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Development and application of gas diffusion denuder sampling techniques with in situ derivatization for the determination of hydrogen halides in volcanic plumes

Alexandra Gutmann (1), Julian Rüdiger (1), Nicole Bobrowski (2), and Thorsten Hoffmann (1)

(1) Johannes Gutenberg-University, Institute of Anorganic and Analytical Chemistry, Mainz, Germany (gutmann@uni-mainz.de), (2) Johannes Gutenberg-University, Institute of Geoscience, Mainz, Germany

Volcanoes emit large amounts of gases into the atmosphere. The gas composition in volcanic plumes vary, driven by subsurface processes (such as magma rising) as well as by chemical reactions within the plume after mixing with ambient air. The knowledge of the gas composition can be a useful tool to monitor volcanic activity changes. However, to use the plume composition as a monitoring parameter, it is essential to understand the chemical reactions inside volcanic plumes, in particular when interpretation of volcanic activity changes is based on reactive gas species, such as bromine monoxide or molecular halogens.
Changes in BrO/SO_2-ratios, measured by UV spectrometers, have already been interpreted in connection with increasing volcanic activity prior to eruptions. But the abundance of BrO changes as a function of the reaction time, and therefore with distance from the vent, as well as the spatial position in the plume. Actually model and field studies assume a non-direct emission of BrO, but its formation due to photochemical and multiphase reactions involving gas and particle phase of volcanic emission mixed with the surrounding atmosphere. However, same models presume HBr as initially emitted species. Therefore, HBr is an important species linking BrO to geophysical processes in volcanic systems. Due to the lack of analytical methods for the accurate speciation of certain halogens (HBr, Br2, Br, BrCl, HOBr, etc.) there are still large uncertainties about the magnitude of volcanic halogen emissions, and in the understanding of the bromine chemistry in volcanic plumes.

Since the concentrations of hydrogen halides are not directly accesable by remote sensing techniques, an in situ method with coated gas diffusion denuder was developed. The method uses selective derivatization reaction of gaseous hydrogen halides with an organic compound for the enrichment and immobilization. For this task 5,6-Epoxy-5,6-dihydro-1,10-phenanthrolin was identified as a suitable derivatization agent. The reaction with HBr results in the formation of 5-Bromo-5,6-dihydro-6-hydroxy-1,10-phenanthrolin. Other hydrogen halides give corresponding products.
Using a denuder based sampling system with in situ derivatization it is also possible to differentiate even between gaseous and particulate hydrogen bromine. The derivatized analytes were analyzed with high pressure liquid chromatography-mass spectrometry.

We applied this approach to measure hydrogen halide mixing ratios (ppt to ppb range depending on plume age) in the plumes of different volcanoes: Stromboli, Italy; Masaya, Nicaragua; Turrialba, Costa Rica. The results of this measurements will be presented. Samples were taken at various distances to the emission source and have been compared with complementary data (e.g. SO_2 from alkaline traps or gas sensors). Furthermore, the sampling method has been applied on an unmanned aerial vehicle for downwind sample collection.