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

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Abstract. The chemical characterization of volcanic gas emissions gives insights into the interior of volcanoes. Monitoring of BrO/SO_2-ratios has 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, BrO is not a primary emitted volcanic volatile and there exist still uncertainties about the formation

15 of BrO in volcanic plumes, mostly due to the lack of analytical approaches for the accurate speciation of certain key compounds.

This study describes a new method for the determination of the BrO precursor, the gaseous hydrogen bromide (HBr), by quantitative collection in denuder samplers. Gas diffusion denuders use the difference in diffusion coefficients to separate gaseous from particle-phase compounds. Gaseous HBr molecules are immobilized with an organic coating at the inner walls

20 of the denuder tubes when pumped through the denuders.

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 analyzed by high-performance liquid chromatography coupled to electrospray ionization mass spectrometry (*in situ* derivatization). Coating

25 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 comparison of HBr determination using EP-coated denuders and Raschig Tubes as alkaline traps 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)

30 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

35   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 previous estimations of the HBr conversion from the chemistry box model (CAABA/MECCA).

1 Introduction

Since the formation of the atmosphere, volcanic eruptions and volcanic passive degassing contribute to an exchange of Earth's

40   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).

45   Besides H_2O, CO_2 and sulfur species, also halogens are among the not negligible constituents of volcanic emissions (Textor et al., 2004). Monitoring of halogens in volcanic plumes has been correlated with volcanic activity for decades. Already 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

50   (e.g. Lübcke et al., 2014) made BrO/SO_2 a promising monitoring tool. Even inaccessible volcanoes can be observed with satellite-based remote sensing instruments (e.g. Hörmann et al., 2013).

However, 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

55   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) and

60   references therein.

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

65 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

70 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 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 from the denuder tubes and are detected and quantified by mass spectrometry, the

75 presented technique represents an *in situ* derivatization HPLC-MS method.

2 Methods

For method development, different organic coatings were 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

80 coating. All reagents used are listed in the supplementary material. 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 were synthesized. Synthesis descriptions are also included in the supplementary material.

2.1 Test gas sources and experimental setup

A diffusion gas source using a brown glass vial with septum cap as described in Rüdiger et al. (2017) was filled with 48 %

85 aqueous HBr or 30 % aqueous hydrogen chloride (HCl) and stored under nitrogen flow at 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.

90 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. All connecting pieces were realized by 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

95 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 and later in the field for total bromine determination. For the method validation in the laboratory a standard gas bottle with 102.8 ± 3.1 ppm HBr 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

100 denuder and Raschig Tube were connected with PTFE tubes, which ended at the bottom of the second flask. Although HBr concentrations between 13 and 31 ppb were established in this way, the downstream analysis revealed concentrations between 3 and 20 ppb. Apparently, fractional amounts of HBr are lost due to losses on the glass surfaces or flowmeters used in the laboratory setup indicate inaccurate gas flows or fluctuate. 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

105 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.
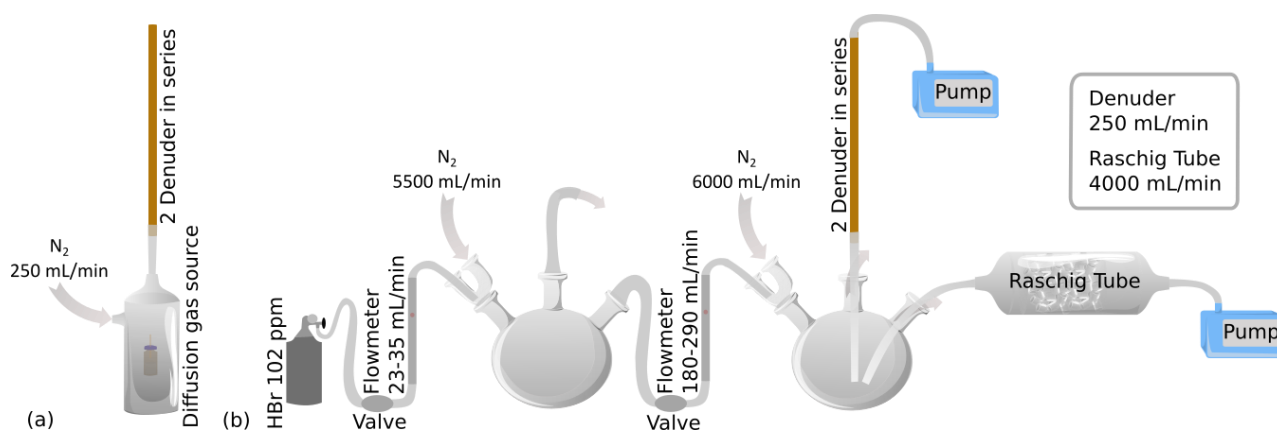
Figure 1: Experimental sampling setups in the laboratory.
(a) Denuders were connected to a diffusion test gas source with PTFE tubes. The test gas source was heated to 50° C. Entering
110 **nitrogen was thermostated before it reached the diffusion source.**
(b) Experimental Setup for comparison of denuder and Raschig Tube technique for HBr determination.

2.2 Denuder preparation and treatment

The denuder tubes were made of brown borosilicate glass to avoid photochemical reactions. They were 50 cm long and had 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

115 (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 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. The coated denuders were closed

120 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 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

125 derivatized product (no isomers or multiple derivatizations). In addition, the coating substrate must be suitable for the coating process. To ensure low volatility and to avoid evaporation during sampling, epoxides containing carboxy groups were selected. Low 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 from the denuders in five steps each with 2 mL of solvent. All analytes were eluted with

130 ethyl acetate, except for EP-coated denuders, as these showed better solubility in methanol. The elution efficiency was investigated with EP-coated denuders doped with 0.01 mmol of the bromine product EPBr. In a second elution step with five times 2 mL solvent after the first elution step, less than 0.05 % EPBr was found. As a consequence, the second elution step was omitted.

Eluates were concentrated to approximately 100 µL under a gentle nitrogen stream at 35° C. For adjustment of varying

135 evaporated volumes and for compensation of evaporation losses, 100 µL of an internal standard was added to the eluates before the concentration step. Samples analyzed by GC-MS were doped with 100 µL 2,4,6-tribromanisole (6 mg/L) as internal standard, while EP-coated denuder samples analyzed by LC-MS were doped with neocuproine (5 mg/L). The recovery rate of the processing method for EPBr was determined to be 99 ± 4 % (*n* = 6) when formic acid was added to the eluate before the evaporation process. For EPBr samples, the flasks were rinsed with an additional 100 µL methanol after evaporation.

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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.

145 **2.3.1 Gas chromatography-mass spectrometry**

To increase the volatility of the analytes, 30 µL *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 7 µL pyridine were added to GC-samples containing carboxylic acids. Samples were stored 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

150 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 and the ions used for quantification are summarized in the supplementary material (Tables S1-4).

2.3.2 High-performance liquid chromatography-mass spectrometry

155 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 %

160 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.

165 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. 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 31.4 min.

3 Results and Discussion

3.1 Selection of derivatizing coating

The suitability of the different denuder coatings is summarized in Table 1. One of the coatings tested was 2,3-epoxycyclooctane. Although it is solid at room temperature, a significant loss of the compound was observed during sampling. Obviously, 2,3-epoxycyclooctane is too volatile. Although 2-bromocyclooctanol could be determined in the denuder eluates, 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, 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 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).

EP (Fig. 2) was observed to be a suitable coating agent for the enrichment and derivatization of HBr. Performance and characterization are described in the following chapters.
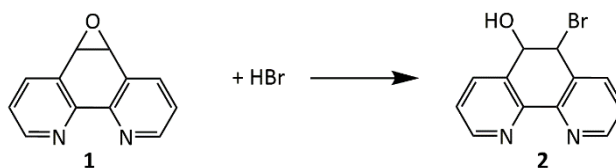
Figure 2: Derivatization of hydrogen bromide (HBr) with 5,6-epoxy-5,6-dihydro-1,10-phenanthroline (1, EP) yielding 5-Bromo-6-hydroxy-5,6-dihydro-[1,10]-phenanthroline (2, EPBr).

3.2 Denuder performance

According to Rüdiger et al. (2020), about 0.5-5.9 ppb total bromine was detected in ground-based samples in the volcanic plume of Masaya volcano using alkaline traps. Therefore, the breakthrough behavior for 1 ppm HBr was investigated (assumed maximum concentration taking into account variations between different volcanoes and sampling conditions). The collection efficiency was tested with three denuders connected in series (Fig. 1a). 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

200 EP 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 45.0 μmol EP coating, the breakthrough for 1 ppm HBr was below 1 %. However, higher amounts of coating are disadvantageous since EP started to precipitate in concentrated samples during sample preparation. Finally, 15 mmol/L EP coating solutions resulting in a total amount of 45.0 μmol EP within one denuder was used as a coating.

The influence of EP on the EPBr determination was investigated by a test series with 450 mmol/L EP and EPBr concentrations

205 in the range of 5 to 73 mg/L (n = 6). We determined deviations of only 2 ± 3 % compared to samples without EP, concluding that no matrix effects were found.

Eluted and constricted denuder samples were stored in the freezer at -4° C. The analysis of the samples was repeated within a time frame of two years. When comparing the analyzed EPBr/NC ratios, 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

210 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

215 evaporation volume, their values were calculated separately for each sample (Table 2).

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) would be at least conceivable as a cross-interference. However, 9,10-epoxystearic acid and EP-coated denuder 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

220 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 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

225 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) (Swain and Scott, 1953). 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

230 (Rüdiger et al., 2020)) 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

235 Since gaseous HBr can also be determined by other methods and total bromine concentrations in volcanic studies are usually determined by alkaline traps, the results of HBr-selective denuders and a Raschig Tube setup for total bromine determination using an artificial bromine source were compared. The experimental setup is described in section 2.1 and shown in Fig. 1b. In five experimental series, HBr concentrations between 3 and 20 ppb were determined simultaneously with both methods. On average, the results of the determinations with alkaline traps yielded 102 ± 11 % of the HBr values determined by denuder

240 sampling (Fig. 3). Since the agreement of the values obtained by both methods is good, the HBr values determined in volcanic plume samples can be considered a fraction of the total bromine determined with the Raschig Tubes.
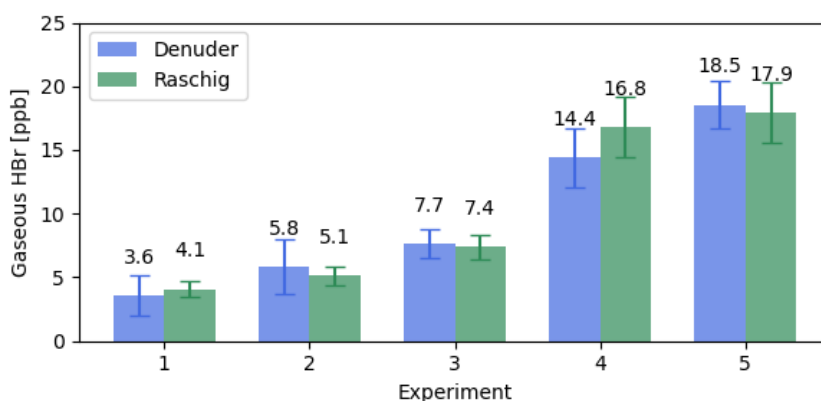
Figure 3: Comparison of simultaneously applied EP coated denuders (blue) and Raschig Tubes (green) for gaseous HBr determination.

245 **The determined HBr concentrations of the sampled test gas (in ppb) are shown for five consecutive comparison experiments. The error bars were calculated from the propagation of the errors of the analytical procedure and the sampling parameters. In total, the determination of test gases with Raschig Tubes yielded in 102 ± 11 % (standard deviation) compared to results obtained with EP coated denuders.**

3.5 Field application at Masaya 2016

250 Denuders coated with 45 μmol EP were used between 18.-21. of July 2016 at the Santiago Crater of the Masaya volcano (Nicaragua). Eight ground-based and two UAV-based samples were taken and subsequently analyzed. 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

255 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. (2020). A detailed description of the UAV system and flight descriptions can be obtained from Rüdiger et al. (2018) and Rüdiger et al. (2020).

In ground-based sampling sets, two denuders were used in series (Fig. 4a). Sampling was performed by a Gilian GilAir Plus pump with a flow rate of 250 ml/min for about 1-1.5 hours for each denuder. In drone-based sampling setups, individual
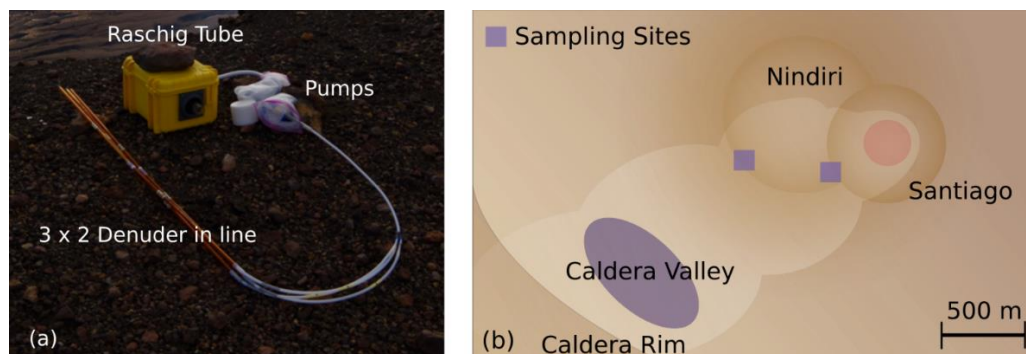
Figure 4: Field campaign at Masaya volcano in July 2016
(a) Sampling setup containing TMB- and EP-denuders, two in series each, and Raschig Tube.
(b) Overview on sampling locations (purple areas) during the field campaign at Santiago crater, on Nindiri rim and in the caldera valley.

260 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).

In ground-based samples, gaseous HBr concentrations were detected in the range of 0.44 to 1.97 ppb. Unfortunately, the two UAV-based samples were below their LOD. The higher LOD in UAV-based measurements is due to a much shorter sampling time of 5-10 minutes compared to ground-based measurements (1-1.5 h). LOD and LOQ were calculated based on the signal-

265 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.

The reproducibility of the results was tested with two sets of two EP-coated denuders, which were sampled simultaneously side by side on July 21 (2x2 denuders at the Santiago rim and 2x2 denuders at the Nindiri rim). At the Santiago rim, the denuder measurements resulted in HBr concentrations of 1.97 ± 0.11 and 1.82 ± 0.10 ppb, at the Nindiri rim 1.17 ± 0.07 and $0.97 \pm$

270 0.09 ppb. 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 HBr concentrations show a decrease in concentration with increasing distance from the emission source, which is caused by dilution and conversion effects. A comparison of the HBr concentrations with the simultaneously determined total bromine concentrations (Table 2) for ground-based sampling sets allows the differentiation of dilution effects and the influence of

275 conversion reactions on the measured concentrations.

The total bromine, total reactive bromine and 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. (2020). This model predicted for a Br/S ratio of 7.4×10^{-4} (for detailed parameterization see Rüdiger et al., 2020) a decrease of about 70 to 35 % HBr between 1 to 3 minutes after gas release. The total bromine to sulfur ratio for these days averaged $6.2 \pm 1.0 \times 10^{-4}$ (Raschig

280 Tubes, Table 2). At an estimated wind speed of 5 m/s (Rüdiger et al., 2020) the proportion of 75 ± 11 % HBr 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). This is in very good agreement with the results obtained with the model's estimations.

Table 2: HBr concentrations in ppb, determined by EP-coated denuders, and their respective limits of detection (LOD) and quantification (LOQ). Samples were taken at various distances to Masaya's emission source. Notice that samples collected at 2000 m distance are below detection limits.

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	1.39	3.99	5.9 ± 0.3
							0.37 ± 0.13	1.46	3.81	
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 (Rüdiger et al., 2020)
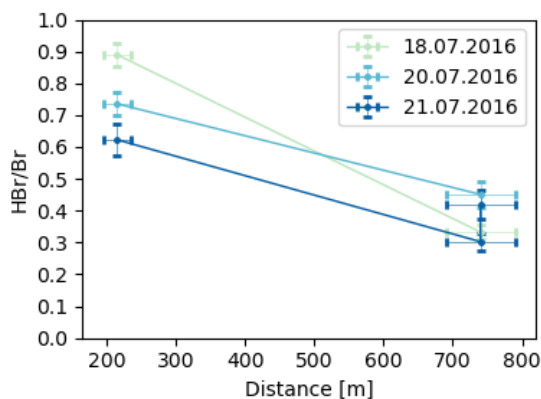
Figure 5: Fraction of HBr determined by EP-coated denuders of total bromine determined by Raschig Tubes. On average, fractions decreased from 0.75 ± 0.11 at 214 m distance from the Masaya emission source to 0.36 ± 0.08 at 740 m distance.

4 Conclusion

The presented study describes a new method for the quantitative determination of gaseous hydrogen halides based on gas diffusion denuders. The hydrogen halides reacted during sampling with appropriate epoxides applied to the denuder walls. After elution and enrichment steps in the laboratory, this *in situ* derivatization allows the separation and detection of the acids 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 to be suitable for the determination of the expected HBr concentrations under ground-based sampling conditions in the presence of other volcanic gases such as HCl.

A laboratory comparison using HBr test gas sources with EP-coated denuders and Raschig Tubes showed a deviation of 2

300 ± 11 % between the two methods. 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.

305 The denuder sampling assembly was deployed in the volcanic plume of Masaya, Nicaragua, in July 2016. 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

310 decreased from 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). 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).

In summary, the study presented here describes a new method as a promising approach to allow better speciation of bromine in volcanic plumes and thus to gain a better understanding of bromine activation. The knowledge of bromine chemistry in

315 volcanic plumes will contribute to the future use of remote sensing BrO measurement systems as monitoring instruments for volcanic activity.

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

320 *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.

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

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