentrations, despite their importance in terms of volcanic surveillance.

This study presents a new approach to analyse both SO_2 and H_2S and S_8^0 in volcanic gases by oxidation of each species (after physical-chemical separation) to SO_4^{2-} and, as a consequence, their determination by ion-chromatography. In the field, gas entrapment carries out through titanium tubes inserted into the vent and attached to dewarded tube to prevent or, at least, minimise condensation. The dewar end is connected to pre-weighted and pre-evacuated 50 ml thorion-tapped tubes at which 20 ml of a solution of 0.15 M $Cd(OH)_2$ and 4 M NaOH were previously added. During fumarole sampling, S_8^0 does not react with the alkaline solution while H_2S reacts with Cd^{2+} to form CdS as insoluble precipitate and SO_2 turns into SO_3^{2-} and SO_4^{2-}. In the laboratory, the solid phase, mainly consisting of $Cd(OH)_2$ with CdS and S_8^0, is separated with a high-speed centrifuge from the supernatant. Here, SO_2 is completely transformed into SO_4^{2-} by oxidising the solution with H_2O_2 (30% w/w). An aliquot (generally 25 ml) of this solution can conveniently be used for CO_2 (acidimetric titration), Cl^- (ion-chromatography), Br^- and F^- (specific electrode potentiometry) determination, as well.

Sulphur from CdS gets converted to SO_4^{2-} by dissolution with H_2O_2 and KOH in ultra-high quality water, while S_8^0 is insoluble and stable in this medium and can successively be separated by centrifugation. Eventually, the last step involves CCl_4, to solubilise S_8^0, and HCl to dissolve the unreacted $Cd(OH)_2$. A solution made up of KOH, $KBrO_3$ and KI in ultra-high quality water allows S_8^0 to be extracted from CCl_4 and converted to SO_4^{2-}. All the obtained solutions containing SO_4^{2}, previously buffered with the addition of H_3BO_3, can easily be analysed by ion-chromatography, sensitively lowering the detection limits (ca. 0.1 ppm SO_4^{2-} in each of the solutions prepared) with respect to similar analytical studies.

As SO_2, S_8^0 and H_2S contents can be affected by many physical-chemical parameters, e.g. temperature, flow rate, presence and thickness of a water table, oxidation-reduction processes, the method proposed has been applied to fumaroles from volcanoes located in different geographical, geodynamical and geological contests such as the Phlegrean Fields and Vulcano (Italy), Kilauea (Hawaii), Poas (Costa Rica) and El Chichon (Mexico). Furthermore, repeated and time-controlled gas sampling has been performed to test both the reproducibility and the precision. Comparison with other methodologies such as those proposed by Martini et al. (1986) and Giggenbach & Gougel (1989) has been carried out, as well.

The analyses obtained have permitted to reveal the presence of SO_2 although at very low concentrations, in the range of 0.0000009 and 0.000016% by vol. at El Chichon volcano. Such low abundances, despite of their importance for the evaluation of the eruptive status of a volcanic system, cannot be detected by using other analytical methodologies proposed so far.

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