Bromine Speciation in Volcanic Plumes: New in-situ Derivatization LC-MS Method for the Determination of Gaseous Hydrogen Bromide by Gas Diffusion Denuder Sampling

Alexandra Gutmann[1,2,3], Nicole Bobrowski[~~2,~~3,4], Marcello Liotta[5~~4~~], Thorsten Hoffmann[1]

[1]Department Chemie, Johannes Gutenberg-University, Mainz, Germany
[2]Institut of Geosciences, Johannes Gutenberg-University, Mainz, Germany
[3]Max-Planck Institute for Chemistry, Mainz, Germany
[4~~2~~]Institute for Environmental Physics, University of Heidelberg, Heidelberg, Germany
[5~~3~~]~~Max-Planck Institute for Chemistry, Mainz, Germany~~
[~~3~~]Instituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy

Correspondence to: Alexandra Gutmann (alexandragutmann@web.de), Thorsten Hoffmann (t.hoffmann@uni-mainz.de~~)~~

Abstract. The chemical characterization of volcanic gas emissions gives insights into the interior of volcanoes. ~~Monitoring of BrO/SO$_2$ ratios~~Bromine species have~~s~~ ~~recently~~ been correlated with changes in the activity of a volcano. ~~BrO and SO$_2$ can both be measured autonomously and simultaneously with the same instruments from a safe distance, making their ratio potentially a strong monitoring tool. However,~~ In order to exploit the volcanic bromine gases, we need to understand what happens to them after they are outgassed into the atmosphere. ~~BrO is not a primary emitted volcanic volatile and there exist still uncertainties about the formation of BrO in volcanic plumes, mostly due to the lack of analytical approaches for the accurate speciation of certain key compounds.~~

This study aims to shed light on the conversion of bromospecies after degassing. ~~describes a new~~The method presented here ~~for the determination of the BrO precursor, the~~ allows the specific analysis of gaseous hydrogen bromide (HBr) in volcanic environments.~~,~~ ~~by quantitative collection in denuder samplers. Gas diffusion denuders use the difference in diffusion coefficients to separate gaseous from particle-phase compounds. Gaseous~~ HBr is ~~molecules are~~ immobilized by reaction with ~~an organic coating~~ 5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (EP), which acts as an ~~at the~~ inner coating inside ~~walls~~ of ~~the diffusion~~ denuder tubes ~~when pumped through the denuders~~(*in situ* derivatization). ~~Five different coatings using 1,2-epoxycyclooctane, *trans*-oxirane-2,3-dicarboxylic acid, 2,3-epoxy-3-phenylpropanoic acid, 9,10-epoxystearic acid, 5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (EP) were tested as denuder coatings. EP proved to be a suitable coating reagent, which at the same time, transfers the analyte into an appropriate derivate To be~~ The derivative is analyzed by high-performance liquid chromatography coupled to electrospray ionization mass spectrometry (HPLC-ESI-MS). ~~(*in situ* derivatization). Coating amount, breakthrough, matrix effects and the storage behavior have been characterized. No considerable cross-sensitivity with hydrogen chloride or other bromine species such as molecular bromine was observed.~~

The collection efficiency for HBr (99.5 %), collection efficiency for HBr alongside HCl (98.1%) and the relative standard deviation of comparable samples (8 %) have been investigated. The comparison of the new ~~HBr determination using EP-coated~~ denuder~~s~~-based method and Raschig Tubes as alkaline trap~~s~~ resulted on average in a relative bias between both methods of 10 ± 6 %.. ~~in the laboratory showed a deviation of 2 ± 11 % for gaseous HBr between the two methods. This allows considering HBr determined by denuders as a fraction of total bromine determined by Raschig Tubes. Since other bromine species (e.g. elemental bromine, bromine oxides) are also collected and determined as bromide by Raschig Tubes, but exclusively HBr in EP-coated denuders, the method presented here allows more accurate speciation of gaseous bromine compounds and their application in volcanic plumes.~~

The denuder sampling setup was applied ~~with complementary denuder systems and alkaline traps~~ in the plume of Masaya (Nicaragua) in 2016. HBr concentrations in the range between 0.44 and 2.27 ppb were measured with limits of detection and quantification below 0.1 and 0.3 ppb respectively~~ at typical ground-based sampling conditions~~. The relative contribution of HBr as a fraction of total bromine decreased from 75 ± 11 % at Santiago rim (214 m distance to the volcanic emission source) to 36 ± 8 % on Nindiri rim (740 m distance).

~~Our findings are in good agreement with~~ A comparison between our data and the previously ~~estimations of the~~calculated HBr, based on the ~~conversion from the chemistry~~ CAABA/MECCA box model, ~~(CAABA/MECCA)~~showed a slightly higher trend for the HBr fraction on average than expected from the model. Data gained from this new method can further refine model runs in the future.

1 Introduction

Since the formation of the atmosphere, volcanic eruptions and volcanic passive degassing contribute to an exchange of Earth's interior and the atmosphere (Brown, 1952; Schmincke, 1993; Halmer et al., 2002) with impacts extending from the local environment to the global climate (Shaw, 2008; Saturno et al., 2018). Besides their environmental and climatic impacts, volcanic gases can be indicators for processes occurring within volcanoes. For example, in 1991, volcanologists observed a significant increase of sulfur dioxide (SO_2) emissions at Mt. Pinatubo which influenced the decision to evacuate ten thousands of people prior to the onset of major volcanic activity (Daag, 1996; Harlow et al., 1996).

Besides H_2O, CO_2 and sulfur species, also halogens are ~~among the not negligible~~ constituents of volcanic emissions e.g. in arc volcanoes 0.84% HCl, 0.061% HF, 0.0025% HBr (Textor et al., 2004; Gerlach, 2004). Monitoring of halogens in volcanic plumes has been correlated with volcanic activity for decades. ~~Already~~ For example, Noguchi and Kamiya determined the plume composition of Mt. Asama over months and observed a decreasing Cl/S ratio before an eruption in 1958 (Noguchi and Kamiya, 1963). The discovery of bromine monoxide (BrO) in volcanic plumes and the observed correlation between the simultaneously determined BrO/SO_2 ratio and volcanic activity by automated instruments (e.g. Lübcke et al., 2014) made BrO/SO_2 a promising monitoring tool. A major advantage of BrO is a typically negligible background in the atmosphere, concluding that findings clearly derive from magma degassing. The BrO/SO_2 ratio is measurable simultaneously by remote sensing instruments which facilitates the applicability for monitoring volcanic activity compared to in situ sampling techniques. Even inaccessible volcanoes can be observed with satellite-based remote sensing instruments (e.g. Hörmann et al., 2013). If the informative value of Br emissions about volcanic activity is confirmed, then it may be possible to provide greater forewarning regarding volcanic eruptions via BrO monitoring through the use of remote sensing instruments. It is therefore important to have methods to determine how bromine species are transformed in volcanic plumes. ~~However,~~ ~~g~~Gas composition and gas amount of distinct halogen species vary not only due to volcanic activity changes but also because of photochemical and multiphase reactions in the plume. It is assumed that bromine is mainly released from volcanoes as hydrogen bromide (HBr) and, depending on various conditions (e.g. total bromine emission, plume-air-mixing), is gradually converted into other bromine species (including BrO) in the volcanic plume. To use the BrO/SO$_2$ ratios for monitoring volcanic activity, a perfect understanding of ongoing bromine chemistry in the plume is essential. Chemical models have already been developed to explain BrO formation in certain plume environments. However, due to the lack of applicable measurement techniques for individual bromine species, comparison of expected bromine species conversion rates with measurements are still hypothetical~~. For an overview of the discussion of bromine chemistry in volcanic plumes see~~ ~~-~~(Gutmann et al., 2018 ~~(2018)~~ and references therein).

A promising approach for the revelation of the bromine speciation are gas diffusion denuder techniques. The gas diffusion denuder technique has already been developed for reactive halogens (e.g. Br$_2$, BrCl, HOBr) (Huang and Hoffmann, 2008, 2009) and has been adapted to volcanic plumes (Rüdiger et al., 2017) and even applied using UAV in volcanic plumes (Rüdiger et al., 2018). The gas diffusion denuder technique differentiates between gaseous compounds and compounds in the particle phase, e.g. HBr and particulate bound bromides (Kloskowski et al., 2002). To function as a sampling unit, the denuder surface should be a perfect sink for the compounds to be analyzed (i.e. assuming an irreversible uptake), which diffuses to the coated inner walls of the denuder as the sampling air passes through the device. The sampling efficiency depends on the denuder dimensions, the flow velocity and the diffusion coefficient of the analyte of interest, but is > 99 % under normal sampling conditions (Fick, 1855; Gormely, P.G. and Kennedy, M., 1948; Townsend, 1900; Tang et al., 2014). Which gaseous analytes are enriched, depends on the organic reagent used as a coating for the denuder tubes. Epoxides are effective reagents for a rapid reaction with gaseous HBr, since they show acid-catalyzed ring-opening reactions with nucleophilic reagents, in the case of HBr both properties being present in one molecule. ~~As products~~ Therefore, as products from the reaction of epoxides with HBr bromohydrins are formed (Becker and Beckert, 2004).

Since the reaction products (besides bromohydrins also other halohydrins) are formed during sampling and are finally separated by liquid chromatography after ~~elution~~ extraction from the denuder tubes and are detected and quantified by mass spectrometry, the presented technique represents an *in situ* derivatization high-performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESI-MS) method.

In this study, the aim was to develop a measurement technique with which it is possible to detect gaseous HBr in volcanic gases. Enrichment of gaseous HBr by chemical bonding to a coating in denuders seemed the most promising method. First, a source of HBr test gas was developed, which is included in the methods section. Followed by the experimental setup, handling of the denuders, analysis of the samples, and finally the description of the application of the method in Masaya’s plume in 2016. After testing five different coatings, 5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (EP) showed the best conditions for a successful method development. The performance of the EP-coated denuders is described in more detail in the following. In order to see to what extent a supplementation of simultaneously collected field samples with other methods is possible, a comparative measurement of the new denuder method was compared with alkaline samples from a Raschig tube. Finally, the results of the new method applied in the volcanic plume of Masaya volcano are presented.

2 Methods

For the ~~method~~ development of a method based on the reaction with an epoxy coating, the collection efficiency of five different ~~organic~~ coatings ~~were~~ was tested. ~~To check the efficiency of the organic coatings in a controlled laboratory experiment, test gas sources were operated. After sampling and elution, the derivatives were analyzed by gas chromatography-mass spectrometry or high-performance liquid chromatography-mass spectrometry, depending on the type of coating.~~ All reagents used are listed in the supplementary material. The substances 2-bromocyclooctanol, 2,3-epoxy-3-phenylpropanoic acid, 9,10-epoxystearic acid, 10-bromo-9-hydroxystearic acid, and 5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr) were required as coatings or reference products, were not commercially available, and were synthesized. Synthesis descriptions are also included in the supplementary material.

2.1 Test gas sources and experimental setup

2.1.1 Test gas sources

A diffusion gas source using a brown glass vial with septum cap as described in Rüdiger et al. (2017) was filled with 48 % aqueous HBr ~~or 30 % aqueous hydrogen chloride (HCl)~~ and stored under nitrogen flow at 30 or 50° C (Fig. 1a). The incoming gas stream was thermostated before it reached the diffusion source. The vials containing the analytes were weighed regularly to determine output rates. The length and diameter of the capillary, as well as the temperature, controlled the output rate. A 5 cm capillary with 0.32 mm inner diameter was used for the HBr source~~, a 2 cm capillary with 0.64 mm inner diameter for the HCl test gas source~~. Taking advantage of the azeotropic behaviour of the HBr-water-mixture (Haase et al., 1963) we observed a constant output rate for HBr of 108 µg/d and 415 µg/d for 30 and 50 °C respectively (Fig. S2).

For experiments testing the collection efficiency of HBr aside hydrogen chloride (HCl), a vial following the same procedure using a 2 cm capillary with 0.64 mm inner diameter was prepared containing 30 % aqueous HCl. We observed an output rate for HCl of 4.33 mg/day at 50 °C. For the experiments both vials (one each for HBr and HCl) were stored side by side in the test gas storage vessel (Fig 1a).

For Br_2, the permeation source described in Rüdiger et al. (2017) was used with an output rate of 775 µg/d under nitrogen flow.

2.1.2 Experimental setup

For a set of experiments, the test gas sampling was performed with two (or three) denuders in a row using a membrane pump (Gilian Gil Air Plus) located downstream of the denuder (Fig. 1a). A sampling flow rate of 250 mL/min ~~proved to provide ideal sampling efficiency~~was used. All connecting pieces were ~~realized by~~ made of glass or PTFE material. A method often used in volcanic emission studies is ~~the~~ sampling with alkaline traps. We used so-called Raschig Tubes (Wittmer et al., 2014). These are horizontally aligned, rotating glass vessels containing Raschig rings, which are filled with an alkaline solution through which the sample air is sucked by means of membrane pumps. This technique was used here both~~,~~ as a comparative method in the laboratory to compare with the denuder technique (Fig, 1b) and later in the field for total bromine determination. The target HBr concentrations were generated by ~~For the method validation in the laboratory~~ a standard gas bottle with 102.8 ± 3.1 ppm HBr diluted with ~~was connected to two~~ 3-neck flasks~~ connected in series as mixing and dilution chambers. Nitrogen was introduced into both vessels. The HBr-nitrogen mixture of the first vessel was introduced together with additional nitrogen via a Y-tube into the second flask. The denuder and Raschig Tube were connected with PTFE tubes, which ended at the bottom of the second flask~~. ~~Therefore, c~~Care was taken to ensure that the connecting tubes to the entrance of the two sampling arrangements (Raschig Tube and denuder) were identical in length and diameter. ~~However,~~ This ensures that results of~~since this affects~~ both sampling methods are comparable as concentration variations affect both methods equally ~~in the same way, a comparison of the results of both methods is still possible.~~ Although HBr concentrations between 13 and 31 ppb were established in this way, the downstream analysis revealed concentrations between 3 and 20 ppb. The cause is probably the loss of HBr on the surfaces of the experimental setup (e.g. Hanson and Ravishankara (1992), Talukdar et al. (1992), this applies generally to strong acids e.g. HNO_3 (Neuman et al., 1999)). ~~Apparently, fractional amounts of HBr are lost due to losses on the glass surfaces or~~Another inaccuracy of HBr concentrations may also come from incorrect flow meters or ~~used in the laboratory setup indicate inaccurate gas flows or~~ fluctuat~~e.~~ing gas flows. ~~However, since this affects both sampling methods in the same way, a comparison of the results of both methods is still possible. Therefore, care was taken to ensure that the connecting tubes to the entrance of the two sampling arrangements (Raschig Tube and denuder) were identical in length and diameter. The detailed design is shown in Fig. 1b.~~

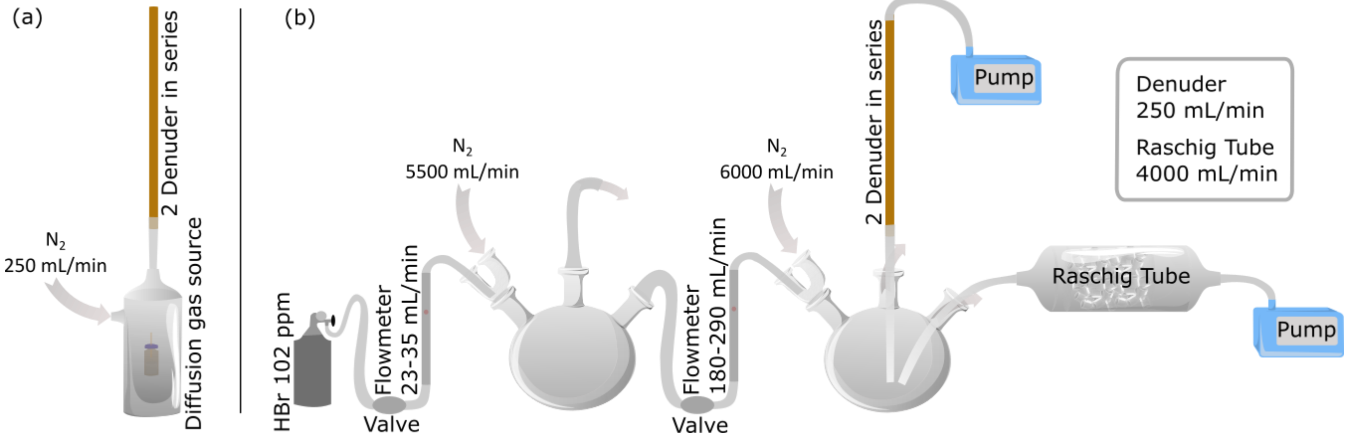


Figure 1: Experimental sampling setups in the laboratory. (a) Denuders were connected to a diffusion test gas source with PTFE tubes. The test gas source was heated to 50° C. Entering nitrogen was thermostated before it reached the diffusion source. (b) Experimental Setup for comparison of denuder and Raschig Tube technique for HBr determination.

2.2 Denuder preparation, extraction and ~~t~~analysis~~reatment~~

The denuder ~~tubes ~~were 50 cm long ~~made of ~~brown borosilicate glass tubes ~~to avoid photochemical reactions. They were 50 cm long and had~~with an inner diameter of 6 mm. Solutions of 1.5 mmol/L, 7.5 mmol/L or 15 mmol/L were used with various coating compounds (Table 1). Besides the amount of coating material, the uniformity of the distribution of the coating inside the denuder influences the collection efficiency of each denuder. To achieve an even coating the coating solution was applied in 6 steps of 0.5 ml. Each aliquot was dried before the application of the next step. ~~6 times 0.5 ml of the respective solutions were pipetted into the denuder.~~ In order to obtain reproducible coating distributions and to standardize the coating process, a system was ~~therefore ~~installed which can hold four denuders horizontally at an adjustable angle of about 10°, to connect the denuders with a gentle stream of nitrogen of about 0.5 L/min/denuder and to rotate them during preparation. A photo of the created drying system is shown in Fig. S3. The coated denuders were closed with polypropylene caps and sealed with PTFE tape and parafilm.

Coating agents for derivatization must have the following properties: The reaction between the coating and gaseous analyte must be sufficiently rapid to achieve high collection efficiencies. Furthermore, the reaction should not require the use of solvents or other additional chemicals. Fixation of ~~educts~~coating reagents to the denuder walls during sampling can be done with glycerine (Finn et al., 2001) and was tested for 1,2-epoxycyclooctane-coated denuders. The coating should preferably provide only one derivatized product (no isomers or multiple derivatizations). In addition, the coating substrate must be suitable for the coating process. Carboxylic acids were used because they entail ~~To ensure ~~low volatility and thus do not~~ to avoid~~ evaporat~~eion~~ during sampling and the concentration step.~~, epoxides containing carboxy groups were selected. ~~ In the further course, attention was paid to l~~L~~ow volatile compounds containing a functional group that exerts a positive inductive effect on the epoxy group to maintain reactivity to HBr were selected to optimize the reactivity of the coating.

After sampling, analytes were ~~eluted ~~dissolved from the denuders ~~with five times~~in five steps using 2 mL solvent each step (Fig. 2a). All analytes were ~~eluted ~~dissolved with ethyl acetate, except for EP-coated denuders, as these showed better solubility in methanol. The ~~elution ~~extraction efficiency was investigated with EP-coated denuders doped with 0.01 µ~~m~~mol of the bromine product EPBr. Therefore, standard calibration solution has been applied and dried on the denuder during the denuder coating process. The extraction process described in Fig. 2a has been performed a second time on a previously extracted denuder. ~~In a~~Analyzing the residue of EPBr in the second ~~elution ~~extraction step~~, with five times 2 mL solvent after the first elution step,~~ less than 0.05 % EPBr compared to the first step was found. ~~As a consequence, the second elution step was omitted.~~

~~Eluates~~ Extracts were concentrated to approximately 100 µL under a gentle nitrogen stream at 35° C. For adjustment of varying evaporated volumes and for compensation of evaporation losses, 100 µL of an internal standard was added to the ~~eluates~~ extracts before the concentration step. Samples analyzed by GC-MS were doped with 100 µL 2,4,6-tribromanisole (TBA, 6 mg/L) as internal standard, while EP-coated denuder samples analyzed by LC-MS were doped with 100 µL neocuproine (NC, 5 mg/L). The suitability of the internal standards was evaluated by investigating the recovery rate.

The recovery rate of the processing method for EPBr showed recovery rates ranging from 110 to 51%. We observed that the high amounts of EP cause precipitation when samples are concentrated for analysis. The addition of formic acid enhances solubility of analytes while not affecting negatively the following LC-ESI-MS analysis. The recovery for EPBr ~~–~~was determined to be 99 ± 4 % ~~(*n* = 6)~~ when formic acid was added to the ~~eluate~~ extracts before the evaporation process (Fig. 2b). ~~For EPBr samples, the flasks were rinsed with an additional 100 µL methanol after evaporation.~~

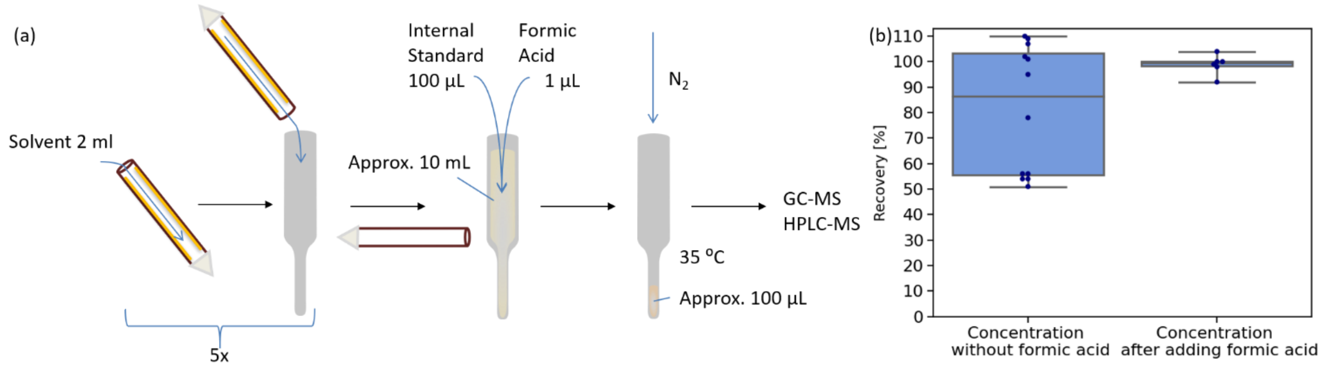


Figure 2: Denuder coating extraction and concentration of samples. **(a) Denuder coating is dissolved 5 times with 2 ml solvent each step. Dissolved coating is collected in glass vessels. 100 µl internal standard (NC for EP-coated denuders, TBA for all others) and 1 µl formic acid for EP-coated denuder samples is added to the approximately 10 ml coating solution before concentration. The samples are concentrated at 35 °C under a gentle nitrogen stream to approximately 100 µl. (b) The investigation of the concentration process without adding formic acid (left side) revealed a mean recovery for EPBr of 81 ± 25 % and a median (grey line) at 86%. Addition of formic acid before the concentration (right side) enhances recovery of EPBr to 99 ± 4 %. The boxes show the 25th and 75th percentiles and the median.**

~~**Table 1: Selected epoxides used as coating reagents**~~

~~Coating~~	~~Derivative~~	~~Result~~
~~1,2-epoxycyclooctane~~	~~2-bromocyclooctanol~~	~~Evaporated during sampling~~
~~*trans*-oxirane-2,3-dicarboxylic acid~~	~~2-bromo-3-hydroxy-butanedioic acid~~	~~No product~~
~~2,3-epoxy-3-phenylpropanoic acid~~	~~2-bromo-3-hydroxy-3-phenylpropanoic acid~~	~~No product~~
~~9,10-epoxystearic acid~~	~~10-bromo-9-hydroxystearic acid~~	~~Water and chloride side product: 9,10-dihydroxystearic acid~~

		~~10-chloro-9-hydroxystearic acid~~
~~5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (EP)~~	~~5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr)~~	~~Suitable~~

2.3 Analysis by chromatography-mass spectrometry

All samples were analyzed by GC-MS, except for EP-related samples, which were analyzed by LC-MS. For all bromine compounds, both isotope masses were measured and taken into account for data processing.

2.3.1 Gas chromatography-mass spectrometry

To increase the volatility of ~~the analytes~~carboxylic acids, the carboxylate functionality was converted to a trimethylsilyl derivative by adding 30 µL *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 7 µL pyridine ~~were added~~ to GC-samples containing carboxylic acids. Samples were ~~stored~~ incubated for 90 min at 70° C before analysis.

For chromatographic analysis, a 6850 Network GC System (Agilent, Waldbronn, Germany) with a fused-silica FS-Supreme-5ms capillary column (30 m x 0.25 mm i.d.; 0.25 µm, CS-Chromatography, Langerwehe, Germany) was used, coupled to a 5973 Network Mass Selective Detector (Agilent, Waldbronn, Germany). The carrier gas was 99.999 % high-purity helium at a constant pressure of 100kPa. 1 µL sample was injected in splitless mode. The injector was heated to 250° C and the transfer line to 300 °C. The Electron Ionization (EI) spectra were acquired at 70 eV and a mass range of *m/z* 45-450 were selected. The oven temperature programs (range from 90-300 °C with total runtimes of 9-30 min) and the ions used for quantification are summarized in the supplementary material (Table~~s~~ S1~~-4~~).

2.3.2 High-performance liquid chromatography-mass spectrometry

Since EP decomposes at usual GC-temperatures, EP-related samples were analyzed by high-performance liquid chromatography coupled to electrospray ionization mass spectrometry (HPLC-ESI-MS). HPLC-ESI-MS was performed with an Agilent 1100 series (Agilent Technologies, Germany) HPLC system coupled to an HCT-Plus ion trap mass spectrometer (Bruker-Daltonics, Germany). The analytical column (Atlantis T3 C18 2.1x150 mm, 3 µm particle size, Waters, Germany) was heated to 35° C during analysis. A flow of 200 µL/min was used. A gradient of eluent A (ultrapure water with 2 % acetonitrile and 0.04 % formic acid) to eluent B (acetonitrile with 2 % ultrapure water) was used, starting with 5 % eluent B that was held for 10 min. Within 23 min eluent B was raised to 14 % and in the following minute raised to 100 % (hold for 11 min). The electrospray ionization source was used in the positive ion mode and resulted in protonated molecular ions ([M+H]$^+$) which were used for quantification. The capillary voltage was +3.5 kV, the dry gas temperature was 350° C, dry gas flow (N_2) was 8.5 L/min, and nebulizer pressure 35 psi. The mass spectrometer was operated in ultra-scan mode.

Under these conditions, EP eluted at 7.9 min retention time, however, with relatively broad peak widths due to the high concentration of the coating material in the concentrated samples. 5-chloro-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline eluted at retention time 20.5 min. In the field samples, the peak widths increased and retention times changed, probably due to ~~matrix effects~~overloading of the column. EPBr eluted at retention time 27.2 min. Depending on the amount of coating material and chloro-derivative, the retention time varied between 25 and 28 min. The internal standard neocuproine eluted at retention time 32.4 min (Fig. S5). A six-point calibration (0.1-10 mg/L) was used to determine the detection limit (LOD) of 0.03 mg/L and the quantitation limit (LOQ) of 0.17 mg/L for EPBr following a standard protocol (DIN 32645:2008-11.).

2.4 Field application at Masaya 2016

A first set of field samples was collected ~~Denuders coated with 45 µmol EP were used~~ between 18.-21. of July 2016 at the Santiago Crater of the Masaya volcano (Nicaragua). A detailed description of the location can be found in Rüdiger et al. (2021). ~~Eight ground-based and two UAV-based samples were taken and subsequently analyzed.~~ In summary, sets from different methods were collected simultaneously together at changing locations with ~~Samples were taken at~~ various distances (200-2000 m, ~~Table 2~~Fig. 3b) ~~from~~to Masaya's emission source at Santiago crater (Fig. 3~~4~~b). ~~During the ground-based sampling periods, EP-coated denuders were used simultaneously with 1,3,5-trimethoxybenzene coated denuders for the determination of reactive bromine as well as Raschig Tubes as alkaline traps for the determination of total bromine and total sulfur.~~

~~The airborne SO_2 concentrations were determined with electrochemical SO_2 sensors, assuming SO_2 as the major sulfur species. The setup was supplemented by DOAS observations of a NOVAC station for BrO and SO_2. Results and method description for reactive and total bromine can be found in detail in Rüdiger et al.. A detailed description of the UAV system and flight descriptions can be obtained from Rüdiger et al. (2018) and Rüdiger et al. (2020).~~

A total of ~~E~~eight ground-based and two UAV-based samples for the newly developed denuder method are presented here. ~~were taken and subsequently analyzed.~~ In ground-based sampling sets, two denuders were ~~used~~ sampled in series ~~-~~(Fig. 3~~4~~a). Both denuders were extracted and results were summarized. Sampling was performed by a Gilian GilAir Plus handheld pump (battery included) with a flow rate of 250 ml/min for about 1-1.5 hours for each denuder. In addition to EP-coated denuders, samples with 1,3,5-trimethoxybenzene coated denuders for the determination of reactive bromine. as well as Raschig Tubes as alkaline traps for the determination of total bromine and total sulfur were collected simultaneously side by side. The results of these samples can also be found in Rüdiger et al. (2021).

First drone-based samples were collected with an UAV using a small four-rotor multicopter with foldable arms (Black Snapper, Globe Flight, Germany) called RAVEN (Rüdiger et al., 2018). For the UAV-based sampling, a remotely controlled sampler (called Black Box) was used and is also described in detail in Rüdiger et al. (2018). The Black Box enabled logging of the sampling duration and SO_2 mixing ratios via the built-in SO_2 electrochemical sensor (CiTiceL 3MST/F, City Technology, Portsmouth, United Kingdom). The Black Box has 20x14x13 cm. With this setup (Black Box + denuder) of approx. 1 kg we achieved flight times of up to 15 min. In drone-based sampling ~~setups~~flights, individual denuders were used with sampling times between 5-10 minutes. ~~Samples were taken at various distances (200-2000 m, Table 2) from Masaya's emission source at Santiago crater (Fig. 4b).~~

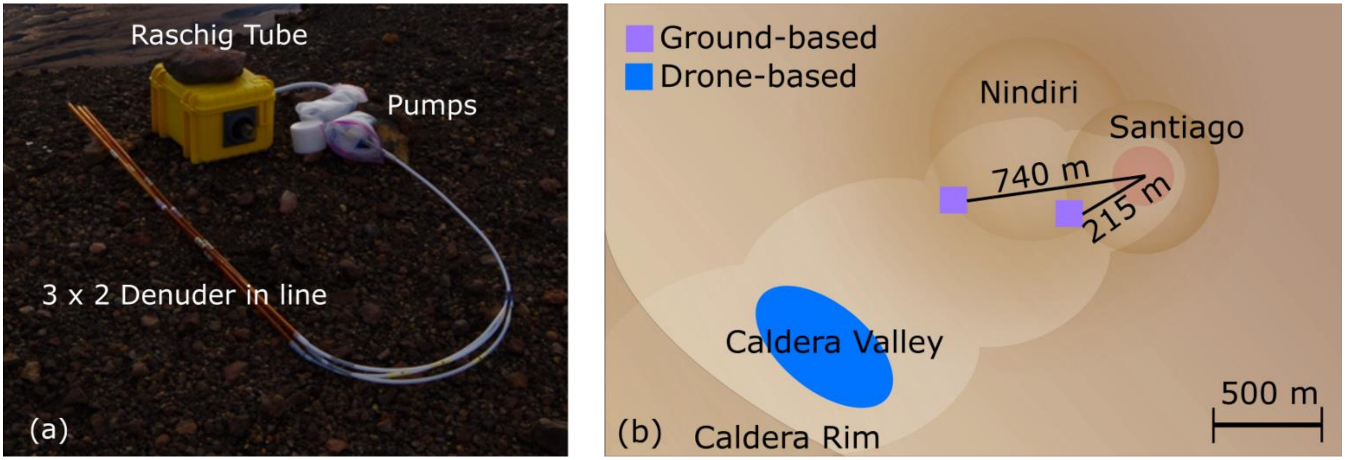


Figure 3: Field campaign at Masaya volcano in July 2016. (a) Sampling setup containing TMB- and EP-denuders, two in series each, and Raschig Tube. (b) Overview on ground-based sampling locations (purple areas) during the field campaign at Santiago crater, on Nindiri rim and UAV-based (blue area) in the caldera valley.

3 Results and Discussion

3.1 Selection of derivatizing coating

For the development of a method based on the reaction with an epoxy coating, the collection efficiency of five different coatings was tested. The ~~suitability~~ observations of the different denuder coatings are~~is~~ summarized in Table 1.

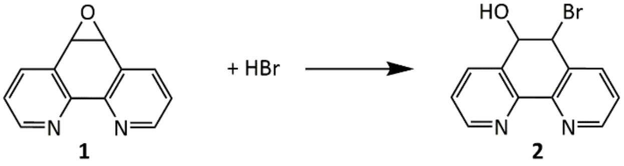
~~One of the coatings tested was 2,3-epoxycyclooctane.~~ Although it is solid at room temperature, 1,2-epoxycyclooctane was not detectable in samples extracted from denuders after ~~a significant loss of the compound was observed during~~ sampling. ~~Obviously, 2,3-epoxycyclooctane is too volatile. Although~~ Nevertheless, traces of the product 2-bromocyclooctanol could be ~~determined~~ detected in the denuder ~~eluates~~extracts.~~,~~ We did not quantify the formation, but this led us to believe in the principle ability of epoxides to react with HBr in our system. ~~which proves the principle suitability of this coating, the observed losses led to the decision not to consider this compound any further, since also the attempt to improve the fixation of the reagent on the denuder walls during sampling with glycerine was not successful.~~

The introduction of carboxy groups into the molecular framework of organic compounds ~~massively~~ reduces the vapor pressure of the substances. Therefore, epoxides with carboxyl groups were subsequently tested as coating materials. ~~However, t~~The selection of compounds with carboxyl groups in the immediate vicinity of the epoxy functionality reduces the reactivity to HBr and accordingly no bromine product of *trans*-oxirane-2,3-dicarboxylic acid and 3-phenyloxirane-2-carboxylic acid could be detected.

The carboxyl group in 9,10-epoxystearic acid also ~~causes low~~reduces volatility but is not near the epoxy group. Technically, two isomeric products were possible, but the influence of the carboxylic acid group resulted in only one detected product (10-

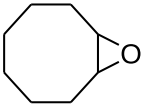
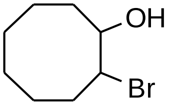
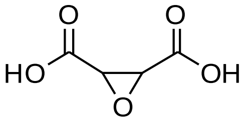
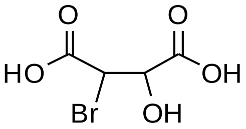
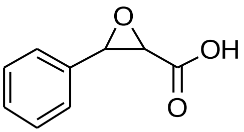
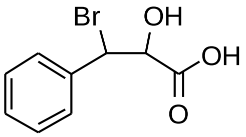
bromo-9-hydroxystearic acid). When 9,10-epoxystearic acid-coated denuders were applied in the plume of Etna, a diol as a result of the reaction of the epoxide with water (9,10-dihydroxystearic acid) and the chloride derivative (10-chloro-9-hydroxystearic acid) were observed. Although derivatized HBr could be analyzed~~ and quantified~~, the *m/z* ratios were overlaid by the water and chloride derivatives (same main *m/z* ratios, Fig. S4). The difficulties this posed for analysis led us to prefer EP, as it also reacted successfully with HBr in our system.

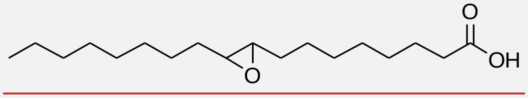
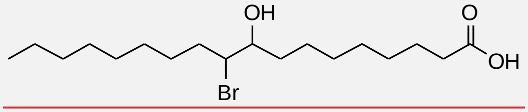
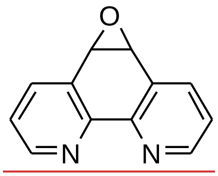
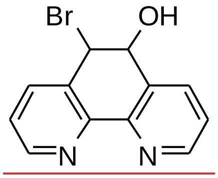
EP ~~(**Fehler! Verweisquelle konnte nicht gefunden werden.**) was observed to be a suitable~~ as a coating agent could retain and ~~for the enrichment and~~ derivatiz~~eation of~~ gaseous HBr passed through denuders and the bromohydrin product could be detected. ~~Performance and~~ The details of the characterization for this coating-compound are ~~described~~ given in the following ~~chapters~~sections.



~~**Figure 2: Derivatization of hydrogen bromide (HBr) with 5,6-epoxy-5,6-dihydro-1,10-phenanthroline (1, EP) yielding 5-Bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (2, EPBr)**~~

~~.~~**Table 1: Selected epoxides used as coating reagentstable**

Coating	Derivative	Observations
1,2-epoxycyclooctane  	2-bromocyclooctanol  	Evaporated during sampling
trans-oxirane-2,3-dicarboxylic acid  	2-bromo-3-hydroxy-butanedioic acid  	No product
2,3-epoxy-3-phenylpropanoic acid  	2-bromo-3-hydroxy-3-phenylpropanoic acid  	No product

9,10-epoxystearic acid	10-bromo-9-hydroxystearic acid	Water and chloride side product: 9,10-dihydroxystearic acid 10-chloro-9-hydroxystearic acid
		
5,6-epoxy-5,6-dihydro-[1,10]-phenanthroline (EP)	5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr)	Chloride side product: 5-chloro-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline Details are described in section 3.2.
		

3.2 Denuder performance

3.2.1 Collection efficiency

According to Rüdiger et al. (2021) and Wittmer et al. (2014), about 0.5-5.9 ppb and 9.5-36 ppb total bromine was detected in ground-based samples in the volcanic plume of Masaya and Etna volcano respectively using alkaline traps. Besides HBr they detected HCl concentrations of 0.5-4.5 ppm and 0.1-20.6 ppm respectively. Other halogen species such as HCl ~~and HI~~ react with EP via the same reaction pathways as HBr. But these form different derivatization products with EP and can, therefore, be easily distinguished by mass spectrometry. Still, HCl can consume the coating reagent. Estimating the speed of the derivatization reaction the nucleophilic reactivity of different hydrogen halides shows that bromide has higher nucleophilic reactivity than chloride (nucleophilic constants in water based on glycidol, H_2O: 0.00, Cl^-: 3.04, Br^-: 3.89, I^-: 5.04) (Swain and Scott, 1953). Accordingly, one could expect a higher reactivity of HBr compared to HCl.

Ensuring that the method will be able to retain all potential gaseous HBr even in high concentrated plumes ~~Therefore,~~ the breakthrough behavior for ~~1 ppm~~0.2 µmol HBr was investigated (0.2 µmol HBr correspond to 1 ppm HBr for 1 h sampling duration). ~~(assumed maximum concentration taking into account variations between different volcanoes and sampling conditions). Therefore~~Further, the collection efficiency for HBr was tested in the presence of about ~~4 ppm~~5 µmol HCl ~~using the sampling arrangement in Fig. 1a.~~ (5 µmol HCl correspond to 4 ppm HCl for 1 h sampling duration).

~~Only 1.9 ± 0.4 % of the bromine product was found in the second denuders.~~The collection efficiency was tested with two or three denuders connected in series (~~Fig. 1a~~Table 2). The amount of product found on the second and third denuder was compared with the values of the first denuder. The collection efficiency tested for denuders coated with ~~22.5 µmol~~ 7.5 mmol/L

EP coating solution ~~clearly~~ revealed a breakthrough of HBr since about 30 % of the amount of the first denuder was observed in the third denuder. In contrast, for denuders coated with ~~45.0 µmol~~15 mmol/L EP coating solution, the breakthrough for 1 ~~-~~ppm HBr was below 1 %. In competition with HCl 1.9 ± 0.4 % of the bromine product was found in the second denuders. ~~However, higher amounts of c~~Coating amounts above 45 µmol EP ~~are disadvantageous since EP started to~~caused precipitat~~ion~~e in concentrated samples during sample preparation (see section 2.2). ~~Finally,~~Concluding from this, 15 mmol/L EP coating solutions were used to coat denuders ~~resulting in~~ a ~~total~~ theoretical amount of 45.0 µmol EP~~ within one denuder was used as a coating~~. The second denuder in series during sampling ensures that we will at least notice a relevant breakthrough of analytes.

Table 2: Experimental details for the determination of collection efficiency for denuders coated with 7.5 and 15.0 mmol/L EP coating

Experiment (Fig. 1a)	EP-Coating Solution [mmol/L]	EP theoretical on denuder [µmol]	EP concentrated to 100 µL [mmol/L]	Approx. applied gases:		Breakthrough	
				HBr [µmol]	HCl [µmol]	2. denuder [%]	3. denuder [%]
3 denuder in series	7.5	22.5	225	0.2	None	105 ± 5	30 ± 5
3 denuder in series	15.0	45.0	450	0.2	None	0.6 ± 0.4	<0.1
2 denuder in series	15.0	45.0	450	0.2	5	1.9 ± 0.4	-

3.2.2 Matrix effects, precision, LOD and LOQ

The influence of abundant EP on the EPBr determination was investigated by a test series with 450 mmol/L EP (corresponds to EP concentrations in concentrated denuder samples) and EPBr concentrations in the range of 5 to 73 ~~-~~mg/L (n = 6, Fig. S7). We determined a relative bias between the both sample types ~~deviations~~ of ~~only~~ 2 ± 3 %~~ compared to samples without EP~~, concluding that no matrix effects were found.

Repeated measurements of the same gas composition using the setup shown in Fig. 1b resulted in a relative standard deviation of 8 % (see Fig. S8)

~~For field samples, the LOD and LOQ were determined by 3 and 10-fold deviation (Kromidas et al., 1995) from coated denuders transported and stored in the same way as denuder samples.~~ To ensure that results remain from detected analytes but not a higher noise (Fig. S5), the LOD and LOQ for denuder samples have been determined from blank denuders. The LOD and LOQ were determined by 3 and 10-fold deviation (Kromidas et al., 1995) from coated denuders transported and stored in the same way as denuder samples (3 coated but not sampled denuders for the field samples presented here). A ~~detection limit (~~LOD~~)~~ of 0.1 mg/L and a ~~limit of quantification (~~LOQ~~)~~ of 0.3 mg/L were calculated for EPBr. Since LOD and LOQ for HBr in the atmosphere depend on sampling time and ~~evaporation~~sample volume after evaporation to concentrated samples, their values were calculated separately for each sample (Table 4~~2~~).

3.2.3 Stability of extracted samples

~~Eluted~~ We tested the stability of extracted and ~~constricted~~ concentrated~~denuder~~ samples with field sample like approaches that were stored in the freezer at -4° C (Table S3 and Fig. S9). Within the first two months of storage no systematic loss could be observed ~~The analysis of the samples was repeated within a time frame of two years. W~~when comparing the analyzed EPBr/NC ratios.~~,~~ After long term storage of 2-3 years remeasuring the field samples (listed in section 3.5) revealed an average loss of 0.03 ± 0.01 % EPBr per day~~an average loss of 0.030 ± 0.003 % EPBr per day was observed in samples ranging from 0.4-4 mg/L (this project's field samples). This is negligible for samples measured directly after pretreatment but must be taken into account for samples stored for a certain time~~ (about 11 % loss after 1 year of storage).

~~For field samples, the LOD and LOQ were determined by 3 and 10-fold deviation (Kromidas et al. 1995) from coated denuders transported and stored in the same way as denuder samples. A detection limit (LOD) of 0.1 mg/L and a limit of quantification (LOQ) of 0.3 mg/L were calculated for EPBr. Since LOD and LOQ for HBr in the atmosphere depend on sampling time and evaporation volume, their values were calculated separately for each sample (Table 2).~~

3.2.4 Interferences

If the denuder coating reacts with other types of bromine, resulting in the same product, this would lead to HBr overdetermination. Elemental bromine (Br_2) is the most likely ~~would be at least conceivable as a~~ cross-interference. ~~However,~~ 9,10-epoxystearic acid and EP-coated denuder collected the output of the Br_2 source for one hour following the setup in Fig. 1a. No bromine product was found. ~~were tested with gases containing Br_2 using the Br_2 sources described in Rüdiger et al. (2017). No corresponding bromine products were found, therefore cross-interference by Br_2 can be excluded. A product formation with alkyl halides, e.g. methyl bromide, is also not expected and would anyway lead to easily distinguishable methoxy bromides. No such product was found in field samples either. Also, with o~~Other bromine species such as bromine oxides (e.g. BrO) with their positively polarized bromine atoms, no nucleophilic attack on the epoxide reaction center leading to bromohydrin is expected.

~~Other halogen species such as HCl and HI form different derivatization products with EP and can, therefore, be easily distinguished by mass spectrometry. Another aspect to be considered is the speed of the derivatization reaction compared to that of competitive reactions. Estimating the nucleophilic reactivity of different hydrogen halides shows that bromide has higher nucleophilic reactivity than chloride (nucleophilic constants in water based on glycidol, H_2O: 0.00, Cl^-: 3.04, Br^-: 3.89, I^-: 5.04. Accordingly, one could expect a higher reactivity of HBr compared to HCl. Nevertheless, HCl may be present in abundant amounts compared to HBr (0.5-4.5 ppm HCl in alkaline traps taken from Masaya volcano) and thus consume the coating reagent despite the slower reaction rate. Therefore, the collection efficiency for HBr was tested in the presence of about 4 ppm HCl using the sampling arrangement in Fig. 1a. Only 1.9 ± 0.4 % of the bromine product was found in the second~~

~~denuders. Therefore, the method was considered suitable to quantitatively analyse HBr in addition to other volcanic halogen emissions.~~

3.4 Comparison between denuder and Raschig method

~~Since~~Alkaline traps determine the total bromine content, gaseous HBr ~~can~~ is thus measured here ~~also be determined by other methods and~~ as a part of the total bromine ~~concentrations in volcanic studies are usually determined by alkaline traps~~. Speciation of the individual bromine species is not possible with alkaline traps, but if only gaseous HBr is sampled by both methods in the laboratory, denuder method and alkaline traps should produce the same results.~~,~~ Therefore, a comparative measurement of the denuder method with ~~the results of HBr-selective denuders and~~ a Raschig Tube as an alkaline trap was set up to check the accuracy of the newly developed denuder method~~setup for total bromine determination using an artificial bromine source were compared~~. The experimental setup is shown in Fig. 1b. In five experimental series, HBr concentrations between 3 and 20 ppb were determined simultaneously (Table 3)~~with both methods~~. A Dean-Dixon outlier test was applied in order to evaluate possible outliers (Dixon, 1950). No outlier was identified for α=0.05 (If the significance level was changed to α=0.01, experiment 4 could be considered an outlier.). Consequently, all the results were taken into account.

On average, the results ~~of the determinations with~~ related to denuder sampling ~~alkaline traps~~ yielded 99~~102~~ ± 11 % of the HBr values determined by the Raschig Tube~~denuder sampling (Fig. 3)~~. An orthogonal distance regression was performed and is shown in Fig. 4. Based on the line equation obtained, small values, such as those observed here in the field samples, can yield higher results from denuder determinations than expected via the Raschig Tube. We have concluded, that ~~Since the agreement of the values obtained by both methods is good,~~ the HBr values determined by denuders in ~~volcanic plume~~field samples can be considered a fraction of the total bromine determined ~~with~~ by the Raschig Tubes. To account for the comparison studied, the deviation found is included as an error of the denuder field samples in Table 4.

Table 3: Comparison of simultaneously test gas sampling of EP coated denuders and Raschig Tubes for gaseous HBr determination. The setup is shown in Fig. 1b.

Experiment	Denuder		Raschig	
	Sampled amount of HBr [nmol]	Calculated HBr in sampled test gas [ppb]	Sampled amount of HBr [nmol]	Calculated HBr in sampled test gas [ppb]
1	1.8 ± 0.6	3.6 ± 1.6	26.0 ± 3.6	4.1 ± 0.6
2	2.3 ± 0.7	5.8 ± 2.2	28.1 ± 3.9	5.1 ± 0.7
3	3.0 ± 0.4	7.7 ± 1.2	41.6 ± 5.3	7.4 ± 1.0
4	4.8 ± 0.7	14.4 ± 2.3	83.0 ± 11.7	16.8 ± 2.4
5	7.6 ± 0.7	18.5 ± 1.8	111.7 ± 14.7	17.9 ± 2.4

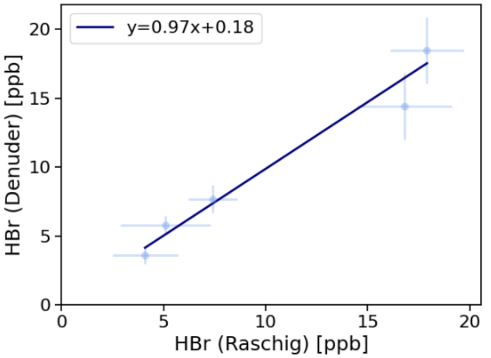
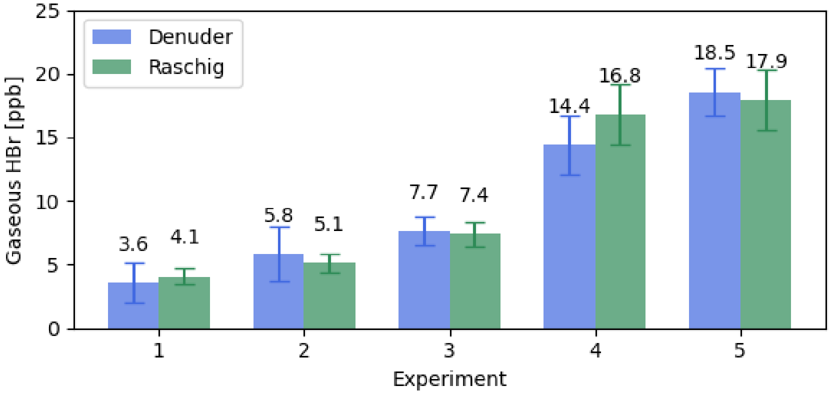


Figure 4: Denuder results are plotted against Raschig results. The orthogonal distance regression model resulted in: y = 0.97 (± 0.10) * x + 0.18 (± 0.10) and a residual variance of 0.25.



~~**Figure 3: Comparison of simultaneously applied EP coated denuders and Raschig Tubes for gaseous HBr determination.**~~

3.5 Field application at Masaya 2016

Here we present a first set of field samples using the new denuder method. The eight sets of~~In~~ ground-based ~~samples~~measurements ~~, gaseous HBr concentrations were detected in the~~ range ~~of~~ from 0.44 to 1.97 ppb (Table 4). ~~Unfortunately, the t~~ Two UAV-based ~~samples~~ measurements ~~were~~ are below their LOD. In UAV-based samples, t~~T~~he higher LOD in UAV-based measurements ~~is due to~~result from a much shorter sampling time of 5-10 minutes (limited by maximum possible flight time) compared to ground-based measurements (1-1.5 h). ~~LOD and LOQ were calculated based on the signal-to-noise approach using 3- and 10-times the standard deviation of the blank samples (n=4).~~ ~~Table 2 assigns the samples according to their sampling location and gives an overview of the calculated LOD and LOQ.~~

To get an idea about the reproducibility of these field measurements ~~results was tested with two~~ a duplicate set~~s~~ of two EP-coated denuders each~~, which were sampled simultaneously~~ was collected in parallel side by side on July 21 ~~(2x2~~. ~~denuders at the Santiago rim and 2x2 denuders at the Nindiri rim). At the Santiago rim, t~~The parallel denuder measurements resulted in HBr concentrations of 1.97 ± 0.11 and 1.82 ± 0.10 ppb at the Santiago rim ~~,~~and ~~at the Nindiri rim~~ 1.17 ± 0.07 and 0.97 ± 0.09 ppb at the ~~. This results in a deviation of 0.09 ± 0.01 ppb for denuders sampling the same plume. Table 2 lists the mean values of 1.90 ± 0.15 and 1.07 ± 0.11 ppb for the Santiago crater and the~~ Nindiri rim~~, respectively~~. The mean values and standard deviations of 1.90 ± 0.11 and 1.07 ± 0.14 ppb of the two parallel samples result in a relative standard deviation of 6 and 13 %, respectively. While the deviation from the Santiago rim samples is within those also found for laboratory samples (8 %), possible causes leading to larger errors and affecting simultaneously collected samples differently may be passive diffusion during installation of the tubes or ash blowing in.

Based on the changes in t~~T~~he HBr concentrations ~~show a decrease in concentration with increasing~~at different ~~-~~distance from the emission source, we can observe a decrease in HBr concentrations with increasing distance.~~,~~ A cause for the decreasing concentrations can be, of course, a dilution of the plume.~~ which is caused by dilution and conversion effects.~~ To compensate for this effect in our observations, we look at the ratio ~~A comparison~~ of the HBr ~~concentrations with the simultaneously determined~~ to the total bromine detected by the Raschig Tube. ~~concentrations (Table 2)~~Since both methods collected their samples side by side at the same time, we assume that a ~~for ground-based sampling sets allows the differentiation of~~ dilution of the plume effects ~~and the influence of conversion reactions on the measured concentrations~~equally both samples. The relevant Raschig Tube results for the total bromine from Rüdiger et al. (2021) are summarized in Table 4. We have also adopted the~~At an~~ estimated wind speed of 5 m/s.

Thus, we observed HBr fractions of 60 to 89 % of total bromine at Santiago Rim and 30 to 46% at Nindiri Rim. This results in an average~~the proportion~~ of 75 ± 11 % HBr of the total bromine at a plume age of 0.7 min (214 m at the Santiago crater) decreases on average to 36 ± 8 % at 2.5 min (740 m at the Nindiri rim) further downwind (Fig. 5).

In the work of Rüdiger et al. (2021) the results of ~~The~~ total bromine, total reactive bromine and bromine monoxide from accompanying methods ~~BrO data from this campaign~~ were used to run the atmospheric box model CAABA/MECCA, which was initialized by a high-temperature equilibrium model~~ in Rüdiger et al. (2021)This model predicted for a~~. The model run that best described the data in Rüdiger et al. (2021) was used here for comparison and is highlighted in light blue for the ratio of HBr/total Br in Fig. 5. This run was based on a Br/S ratio of 7.4 x10^{-4}. The Br/S ratio for the measurements considered here on 18.-21.7. was on averaged 6.2 ± 1.0 x10^{-4}.~~ (for detailed parameterization see Rüdiger et al. 2020).~~ Even though the general trend between measured values and model predictions is consistent, on average the measured values appear to be slightly higher than those calculated by this model run. Following the observations in Rüdiger et al. (2021), a cause may be the influence of aerosol. Aerosol was not measured simultaneously, smaller particle number concentrations and diameters than assumed may lead to slower HBr loss than expected. Also, deviation from the assumed wind speed can lead to a horizontal shift of the measurements while the deviations between Denuder and Raschig method cause a vertical shift. Overall, the trend observed would have to be confirmed by further samples. These samples give us a first idea that we can confirm our general idea about the HBr consumption. Of course, a solid foundation will require many field samples and further consideration of the two methods used and their joint application at the expected concentrations.

Table 4: Results of denuder measurements sampled in Masaya's plume on three days in July 2016. Sampling has been performed at three different locations with the following distances to the emission source: Santiago Rim 215 ± 50 m, Nindiri Rim 740 ± 50 m and in the Caldera Valley 2000 ± 150 m (Fig. 3b). Total Bromine has been determined by simultaneously applied Raschig Tubes (details in Rüdiger et al. 2021). ~~–~~HBr concentrations (in ppb)~~,~~ were determined by EP-coated denuders. ~~, and t~~Their respective ~~limits of detection (~~LOD~~)~~ and ~~quantification (~~LOQ~~)~~. ~~LOD and LOQ~~ were calculated based on the signal-to-noise approach using 3- and 10-times the standard deviation of the blank samples (n=3). ~~–~~ The Raschig bias is the calculated differences obtained from the line equation of the orthogonal distance regression. The determined amount of HBr (in nmol) is given for comparison with lab experiments.~~Values colored in red are below detection limits. Samples were taken at various distances to Masaya's emission source.~~

Date	Total Br* [ppb]	HBr [ppb]	LOD [ppb]	LOQ [ppb]	Raschig bias [ppb]	HBr on denuder [nmol]	HBr/ total Br [%]	Comment
18.07.2016								
Santiago Rim	1.85 ± 0.04	1.65 ± 0.05	0.04	0.12	- 0.13	1.42 ± 0.04	89	
Nindiri Rim	1.31 ± 0.03	0.44 ± 0.03	0.02	0.06	- 0.17	0.38 ± 0.02	34	
20.07.2016								
Santiago Rim	1.55 ± 0.03	1.14 ± 0.05	0.07	0.24	- 0.15	0.92 ± 0.04	74	
Nindiri Rim	1.22 ± 0.03	0.55 ± 0.05	0.09	0.29	- 0.17	0.45 ± 0.04	45	
Caldera Valley	Not available	<LOD <LOD	1.39 1.46	3.99 3.81		0.03 ± 0.01 0.02 ± 0.01		UAV-based sampling
21.07.2016								
Santiago Rim	3.05 ± 0.05	1.97 ± 0.11	0.08	0.27	- 0.12	1.53 ± 0.09	65	Simultaneous
		1.82 ± 0.10	0.06	0.26	- 0.13	1.42 ± 0.08	60	
Nindiri Rim	1.81 ± 0.04	0.55 ± 0.05	0.05	0.15	- 0.17	0.58 ± 0.05	30	
	2.56 ± 0.06	1.17 ± 0.07	0.07	0.23	- 0.15	0.91 ± 0.05	46	Simultaneous
		0.97 ± 0.09	0.09	0.30	- 0.16	0.75 ± 0.07	38	

* Total Bromine determined by Raschig Tube samples adopted from Rüdiger et al. (2021)

~~Distance [m]~~	~~214 ± 50 (Santiago rim)~~			~~740 ± 50 (Nindiri rim)~~			~~2000 ± 150 (Caldera Valley)~~			~~214 ± 50~~
~~Date~~	~~[ppb]~~	~~LOD~~	~~LOQ~~	~~[ppb]~~	~~LOD~~	~~LOQ~~	~~[ppb]~~	~~LOD~~	~~LOQ~~	~~Br/S* x10^{-4}~~
~~18.07.2016~~	~~1.65 ± 0.05~~	~~0.04~~	~~0.12~~	~~0.44 ± 0.03~~	~~0.02~~	~~0.06~~				~~5.1 ± 0.3~~
~~20.07.2016~~	~~1.14 ± 0.05~~	~~0.07~~	~~0.22~~	~~0.55 ± 0.05~~	~~0.09~~	~~0.15~~	~~0.57 ± 0.14~~ ~~0.37 ± 0.13~~	~~1.39~~ ~~1.46~~	~~3.99~~ ~~3.81~~	~~5.9 ± 0.3~~

~~21.07.2016~~	~~1.90 ± 0.15~~	~~0.08~~	~~0.27~~	~~1.07 ± 0.11~~	~~0.07~~	~~0.23~~		~~7.5 ± 0.4~~
				~~0.55 ± 0.05~~	~~0.05~~	~~0.15~~		

~~* Total Bromine to total sulfur ratio determined by Raschig Tube samples~~

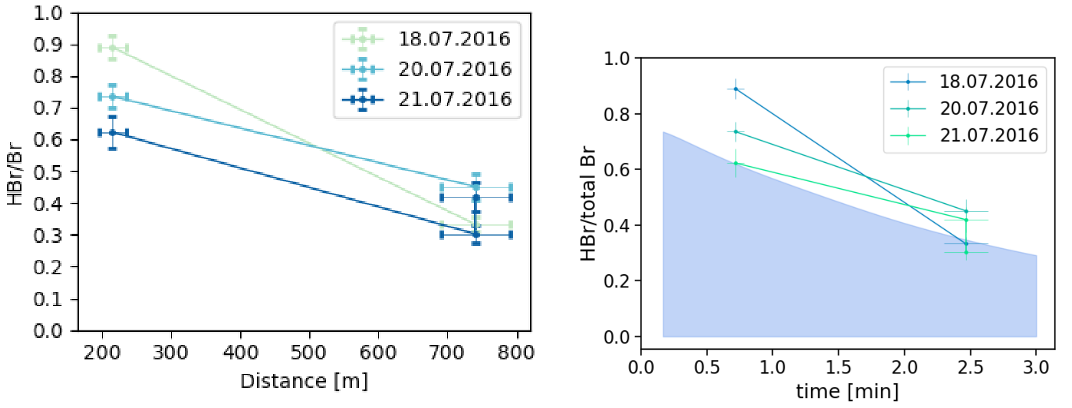


Figure 5: Fraction of HBr (determined by EP-coated denuders) ~~of~~ to total bromine (determined by Raschig Tubes). Assuming a windspeed of 5 m/s, ~~On average,~~ HBr fractions decrease~~d~~ on average from 0.75 ± 0.11 at 0.7 min ~~214 m distance~~ at Santiago Rim ~~from the Masaya emission source~~ to 0.36 ± 0.08 at 2.5 min ~~740 m distance~~ on Nindiri Rim. The colored area in light blue describes the fraction of HBr calculated by the model of Rüdiger et al. (2021) (model parameter to identify the selected run: An initial ratio of 10:90 of atmospheric and magmatic gas was assumed at high temperatures. The output was then quenched to 30 ppm SO_2 for the start of the low temperature chemistry. The proportions of hydroxyl radicals (OH), hydrogen peroxide (H_2O_2) and hydroperoxyl radicals (HO_2) and nitric oxide radicals (NOx) correspond to the atmospheric background composition. Within 10 minutes, dilution by a factor of 1/e (0.37) occurred. The number of particles per m^3 was 3 x10^9, their radius 300 nm.)

4 Conclusion

Our goal is to be able to make a statement about the inner life of the volcano by monitoring the volcanic gases. Bromine has shown to be a potentially suitable candidate and has been correlated with changes in the activity of a volcano. Particularly attractive is the monitoring of BrO, which can be detected with remote sensing techniques. However, in order to draw conclusions about the volcanic activity by observing the volcanic bromine outgassing, we need to understand what happens to the bromine speciation after they are released in the atmosphere.

In order to get closer to this goal, a measurement method was drafted, which is able to make a certain bromine species measurable: ~~The presented study describes a new method for the quantitative determination of gaseous hydrogen halides based on gas~~ The diffusion denuder~~s~~-based method uses an internal coating that can chemically derivatize a certain species.

~~The hydrogen halides reacted during sampling with~~ To make the method applicable to HBr, different coatings were tested. The coatings were based on the reactivity of appropriate epoxides towards HBr and the immobilization of HBr ~~applied to~~ on the denuder walls by formation of a bromohydrin. After ~~elution~~ extraction and enrichment steps in the laboratory, this *in situ* derivatization allows the separation and detection of ~~the acids~~derivate by means of high-performance liquid chromatography-mass spectrometry. ~~Motivated by the special interest in bromine chemistry in volcanic plumes, the method was optimized for sampling and detection of HBr.~~

~~In laboratory studies, the coating process, coating quantity, breakthrough behavior and storage behavior of EP-coated denuders were characterized. The coating proved~~EP was shown to be the most promising~~suitable~~ substance for the determination of the expected HBr concentrations under ground-based sampling conditions~~ in the presence of other volcanic gases such as HCl~~. The collection efficiency of a denuder coated with 45 µmol EP was 99.5 ± 0.4 % for 0.2 µmol HBr. Also, besides 5 µmol HCl, 0.2 µmol HBr could be retained to 98.1 ± 0.4 %. The relative standard deviation of comparable samples was 8 %.

A parallel sampling of the~~laboratory comparison using HBr test gas sources with EP-coated~~ denuder~~s~~ method and Raschig Tubes revealed the comparability of both methods~~s showed a deviation of 2 ± 11 % between the two methods~~. For the prediction of the denuder values from the Raschig results the linear relationship with a slope of 0.97 (± 0.10) and an intercept of 0.18 (± 0.10) with a residual covariance of 0.25 was found. From this we concluded that we can consider measured HBr from denuders as a fraction of the total bromine given from Raschig Tubes. ~~Since alkaline trap sampling (Raschig Tubes) is often used in volcanic studies to determine total bromine concentrations, this method was used here as a complementary method. Analytically interesting is the parallel use of both methods in the field since by comparing the results between selective and non-selective sampling, information about the bromine species can be obtained. This is particularly interesting for a better understanding of bromine activation in volcanic plumes in connection with the development of warning systems for volcanic activity.~~

The denuder sampling assembly was deployed in the volcanic plume of Masaya, Nicaragua, in July 2016. Samples were collected at the Santiago crater rim and on the Nindiri rim. Gaseous HBr in the concentration range of 0.44-1.97 ppb was detected with detection and quantification limits below 0.1 and 0.3 ppb, respectively, under typical ground-based sampling conditions. ~~In the first tests of UAV-based sampling, the results were below the detection limit. However, especially the extension of flight time but possibly also an optimization of the method (e.g. reduction of the amount of coating reagent) should also allow UAV-based HBr measurements in the future.~~ HBr contribution to total bromine decreased from an average of 75 ± 11 % at the Santiago rim with an estimated plume age of 0.7 min (214 m distance to the Masaya emission source) to 36 ± 8 % at 2.5 min at the Nindiri rim (740 m distance). ~~In the first tests of~~The UAV-based ~~sampling~~data at advanced plume ages~~, the results~~ were below the detection limit. ~~However, e~~Especially the extension of flight time but possibly also an optimization of the method (e.g. reduction of the amount of coating reagent) ~~should~~may also allow UAV-based HBr measurements in the future.

~~Our results are in very good agreement with the model calculations of this campaign described in Rüdiger et al (2020) (70 to 35 % at about 1 to 3 min).~~ The recently published model by Rüdiger et al. (2021) is based on data collected simultaneously with those shown here. A comparison shows a slightly higher trend for HBr on average than expected from the model.

~~In summary, the study presented here describes a~~ The new method can now contribute to visualize the transformations ~~as a promising approach to allow better speciation~~ of the bromine species in the volcanic plume~~s and thus to gain a better~~

~~understanding of bromine activation~~. The extension of speciation knowledge may allow model runs to be further refined in ~~of bromine chemistry in volcanic plumes will contribute to~~ the future. It would be a great step if we can predict volcanic activity by monitoring volcanic bromine gases. Even better if these observations can be accomplished with ~~use of remote sensing~~ BrO~~-measurement systems as~~ monitoring by remote sensing methods. ~~instruments for volcanic activity.~~

Data Availability. The data used in this study is available on request from Thorsten Hoffmann (t.hoffmann@uni-mainz.de).

Author contribution. AG and TH designed the framework of the study. AG established the new measurement technique and carried out the experiments and data processing. AG and ML performed the analysis of Raschig Tube samples and processed the data. AG and NB collected the data sets on Masaya volcano. AG led the writing of the manuscript and all co-authors participated in investigating and interpreting results and editing the manuscript.

Competing interest. The authors declare that they have no conflict of interest.

Acknowledgements. AG, NB and TH acknowledge support by the research center “Volcanoes and Atmosphere in Magmatic, Open Systems” (VAMOS) at the University of Mainz, Germany and are thankful for the support by INETER (Nicaragua). The authors also thank Julian Rüdiger for his support on the collection of data sets on Masaya volcano.

References

Becker, H. G. O. and Beckert, R.: Organikum: Organisch-chemisches Grundpraktikum, 22., vollst. überarb. und aktualisierte Aufl., Wiley-VCH, Weinheim, 852 pp., 2004.

Brown, H.: Rare gases and formation of the Earth's atmosphere, in: The Atmospheres of the Earth and Planets, edited by: Kuiper, G. P., University of Chicago Press, Chicago, 258–266, 1952.

Daag, A. S.: Monitoring sulfur dioxide emission at Mount Pinatubo, in: Fire and mud: Eruptions and lahars of Mount Pinatubo, Philippines, edited by: Newhall, C. G., Philippine Inst. of Volcanology and Seismology, Quezon City, 409–414, 1996.

DIN 32645:2008-11.: Chemische Analytik_- Nachweis-, Erfassungs- und Bestimmungsgrenze unter Wiederholbedingungen - Begriffe, Verfahren, Auswertung, Beuth Verlag GmbH, Berlin, https://doi.org/10.31030/1465413.

Dixon, W. J.: Analysis of Extreme Values, aoms, 21, 488–506, https://doi.org/10.1214/aoms/1177729747, available at: https://projecteuclid.org/journals/annals-of-mathematical-statistics/volume-21/issue-4/Analysis-of-Extreme-Values/10.1214/aoms/1177729747.full, 1950.

Fick, A.: Ueber Diffusion, Ann. Phys. Chem., 170, 59–86, https://doi.org/10.1002/andp.18551700105, 1855.

Finn, D., Rumburg, B., Claiborn, C., Bamesberger, L., Siems, W. F., Koenig, J., Larson, T., and Norris, G.: Sampling artifacts from the use of denuder tubes with glycerol based coatings in the measurement of atmospheric particulate matter, Environmental science & technology, 35, 40–44, https://doi.org/10.1021/es001325i, 2001.

Gerlach, T. M.: Volcanic sources of tropospheric ozone-depleting trace gases, Geochem. Geophys. Geosyst., 5, n/a-n/a, https://doi.org/10.1029/2004GC000747, 2004.

Gormely, P.G. and Kennedy, M.: Diffusion from a Stream Flowing through a Cylindrical Tube, in: Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences, edited by: JSTOR, 163–169, 1948.

Gutmann, A., Bobrowski, N., Roberts, T. J., Rüdiger, J., and Hoffmann, T.: Advances in Bromine Speciation in Volcanic Plumes, Front. Earth Sci., 6, https://doi.org/10.3389/feart.2018.00213, 2018.

Haase, R., Naas, H., and Thumm, H.: Experimentelle Untersuchungen über das thermodynamische Verhalten konzentrierter Halogenwasserstoffsäuren, Zeitschrift für Physikalische Chemie, 37, 210–229, https://doi.org/10.1524/zpch.1963.37.3_4.210, 1963.

Halmer, M. M., Schmincke, H.-U., and Graf, H.-F.: The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years, Journal of Volcanology and Geothermal Research, 115, 511–528, https://doi.org/10.1016/S0377-0273(01)00318-3, 2002.

Hanson, D. R. and Ravishankara, A. R.: Heterogeneous chemistry of hydrogen bromide and hydrogen fluoride, J. Phys. Chem., 96, 9441–9446, https://doi.org/10.1021/j100202a069, 1992.

Harlow, D. H., Power, J. A., Laguerta, E. P., Ambubuyog, G., White, R. A., and Hoblitt, R. P.: Precursory seismicity and forecasting of the June 15, 1991, eruption of Mount Pinatubo, in: Fire and mud: Eruptions and lahars of Mount Pinatubo, Philippines, edited by: Newhall, C. G., Philippine Inst. of Volcanology and Seismology, Quezon City, 223–247, 1996.

Hörmann, C., Sihler, H., Bobrowski, N., Beirle, S., Penning de Vries, M., Platt, U., and Wagner, T.: Systematic investigation of bromine monoxide in volcanic plumes from space by using the GOME-2 instrument, Atmos. Chem. Phys., 13, 4749–4781, https://doi.org/10.5194/acp-13-4749-2013, 2013.

Huang, R.-J. and Hoffmann, T.: Development of a coupled diffusion denuder system combined with gas chromatography/mass spectrometry for the separation and quantification of molecular iodine and the activated iodine compounds iodine monochloride and hypoiodous acid in the marine atmosphere, Analytical chemistry, 81, 1777–1783, https://doi.org/10.1021/ac801839v, 2009.

Huang, R.-J. and Hoffmann, T.: A denuder-impinger system with in situ derivatization followed by gas chromatography-mass spectrometry for the determination of gaseous iodine-containing halogen species, Journal of chromatography. A, 1210, 135–141, https://doi.org/10.1016/j.chroma.2008.08.003, 2008.

Kloskowski, A., Pilarczyk, M., and Namieśnik, J.: Denudation — A Convenient Method of Isolation and Enrichment of Analytes, Critical Reviews in Analytical Chemistry, 32, 301–335, https://doi.org/10.1080/10408340290765588, 2002.

Kromidas, S., Klinkner, R., and Mertens, R.: Methodenvalidierung im analytischen Labor, Nachr. Chem. Tech. Lab., 43, 669–676, https://doi.org/10.1002/nadc.19950430609, 1995.

Lübcke, P., Bobrowski, N., Arellano, S., Galle, B., Garzón, G., Vogel, L., and Platt, U.: BrO/SO_2 molar ratios from scanning DOAS measurements in the NOVAC network, Solid Earth, 5, 409–424, https://doi.org/10.5194/se-5-409-2014, 2014.

Neuman, J. A., Huey, L. G., Ryerson, T. B., and Fahey, D. W.: Study of Inlet Materials for Sampling Atmospheric Nitric Acid, Environ. Sci. Technol., 33, 1133–1136, https://doi.org/10.1021/es980767f, 1999.

Noguchi, K. and Kamiya, H.: Prediction of volcanic eruption by measuring the chemical composition and amounts of gases, Bull Volcanol, 26, 367–378, https://doi.org/10.1007/BF02597298, 1963.

Rüdiger, J., Gutmann, A., Bobrowski, N., Liotta, M., Moor, J. M. de, Sander, R., Dinger, F., Tirpitz, J.-L., Ibarra, M., Saballos, A., Martínez, M., Mendoza, E., Ferrufino, A., Stix, J., Valdés, J., Castro, J. M., and Hoffmann, T.: Halogen activation in the plume of Masaya volcano: field observations and box model investigations, Atmos. Chem. Phys., 21, 3371–3393, https://doi.org/10.5194/acp-21-3371-2021, 2021.

Rüdiger, J., Tirpitz, J.-L., Moor, J. M. de, Bobrowski, N., Gutmann, A., Liuzzo, M., Ibarra, M., and Hoffmann, T.: Implementation of electrochemical, optical and denuder-based sensors and sampling techniques on UAV for volcanic gas measurements: examples from Masaya, Turrialba and Stromboli volcanoes, Atmos. Meas. Tech., 11, 2441–2457, https://doi.org/10.5194/amt-11-2441-2018, 2018.

Rüdiger, J., Bobrowski, N., Liotta, M., and Hoffmann, T.: Development and application of a sampling method for the determination of reactive halogen species in volcanic gas emissions, Analytical and bioanalytical chemistry, 409, 5975–5985, https://doi.org/10.1007/s00216-017-0525-1, 2017.

Saturno, J., Ditas, F., Penning de Vries, M., Holanda, B. A., Pöhlker, M. L., Carbone, S., Walter, D., Bobrowski, N., Brito, J., Chi, X., Gutmann, A., Hrabe de Angelis, I., Machado, L. A. T., Moran-Zuloaga, D., Rüdiger, J., Schneider, J., Schulz, C., Wang, Q., Wendisch, M., Artaxo, P., Wagner, T., Pöschl, U., Andreae, M. O., and Pöhlker, C.: African volcanic emissions influencing atmospheric aerosols over the Amazon rain forest, Atmos. Chem. Phys., 18, 10391–10405, https://doi.org/10.5194/acp-18-10391-2018, 2018.

Schmincke, H.-U.: Transfer von festen, flüssigen und gasförmigen Stoffen aus Vulkanen in die Atmosphäre, UWSF - Z Umweltchem Ökotox, 5, 27–44, https://doi.org/10.1007/BF02945888, 1993.

Shaw, G. H.: Earth's atmosphere – Hadean to early Proterozoic, Geochemistry, 68, 235–264, https://doi.org/10.1016/j.chemer.2008.05.001, 2008.

Swain, C. G. and Scott, C. B.: Quantitative Correlation of Relative Rates. Comparison of Hydroxide Ion with Other Nucleophilic Reagents toward Alkyl Halides, Esters, Epoxides and Acyl Halides 1, J. Am. Chem. Soc., 75, 141–147, https://doi.org/10.1021/ja01097a041, 1953.

Talukdar, R. K., Warren, R. F., Vaghijiani, G. L., and Ravishankara, A. R.: Kinetics of the reaction of H(2S) with HBr, Int. J. Chem. Kinet., 24, 973–982, https://doi.org/10.1002/kin.550241107, 1992.

Tang, M. J., Cox, R. A., and Kalberer, M.: Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds, Atmos. Chem. Phys., 14, 9233–9247, https://doi.org/10.5194/acp-14-9233-2014, 2014.

Textor, C., Graf, H.-F., Timmreck, C., and Robock, A.: Emissions from volcanoes, in: Emissions of Atmospheric Trace Compounds, edited by: Granier, C., Artaxo, P., and Reeves, C. E., Springer, Dordrecht, 269–303, https://doi.org/10.1007/978-1-4020-2167-1_7, 2004.

Townsend, J. S. E.: IV. The diffusion of ions into gases, Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character, 193, 129–158, https://doi.org/10.1098/rsta.1900.0004, 1900.

Wittmer, J., Bobrowski, N., Liotta, M., Giuffrida, G., Calabrese, S., and Platt, U.: Active alkaline traps to determine acidic-gas ratios in volcanic plumes: Sampling techniques and analytical methods, Geochem. Geophys. Geosyst., 15, 2797–2820, https://doi.org/10.1002/2013GC005133, 2014.

Supplement of "Bromine Speciation in Volcanic Plumes: New in-situ Method for the Determination of Gaseous Hydrogen Bromide by Gas Diffusion Denuder Sampling"

Alexandra Gutmann[1], Nicole Bobrowski[2,3], Marcello Liotta[4], Thorsten Hoffmann[1]

[1]Department Chemie, Johannes Gutenberg-University, Mainz, Germany
[2]Institute for Environmental Physics, University of Heidelberg, Heidelberg, Germany
[3]Max-Planck Institute for Chemistry, Mainz, Germany
[3]Instituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Italy

Correspondence to: Alexandra Gutmann (alexandragutmann@web.de), Thorsten Hoffmann (t.hoffmann@uni-mainz.de)

1 Reagents and material

1.1 Chemicals

5,6-Epoxy-5,6-dihydro-[1,10]-phenanthroline (EP), *trans*-cinnamic acid and 2,4,5-tribromanisol were purchased from Aldrich (Steinheim, Germany). Neocuproine (NC), *trans*-oxirane-2,3-dicarbon acid and pyridine were purchased from Sigma-Aldrich (Steinheim, Germany). Oleic acid, (-)-α-pinene and ethylenediaminetetraacetic acid disodium salt were purchased from Fluka (Steinheim, Germany). 1,2-Epoxycyclooctane, sodium hydrogen carbonate and silica gel 60 (F254) were purchased at Merck. 2,4,6-Tribromanilin (98% purity), sodium carbonate and poshphorpentoxide were obtained from Acros Organics (Geel, Belgium). Hydrobromic acid (48%) and *cis*-stilbene were purchased from Alfa Aesar (Karlsruhe, Germany). *Trans*-stilbene was obtained from TCI. All other chemicals were of analytical reagent grade. Deionized water (18 MΩ cm) was used for aqueous solutions.

1.2 Preparation of standards

2-bromocyclooctanol, 2,3-epoxy-3-phenylpropanoic acid, 9,10-epoxystearic acid, 10-bromo-9-hydroxystearic acid and 5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr) were not commercially available and have been synthesized.

1.2.1 2-Bromocyclooctanol

The synthesis followed Haufe et al. (1977). 20 mmol 1,2-epoxycyclooctane were solved in 5 mL chloroform. While vigorous stirring 10 mL hydrobromic acid (48%) were added. After 30 min stirring the organic phase was separated and washed with water, saturated $NaHCO_3$-solution and again water. A yield of 85-90% of an oily colourless liquid was obtained.

1.2.2 3-Phenyloxirane-2-carboxylic acid

Following the synthesis of Corey and Ward (1986) and Shee et al. (2019) to 0.75 mmol trans-cinnamic acid in 500 µL acetone 3.3 mmol $NaHCO_3$ in 500 µL in water was added dropwise. A solution of Oxone (1.4 mmol, 1.8 euiv. $KHSO_3$) in 1.6 mL 0.4 mM ethylenediaminetetraacetic acid disodium salt was added dropwise over an hour while the temperature was kept approximately at. 25 °C and pH 7.5. After another hour of stirring the mixture was cooled to 0 °C and acidified with 12 M HCl to pH 2. After adding 5 mL ethyl acetate with rapid stirring the mixture was filtered and extracted with 3 times 50 mL ethyl acetate. The combined organic fractions were washed with NaCl and dried over $MgSO_4$, filtered and dried under vacuum. 1 mL ethanol was added to the resulting oil and cooled in ice. After adding 3.6 mmol KOH in another 1 mL ethanol the mixture was filtered, washed with ethanol and dried under vacuum. Approximately 75 % of the total yield of the potassium salt was obtained. The crude product was used as a coating material.fi

1.2.3 9,10-Epoxystearic acid

The synthesis of 9,10-epoxystearic acid followed Findley et al. (1945) with optimization of Milchert and Smagowicz (2009) and Milchert et al. (2010). 0.22 g acetic acid and 0.07 g sulfuric acid were added to 3.00 g oleic acid. While stirring for 15 min the solution was heated to 40 °C in a water bath. 1.08 g H_2O_2 were added with continued stirring to the black solution. The solution turned colourless. After 4 hours stirring the phases were separated and 5 mL water was added to the organic phase and stored at 4 °C for 15 min. The colourless precipitation was filtered. And washed with water until the filtrate was pH 7.

6 mL hexane and 2 mL cyclohexane were added to 3.0 g raw product and heated to 50 °C. The product separated as a liquid phase underneath the solvents. After 16 h at 4 °C, colourless precipitation was obtained, filtered and dried. Pure products were isolated by SiO_2 column chromatography with 1:1 of hexane and ethyl acetate as a mobile phase.

1.07-2.11 g product was obtained (37.5-73.9% yield).

1.2.4 10-Bromo-9-hydroxystearic acid

10-Bromo-9-hydroxystearic acid was synthesized following King (1949). 3.0 g diethyl ether and 3.0 mL hydrobromic acid (48%) were added to 0.3 g of 9,10-epoxystearic acid. After stirring for 1 h the organic phase was washed with conc. sodium carbonate and water. The dried product resulted in 81 % yield. SiO_2 column chromatography with 1:1 of hexane and ethyl acetate as a mobile phase resulted in 70 % purity for 10-Bromo-9-hydoxystearic acid (GC/MS determinations).

1.2.5 5-Bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (EPBr)

A solution of 1 mmol EP in 1 mL 48% aqueous HBr was stirred for 1 hour at room temperature. When neutralizing the solution with 8 mL aqueous saturated $NaHCO_3$-solution the EPBr precipitated. The colourless solid has been extracted, washed twice with 2 mL saturated $NaHCO_3$-solution and three times with 3 mL water. The product has been dried under vacuum at room temperature resulting in 72% of the theoretical yield. This is a revised prescription of the principal reported in Chini et al. (1992) and Haufe et al. (1977). Synthesis of EPBr after Porter et al. (1995) did not succeed.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.83 – 8.64 (m, 2H), 8.04 (dd, *J*=7.8, 1.7, 1H), 7.95 (dd, *J*=7.7, 1.7, 1H), 7.58 – 7.42 (m, 2H), 6.20 (d, *J*=4.9, 1H), 5.64 (d, *J*=2.8, 1H), 5.05 – 4.99 (m, 1H). The spectrum is shown in Fig. S1.

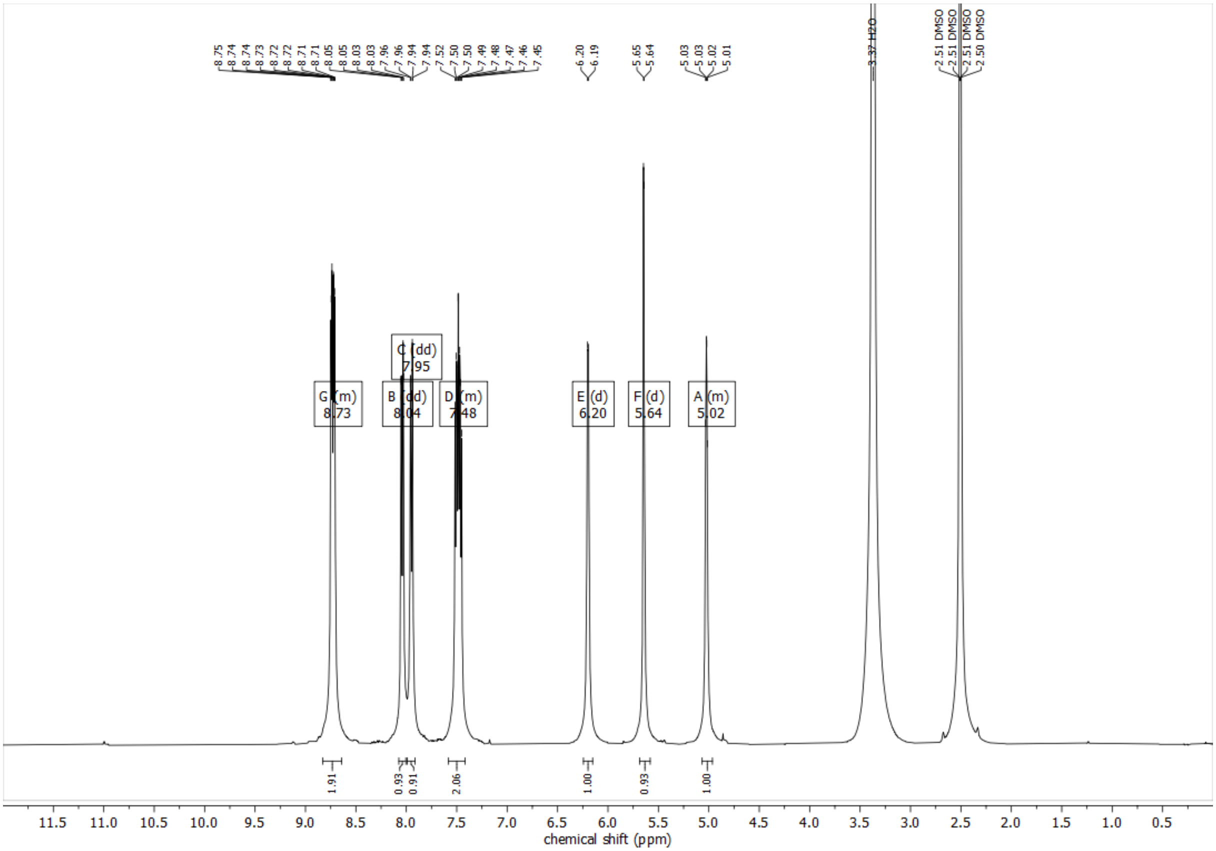


Figure S1~~1~~: H-NMR for 5-bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline

2 Methods

2.1 Testgas sources

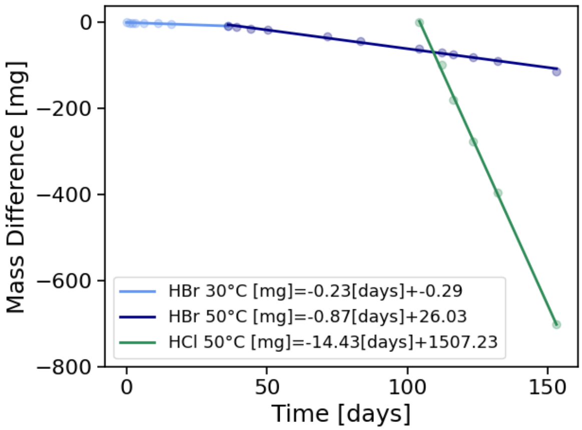


Figure S2: Output of diffusion gas sources of 48% HBr at 30 °C (light blue), 48% HBr at 50 °C (dark blue) and 30% HCl at 50 °C (green).

2.2 Denuder preparation

A system for the parallel coating of four denuders has been created (Fig. S3). The system can hold four denuders at an angle of 10°. The denuders are not fixed tight so a system of a geared motor (Modelcraft, 12 V, 2.1 A) and toothed belts can rotate the denuders with approximately 87 rounds/min. Each denuder is connected to a N_2-stream of approximately 0.5 L/min. The N_2-Stream is drying the applied solution and prevents leaking of the solution on the lower end of the denuder.

Alternatively, denuder can be coated handheld. The denuder has to be connected to a N2-stream. After the application of solution, the denuder has to be rotated until the solution has dried. Particular attention has to be paid on the angle of the denuder to prevent leaking.

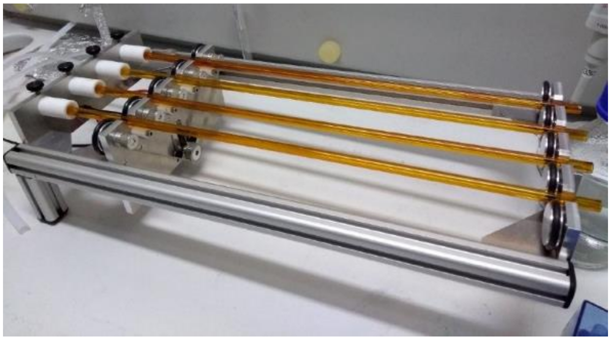


Figure S3: Created system (called “Denudermaster”) for the simultaneous coating of four denuders.

2.3 Gas Chromatography oven temperature programs

Table S 1: GC-temperature programs~~ A, analysis of 1,2-epoxycyclooctane coated denuders~~

Heating rate [°C min^{-1}]	End temperature [°C]	Holding [min]	Duration [min]
Program A, analysis of 1,2-epoxycyclooctane coated denuders			
	90	3.00	3.00
38	210	0.00	6.16
9.5	235	0.00	8.79
30	250	min. 2	min. 11.29
Program B, analysis of 9,10-epoxystearic acid-coated denuders			
	120	0.50	0.50
38	250	0.00	3.92
10	300	0.00	8.92
program C, analysis of trans-oxirane-2,3-dicarboxylic acid and 3-Phenyloxirane-2-carboxylic acid coated denuders.			
	90	3.00	3.00
18	150	3.00	9.33
25	250	17.00	30.33

~~**Table S2: GC-temperature program B, analysis of 9,10-epoxystearic acid-coated denuders**~~

~~Heating rate [°C min-1]~~	~~End temperature [°C]~~	~~Holding [min]~~	~~Duration [min]~~
	~~120~~	~~0.50~~	~~0.50~~
~~38~~	~~250~~	~~0.00~~	~~3.92~~
~~10~~	~~300~~	~~0.00~~	~~8.92~~

~~**Table S3: GC-temperature program C, analysis of trans-oxirane-2,3-dicarboxylic acid and 3-Phenyloxirane-2-carboxylic acid coated denuders.**~~

~~Heating rate [°C min^{-1}]~~	~~End temperature [°C]~~	~~Holding [min]~~	~~Duration [min]~~
	~~90~~	~~3.00~~	~~3.00~~
~~18~~	~~150~~	~~3.00~~	~~9.33~~
~~25~~	~~250~~	~~17.00~~	~~30.33~~

Table S 2: Overview on applied temperature programs, resulting retention times and considered m/z-ratios of analytes obtained by gas chromatography coupled to electron impact ionization and quadrupole mass spectrometry, BSTFA = *N,O*-bis(trimethylsilyl)trifluoroacetamide, TBA = 2,4,6-tribromanisole.

compound	GC-temperature program	Retention Time [min]	m/z used for Quantification	Retention time TBA [min]
1,2-epoxycyclooctane	A	4.93	55	7.57
2-bromocyclooctanol	A	6.41	109	7.57
9,10-epoxystearic acid	B	6.86	75, BSTFA derivatized	4.13
10-bromo-9-hydroxystearic acid	B	8.13	317, BSTFA derivatized	4.13
9,10-dihydroxystearic acid	B	7.43	317, BSTFA derivatized	4.13
trans-oxirane-2,3-dicarboxylic acid	C	9.51	147, BSTFA derivatized	11.82
3-phenyloxirane-2-carboxylic acid	C	7.19	147, BSTFA derivatized	11.82

2.4 Chromatograms and Spectra

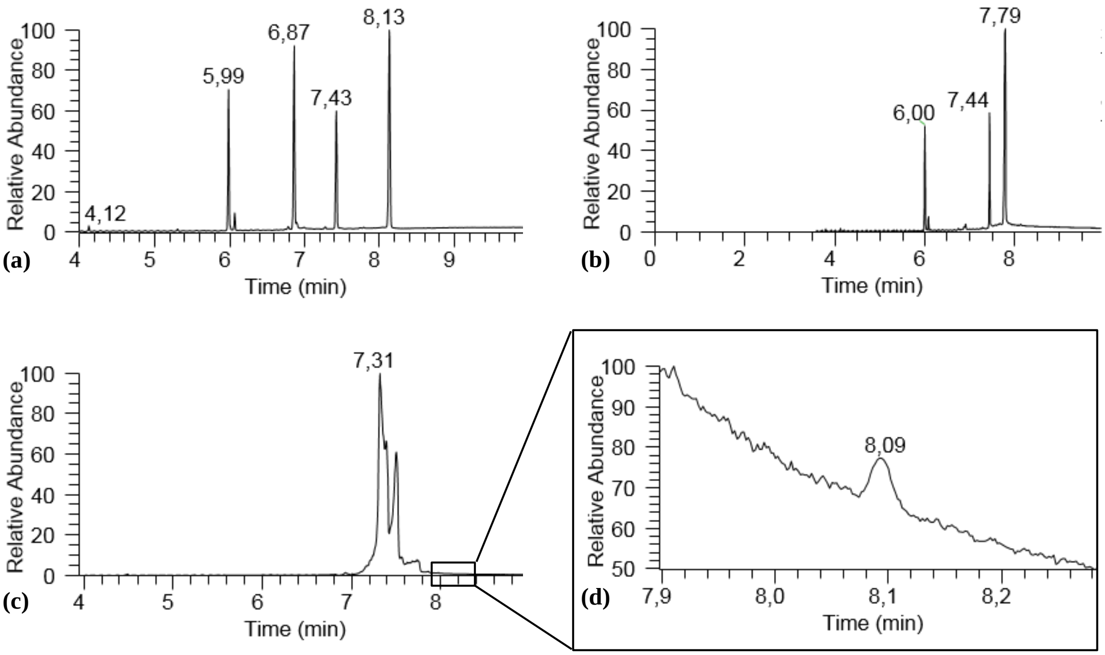


Figure S4: GC-MS Chromatograms following temperature program B describing denuders coated with 9,10-epoxystearic acid. (a) GC-MS chromatogram in full scan showing retention times for oleic acid (5.99 min), 9,10-epoxystearic acid (6.87 min), 9,10-dihydroxystearic acid (7.43 min), and 10-bromo-9-hydroxystearic acid (8.13 min). (b) GC-MS chromatogram in full scan showing retention timed for oleic acid (6.00 min), 9,10-dihydroxystearic acid (7.44 min), and 10-chloro-9-hydroxystearic acid (7.79 min). (c) GC-MS chromatogram with selected ion monitoring (SIM) of m/z 317 of a sample collected with 9,10-epoxystearic acid coated denuder on Mt. Etna in 2015

showing broad peaks between minute 7 and 8 presumably caused by 9,10-dihydroxystearic acid and 10-chloro-9-hydroxystearic acid. Note that the coating 9,10-epoxystearic acid disappeared, presumably has been used up by the reaction with water and HCl. (d) zoom of chromatogram (c) that shows 10-bromo-9-hydroxystearic acid the product of the coating with HBr and the high and variable background. We assume that the shift of retention times to an earlier position is caused by the overload of the analytical column from the coating.

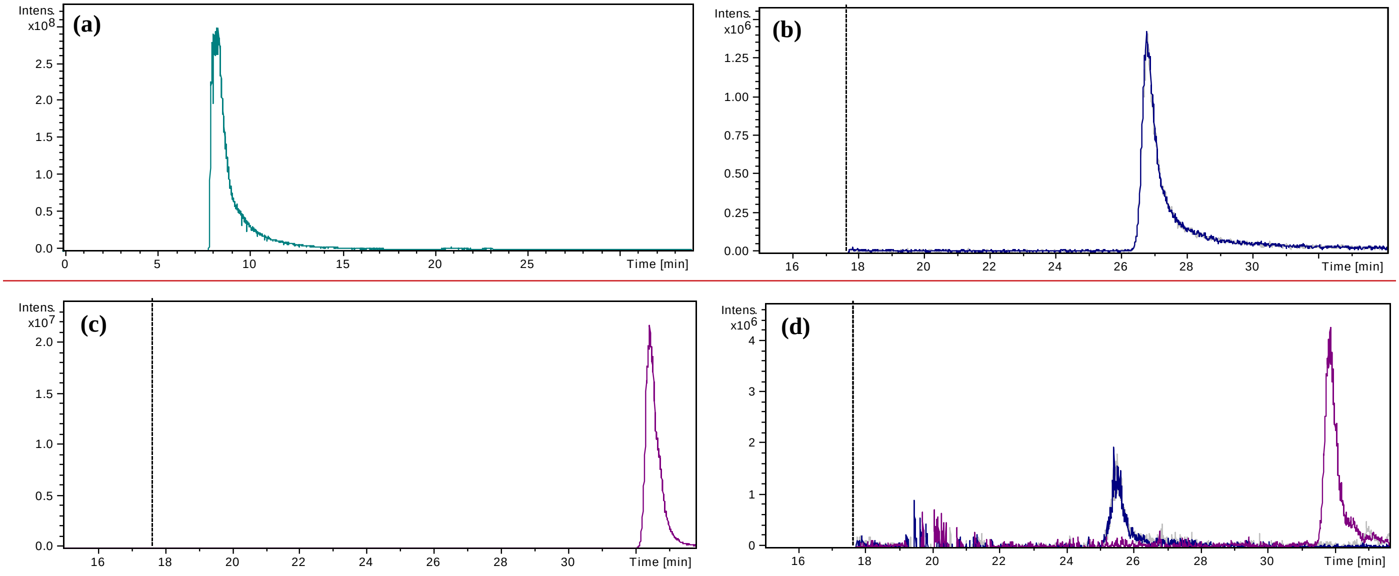


Figure S5: LC-MS Chromatograms describing denuders coated with EP, for details see section 2.3.2 in the main article. (a) Extracted Ion Chromatograms of EP solution in methanol containing 7.5 mmol/L showing the m/z 197 of EP (green) at retention time 8.2 min. Samples extracted from denuders contain about 450 mmol/L. To prevent the MS from an overloading by EP, the output of the LC was led to the MS only after 17.8 min. (b) Extracted Ion Chromatograms of EPBr solution in methanol containing 1.6 mg/L showing the m/z 277 (grey) and 279 (blue) of EPBr at 27.2 min. (c) Extracted Ion Chromatograms of NC solution in methanol containing 5 mg/L showing the m/z 209 of NC (purple) at 32.4 min. (d) Selected Ion Chromatogram (using mass isolation before producing the MS) of front denuder of the field sample taken at Nindiri Rim on 18.07.16 showing EPBr (m/z 277 in grey, 279 in blue) at 25.7 min and NC (m/z 209 in purple) at 31,4 min. We assume that the shift of retention times to an earlier position is caused by the overload of the analytical column from EP-coating.

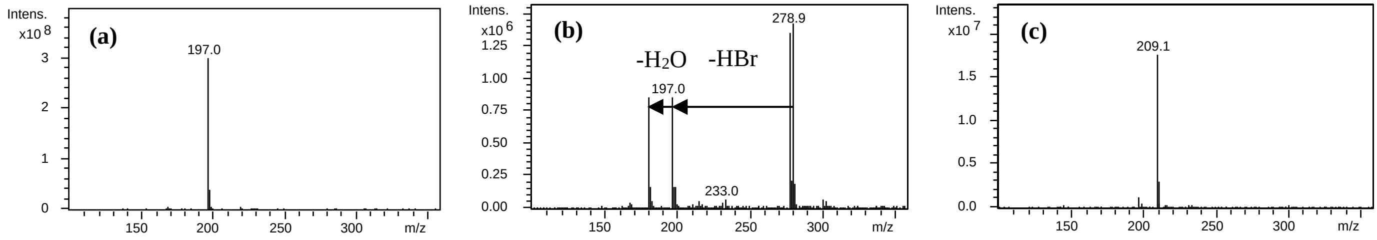


Figure S6: MS spectra, for details the section 2.3.2 of the main article. (a) MS spectrum of EP solution in methanol containing 7.5 mmol/L showing the [m+H]$^+$ m/z 197 of EP at retention time 8.2 min. (b) MS spectrum of EPBr solution in methanol containing 1.6 mg/L showing the [M+H]$^+$ m/z 277 and 279 of EPBr and two fragments of m/z 197 (-HBr) and 181 (-HBr-H_2O) at 27.2 min. (c) MS spectrum of NC solution in methanol containing 5 mg/L showing the [M+H]$^+$ m/z 209 of NC at 32.4 min.

3. Results

3.1 Matrix effects and precision

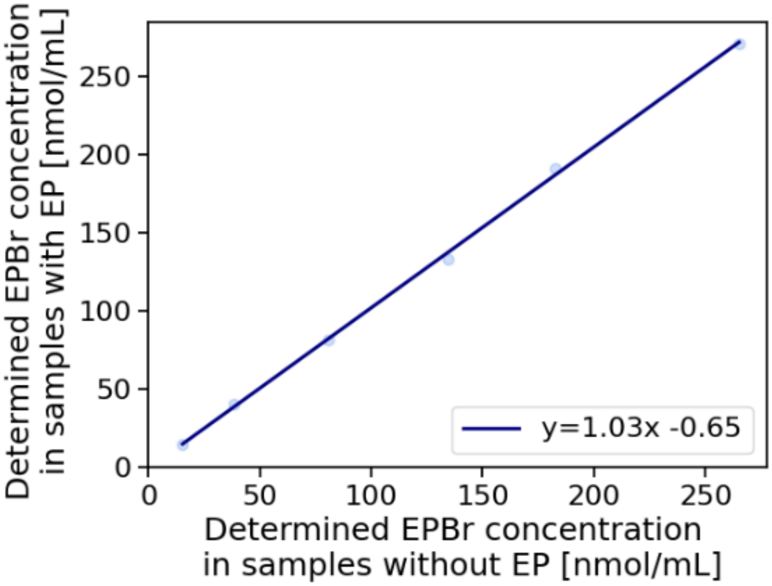


Figure S7: Analysis of matrix effects comparing Samples containing EPBr concentrations with 450 mmol/L EP (+EP) and without EP (-EP) in the sample. The orthogonal distance regression model results in (+EP) = 1.03 x (-EP) – 0.65. The relative bias between the both sample types is 2 ± 3 %.

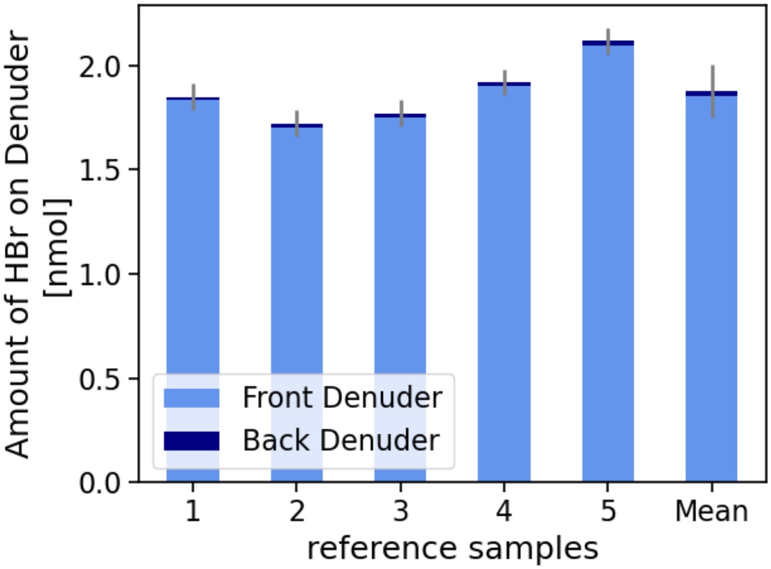


Figure S8: Precision of the method was determined by analysing five times the same test gas denuders coated with 15 mmol/L EP-solution. The experimental setup was performed as described in Fig. 1b. Resulting in a relative standard deviation of 8%.

3.2 Stability of extracted samples

Table S3: Stability of concentrated samples. In Fig. S9 test series 1 are Lab Samples 1-3 and test series 2 are Lab Samples 4-6.

Test series	EP [mmol/L]	EPBr [mmol/L]	EPBr [nmol/sample]	Methanol	Formic Acid	Aliquots
1	450	0.01	1	500 µl	5 µl	3x 100 µl
2	450	0.05	5	500 µl	5 µl	3x 100 µl

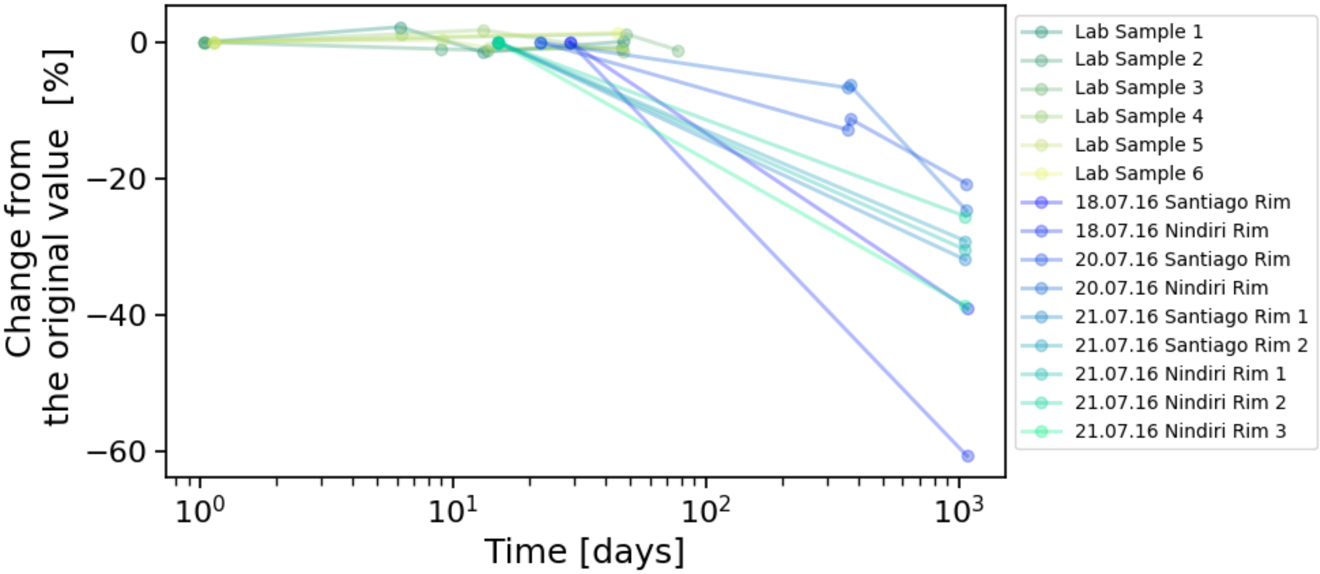


Figure S9: Stability of extracted and concentrated samples. The samples were stored in the freezer at -4°C. Stability of field-like lab samples during the first 80 days. Assignment of the samples can be seen in Table S3. The regression model indicates that a collective significant effect was not found. The field samples described in section 3.5 have been measured again after 2-3 years. All samples revealed a loss of -20 to -40 %. That refers to 0.03 ± 0.01 %/day. Note that the x-axis has a logarithmic scale.

4. References

Chini, M., Crotti, P., Gardelli, C., and Macchia, F.: Regio- and Stereoselective Synthesis of β-Halohydrins from 1,2-Epoxides with Ammonium Halides in the Presence of Metal Salts, Tetrahedron, 48, 3805–3812, https://doi.org/10.1016/S0040-4020(01)92271-9, 1992.

Corey, P. F. and Ward, F. E.: Buffered potassium peroxymonosulfate-acetone epoxidation of .alpha.,.beta.-unsaturated acids, J. Org. Chem., 51, 1925–1926, https://doi.org/10.1021/jo00360a059, 1986.

Findley, T. W., Swern, D., and Scanlan, J. T.: Epoxidation of Unsaturated Fatty Materials with Peracetic Acid in Glacial Acetic Acid Solution, J. Am. Chem. Soc., 67, 412–414, https://doi.org/10.1021/ja01219a018, 1945.

Haufe, G., Mhlstdt, M., and Graefe, J.: Hydroxybromierung und Methoxybromierung von (Z)-Cycloocten, Monatshefte fr Chemie, 108, 803–811, https://doi.org/10.1007/BF00898044, 1977.

King, G.: 389. A contribution to the chemistry, including the stereochemistry, of the ? ? -halogenohydroxystearic acids, J. Chem. Soc., 1817, https://doi.org/10.1039/JR9490001817, 1949.

Milchert, E. and Smagowicz, A.: The Influence of Reaction Parameters on the Epoxidation of Rapeseed Oil with Peracetic Acid, J Am Oil Chem Soc, 86, 1227–1233, https://doi.org/10.1007/s11746-009-1455-7, 2009.

Milchert, E., Smagowicz, A., and Lewandowski, G.: Optimization of the Epoxidation of Rapeseed Oil with Peracetic Acid, Org. Process Res. Dev., 14, 1094–1101, https://doi.org/10.1021/op900240p, 2010.

Porter, D. J., Stewart, A. T., and Wigal, C. T.: Synthesis of a Bromohydrin: An Experiment Demonstrating Markovnikov Addition, J. Chem. Educ., 72, 1039, https://doi.org/10.1021/ed072p1039, 1995.

Shee, P. K., Ratnayake, N. D., Walter, T., Goethe, O., Onyeozili, E. N., and Walker, K. D.: Exploring the Scope of an α/β-Aminomutase for the Amination of Cinnamate Epoxides to Arylserines and Arylisoserines, ACS Catal., 9, 7418–7430, https://doi.org/10.1021/acscatal.9b01557, 2019.