

## Development and application of denuder sampling techniques with in situ derivatization for the determination of hydrogenbromide in volcanic plumes

Alexandra Gutmann, Julian Rüdiger, and Thorsten Hoffmann

Institute of Inorganic and Analytical Chemistry Johannes Gutenberg-Universität, Mainz, Germany (agutmann@uni-mainz.de)

The composition of gases in volcanic plumes shifts with subsurface processes inside volcanoes. For monitoring volcanic activity by studying volcanic plumes it is essential to understand the chemical reactions inside the volcanic plume (Bobrowski and Platt, 2013).

Measurements of BrO/SO<sub>2</sub>-ratio already enable insights into magmatic processes (Bobrowski and Giuffrida, 2012). Both, BrO and SO<sub>2</sub>, are measurable by *Remote Sensing Techniques* at a safe distance. Models suggest not a direct emission of BrO but formation due to photochemical and multiphase reactions in the gas and particle phase. These model presume HBr as first emitted species (Gerlach, 2004). So HBr is an important connecting link between easily measurable BrO/SO<sub>2</sub>-ratios and conclusions on a volcanic system. It is of high importance to know if there is a variation in the amount of HBr transformed into BrO and to gain knowledge on the factor of its dependence. Apart from depletion of surrounded ozone also decreasing or depletion of emitted HBr or even HCl could be responsible for the shift (Bobrowski and Giuffrida, 2012). Knowledge about complex processes in volcanic plumes will simplify interpretation and predictions.

In this study, first applications of coated gas diffusion denuder (similar to Huang and Hoffmann, 2008) to derivatize gaseous HBr were successful. Due to the lack of adequate *remote sensing techniques* an *in situ* method was developed and will be presented in detail. The epoxide of oleic acid was determined as a suitable derivatization agent. The reaction with HBr gives 10-bromo-9-hydroxyoctadecanoic acid. Other hydrogenhalogens give corresponding products. Derivatized analytes were removed from denuder by solvent elution and subsequent analysed with gas chromatography-mass spectrometry. A limit of quantification below 1 ng was achieved. The method was applied on volcanic gas plumes at Mt. Etna in Italy in July and August 2015. The results showed HBr in higher ppt-range. These first proof-of-principle investigations showed the suitability of the method for halogenhalides-analysis.

### References

- Bobrowski, N. and Giuffrida, G.: Bromine monoxide / sulphur dioxide ratios in relation to volcanological observations at Mt. Etna 2006–2009, *Solid Earth*, 3, 433–445, doi:10.5194/se-3-433-2012, 2012.
- Bobrowski, N. and Platt, U.: Den Himmel betrachten, die Hölle verstehen. Telegramm aus dem Inneren der Erde., *Ruperto Carola*, 2013, 2013.
- Gerlach, T. M.: Volcanic sources of tropospheric ozone-depleting trace gases, *Geochem. Geophys. Geosyst.*, 5, n/a, doi:10.1029/2004GC000747, 2004.
- Huang, R.-J. and Hoffmann, T.: A denuder-impinger system with in situ derivatization followed by gas chromatography-mass spectrometry for the determination of gaseous iodine-containing halogen species, *Journal of Chromatography A*, 1210, 135–141, doi:10.1016/j.chroma.2008.08.003, 2008.