Geophysical Research Abstracts
Vol. 17, EGU2015-2392-2, 2015
EGU General Assembly 2015

Development and application of compact denuder sampling techniques with in situ derivatization followed by gas chromatography-mass spectrometry for halogen speciation in volcanic plumes

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Volcanoes are a large source for several reactive atmospheric trace gases including sulphur and halogen containing species. The detailed knowledge of volcanic plume chemistry can give insights into subsurface processes and can be considered as a useful geochemical tool for monitoring of volcanic activity, especially halogen to sulphur ratios (e.g. Bobrowski and Giuffrida, 2012; Donovan et al., 2014). The reactive bromine species bromine monoxide (BrO) is of particular interest, because BrO as well as SO_2 are readily measurable by UV spectrometers at a safe distance. Furthermore it is formed in the plume by a multiphase reaction mechanism under depletion of ozone in the plume. The abundance of BrO changes as a function of the reaction time and therefore distance from the vent as well as the spatial position in the plume. Due to the lack of analytical approaches for the accurate speciation of certain halogens (HBr, Br_2, Br, BrCl, HOBr etc.) there are still uncertainties about the magnitude of volcanic halogen emissions and in particular their specificationtheir species and therefore also in the understanding of the bromine chemistry in volcanic plumes (Bobrowski et al., 2007).

In this study, the first application of a 1,3,5-trimethoxybenzene (1,3,5-TMB)-coated gas diffusion denuder (Huang and Hoffmann, 2008) on volcanic gases proved to be suitable to collect selectively gaseous bromine species with oxidation states of +1 or 0 (Br_2 and BrO(H)), while being ignorant to HBr (OS -1). The reaction of 1,3,5-TMB with bromine gives 1-bromo-2,4,6-trimethoxybenzene (1-bromo-2,4,6-TMB) - other halogens give corresponding products. The diffusion denuder technique allows sampling of gaseous compounds exclusively without collecting particulate matter. Choosing a flow rate of 500 $mL \cdot min^{-1}$ and a denuder length of 0.5 m a nearly quantitative collection efficiency was achieved. Solvent elution of the derivatized analytes and subsequent analysis with gas chromatography-mass spectrometry gives a limit of detection below 1 ng of bromine. The method was applied on volcanic gas plumes at Mt. Etna and Mt. Stromboli in Italy in July 2014 and on fumarolic gas emissions at Mt. Lastarria in Chile in November 2014. The results show significant amounts of the concerning bromine species (lower ppb range). Comprehensive data evaluation and comparison with results of impinger extraction with NaOH solution as well as chamber experiments are still in progress.

References

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