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Development and application of a sampling method for the determination of reactive halogen species in volcanic gas emissions

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Volcanoes are a potential large source of several reactive atmospheric trace gases including sulfur and halogen containing species. Besides the importance for atmospheric chemistry, the detailed knowledge of halogen chemistry in volcanic plumes can help to get insights into subsurface processes. 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 (RHS), was characterized by dilution chamber experiments. The coating proved to be suitable to collect selectively gaseous bromine species with oxidation states (OS) 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. Solvent elution of the derivatized analytes and subsequent analysis with gas chromatography mass spectrometry gives detection limits of 10 ng or less for Br_2, Cl_2, and I_2. In 2015 the method was applied on volcanic gas plumes at Mt. Etna (Italy) giving reactive bromine mixing ratios from 0.8 ppbv to 7.0 ppbv. Total bromine mixing ratios of 4.7 ppbv to 27.5 ppbv were obtained by simultaneous alkaline trap sampling (by a Raschig-tube) followed by analysis with ion chromatography and inductively coupled plasma mass spectrometry. This leads to the first results of in-situ measured reactive bromine to total bromine ratios, spanning a range between 12 ± 1 % and 36 ± 2 %. Our finding is in an agreement with previous model studies, which imply values < 44 % for plume ages < 1 minute, which is consistent with the assumed plume age at the sampling sites.