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Halogen speciation in volcanic plumes - Development of compact denuder sampling techniques with in-situ derivatization followed by gas chromatography-mass spectrometry and their application at Mt. Etna, Mt. Nyiragongo and Mt. Nyamulagira in 2015.

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Volcanoes are a large source for several reactive atmospheric trace gases including sulfur 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 sulfur 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 spectrometer 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. The precursor substance for the formation of BrO is HBr with Br_2as an intermediate product. The reaction of HBr to BrO involves heterogeneous reactions involving aerosol particles, while Br_2 reacts directly with O_3 to form BrO in a UV radiation induced mechanism. Due to the lack of analytical approaches for the species analysis of halogens (HBr, Br_2, Br, BrCl, HOBr) there are still uncertainties about the magnitude of volcanic halogen emissions and in particular their speciation and therefore also in the understanding of the bromine chemistry in volcanic plumes (Bobrowski et al., 2007).

In this study a gas diffusion denuder sampling method using a 1,3,5-trimethoxybenzene (1,3,5-TMB) coating for the derivatization of reactive halogen species (Rüdiger et al., 2015) was characterized by reaction chamber experiments. The coating proved to be suitable to collect selectively gaseous bromine species with oxidation states of +1 or 0 (such as Br_2, BrCl, BrO(H) and $BrONO_2$), while being ignorant to HBr (OS -1). The reaction of 1,3,5-TMB with reactive bromine species 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. 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 in 2015 on volcanic gas plumes at Mt. Etna (Italy), Mt. Nyiragongo and Mt. Nyamulagira (DR Congo) giving reactive bromine mixing ratios from 0.3 ppb (Nyiragongo) up to 22 ppb (Etna, NEC). Compared with total halogen data derived by alkaline trap sampling (Raschig-tube) and ion-chromatography analysis the reactive bromine mixing ratios allow the investigation of the conversion of HBr into reactive species due to plume chemistry with progressing plume age.

The new method will be described in detail and the first results on the reactive halogen to total halogen output will be discussed (for bromine and chlorine) and compared to earlier volcanic plume chemistry model studies.

References

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