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Bromine Chemistry in volcanic plumes – Development of in-situ denuder sampling techniques for hydrogen bromine

Alexandra Gutmann (1), Nicole Bobrowski (2,3), Marcello Liotta (4), Julian Rüdiger (5), and Thorsten Hoffmann (1)

(1) Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany, (2) Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany, (3) Max Planck Institute for Chemistry, Mainz, Germany, (4) Istituto Nazionale di Geo[U+FB01]sica e Vulcanologia, Sezione di Palermo, Italy, (5) Atmospheric Chemistry, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany

Within their large amounts of gas emissions, volcanoes release significant amounts of halogens into the atmosphere. Since subsurface processes may drive varying gas compositions, monitoring ratios of gases in volcanic plumes can be a useful tool to monitor volcanic activity changes. Lately, decreasing BrO/SO_2-ratios, measured by UV spectrometers, have been interpreted in connection with increasing volcanic activity prior to eruptions. However, the amount of BrO changes also as a function of the reaction time and therefore with the distance from the vent, as well as the spatial position in the plume by chemical reactions within the plume after mixing with ambient air. Therefore, it is essential to understand the chemical reactions inside volcanic plumes for using the plume composition as a monitoring parameter.
Actually model and field studies assume the rapid formation of BrO due to photochemical and multiphase reactions involving the gas and particle phase of volcanic emissions mixed with the surrounding atmosphere rather than the direct emission of BrO. The same models presume HBr as major initially emitted bromine species. Therefore, HBr is an important species linking BrO to geochemical processes in volcanic systems. Due to the lack of analytical methods for the accurate speciation of most halogen compounds (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 most bromine species are not directly accessible by remote sensing techniques, in situ methods have been developed. Alkaline traps dissolve and enrich halogens in alkaline solutions. Detected amounts of bromine are used as a reference point for total bromine.
However, alkaline traps cannot distinguish between several bromine species. Therefore, more recently gas diffusion denuder sampling techniques have been improved for this purpose. Enrichment is based on the derivatization of selected species with organic coatings. For hydrogen halides, 5,6-Epoxy-5,6-dihydro-1,10-phenanthroline was identified as a suitable derivatization agent. Because only gaseous species diffuse fast enough to the tube walls and are retained by derivatizing reactions, denuders distinguish additionally between gaseous and particle proportions of a species.

The suitability of epoxide coated gas diffusion denuders for hydrogen bromine determination has been verified and assessed in the lab. Gas diffusion denuder and Raschig tubes have been applied at Stromboli (Italy) and Masaya (Nicaragua). Samples were taken at various distances from the emission source. The evolution of compound ratios with reference to the distance of the source will be presented and discussed.