



*Supplement of*

## **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 et al.**

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

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## 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). Neocuprone (NC), *trans*-oxirane-2,3-dicarbon acid and pyridine were purchased from Sigma-Aldrich (Steinheim, Germany). Oleic acid, (-)- $\alpha$ -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 phosphorpentoxide 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 M $\Omega$  cm) was used for aqueous solutions.

### 10 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 15 10 mL hydrobromic acid (48%) were added. After 30 min stirring the organic phase was separated and washed with water, saturated NaHCO<sub>3</sub>-solution and again water. A yield of 85-90% of an oily colourless liquid was obtained.

#### 1.2.2 3-Phenylloxirane-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  $\mu$ L acetone 3.3 mmol NaHCO<sub>3</sub> in 500  $\mu$ L in water was added dropwise. A solution of Oxone (1.4 mmol, 1.8 equiv. KHSO<sub>3</sub>) in 1.6 mL 0.4 mM 20 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<sub>4</sub>, 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 25 under vacuum. Approximately 75 % of the total yield of the potassium salt was obtained. The crude product was used as a coating material.

### 1.2.3 9,10-Epoxy stearic 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

30 solution was heated to 40 °C in a water bath. 1.08 g H<sub>2</sub>O<sub>2</sub> 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

35 SiO<sub>2</sub> 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

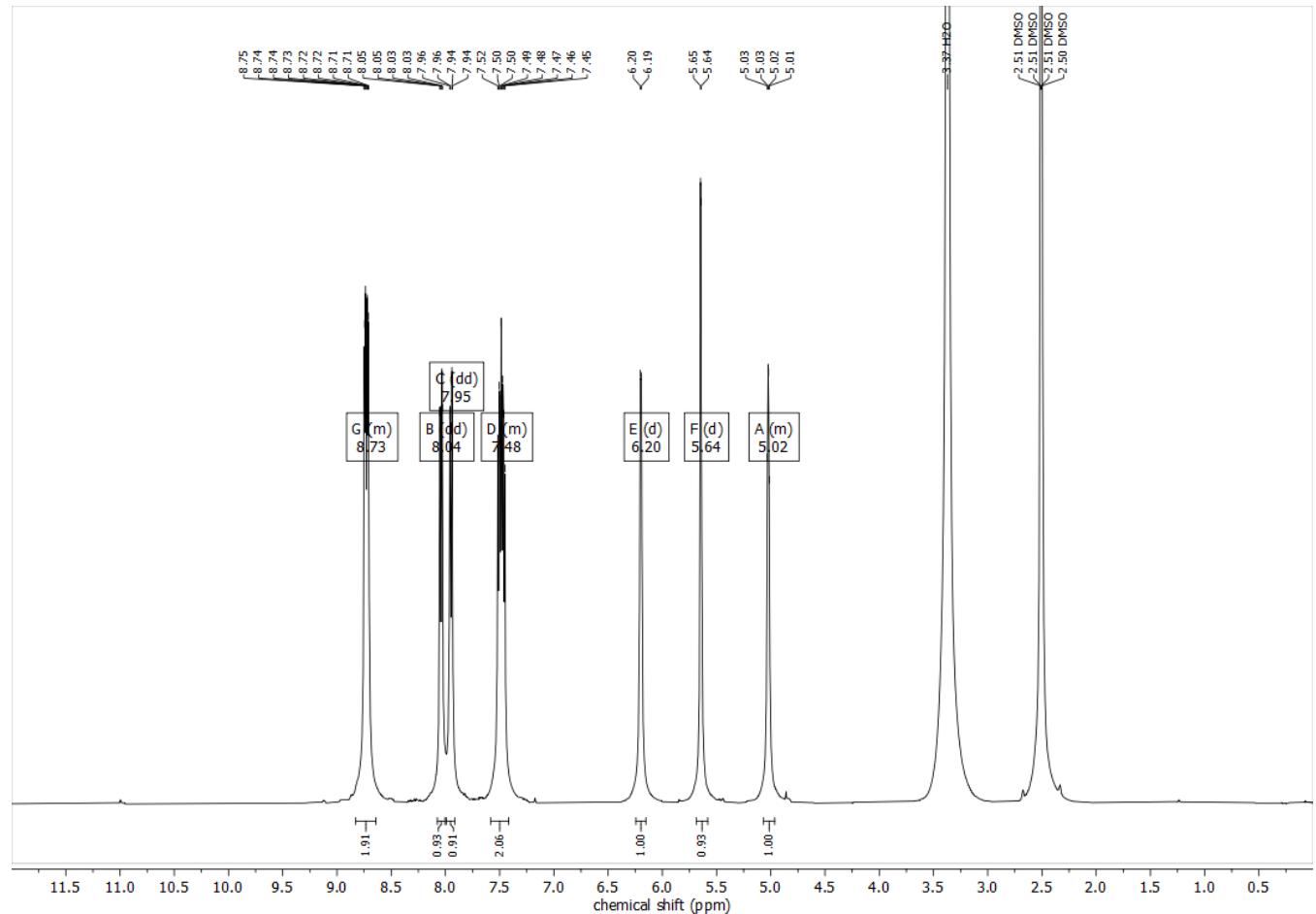
40 water. The dried product resulted in 81 % yield. SiO<sub>2</sub> column chromatography with 1:1 of hexane and ethyl acetate as a mobile phase resulted in 70 % purity for 10-Bromo-9-hydroxystearic acid (GC/MS determinations).

### 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<sub>3</sub>-solution the EPBr precipitated. The colourless solid has been extracted, washed twice with

45 2 mL saturated NaHCO<sub>3</sub>-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.

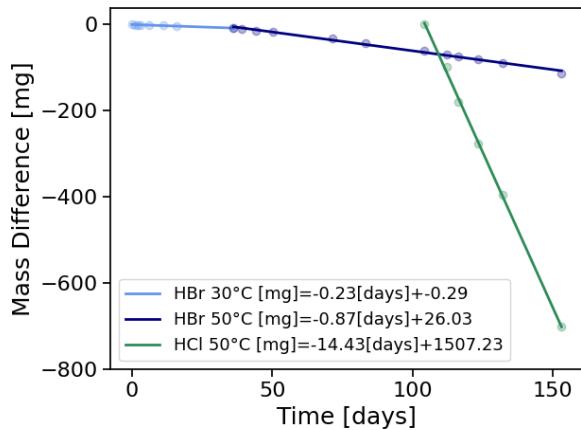
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 8.83 – 8.64 (m, 2H), 8.04 (dd, *J*=7.8, 1.7, 1H), 7.95 (dd, *J*=7.7, 1.7, 1H), 7.58 – 7.42 (m, 2H), 6.20 (d, *J*=4.9, 1H), 5.64 (d, *J*=2.8, 1H), 5.05 – 4.99 (m, 1H). The spectrum is shown in Fig. S1.



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

## 2 Methods

### 2.1 Testgas sources



55 **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<sub>2</sub>-stream of approximately 0.5 L/min. The N<sub>2</sub>-Stream is drying 60 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 N<sub>2</sub>-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.



65 **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

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

70 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-phenylloxirane-2-carboxylic acid	C	7.19	147, BSTFA derivatized	11.82

## 2.4 Chromatograms and Spectra

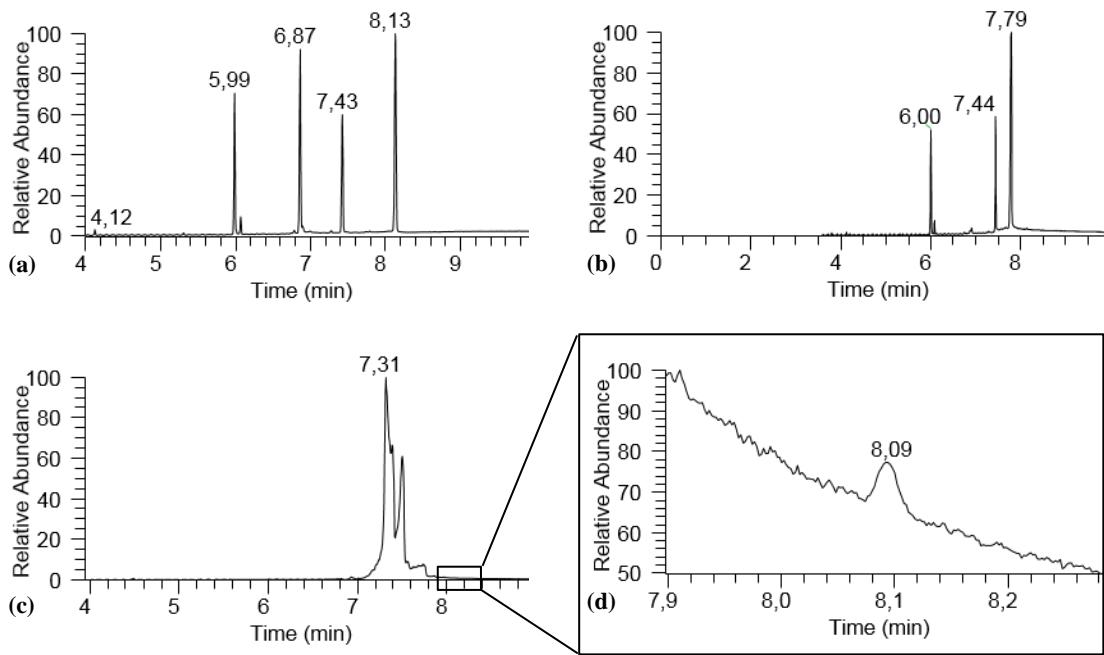


Figure S4: GC-MS Chromatograms following temperature program B describing denuders coated with 9,10-epoxystearic acid. (a) GC-MS chromatogram in full scan showing retention times for oleic acid (5.99 min), 9,10-epoxystearic acid (6.87 min), 9,10-dihydroxystearic acid (7.43 min), and 10-bromo-9-hydroxystearic acid (8.13 min). (b) GC-MS chromatogram in full scan showing retention times 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.

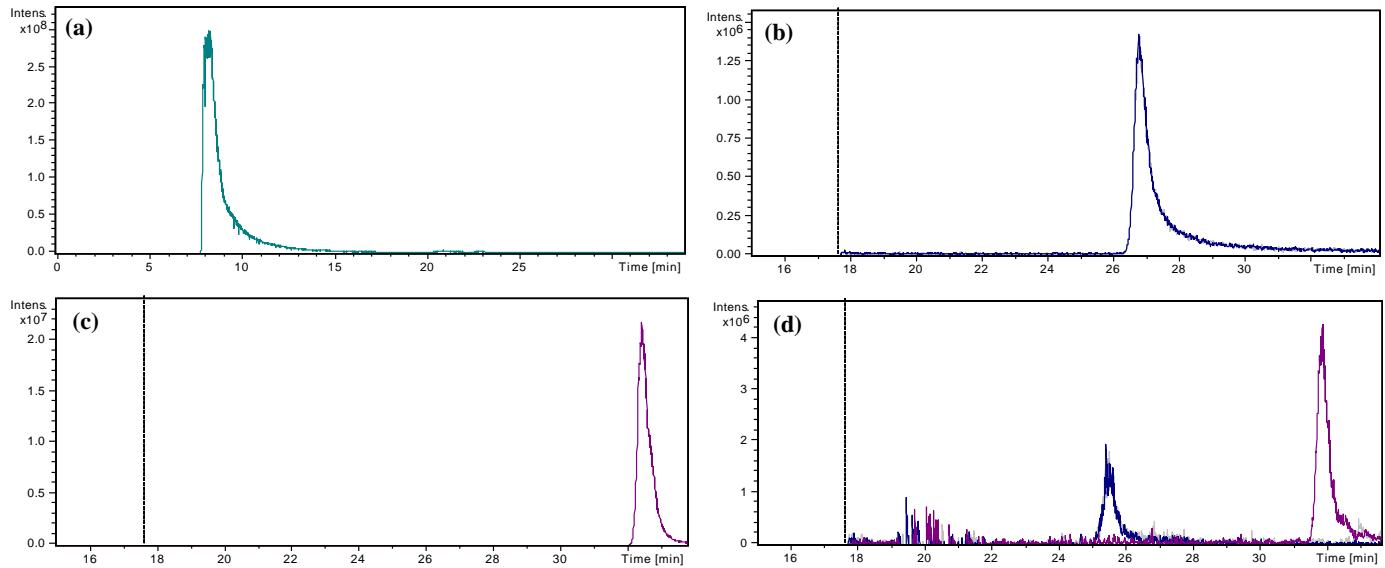


Figure S5: LC-MS Chromatograms describing denuders coated with EP, for details see Sect. 2.3.2 in the main article. (a) Extracted Ion Chromatograms of EP solution in methanol containing 7.5 mmol/L showing the  $m/z$  197 of EP (green) at retention time 8.2 min. Samples extracted from denuders contain 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.

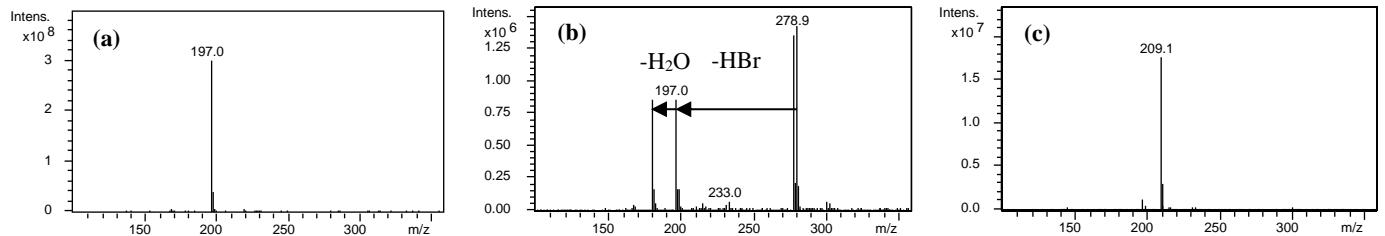


Figure S6: MS spectra, for details the Sect. 2.3.2 of the main article. (a) MS spectrum of EP solution in methanol containing 7.5 mmol/L showing the  $[M+H]^+$   $m/z$  197 of EP at retention time 8.2 min. (b) MS spectrum of EPBr solution in methanol containing 1.6 mg/L showing the  $[M+H]^+$   $m/z$  277 and 279 of EPBr and two fragments of  $m/z$  197 (-HBr) and 181 (-HBr-H<sub>2</sub>O) 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

#### 105 3.1 Matrix effects and precision

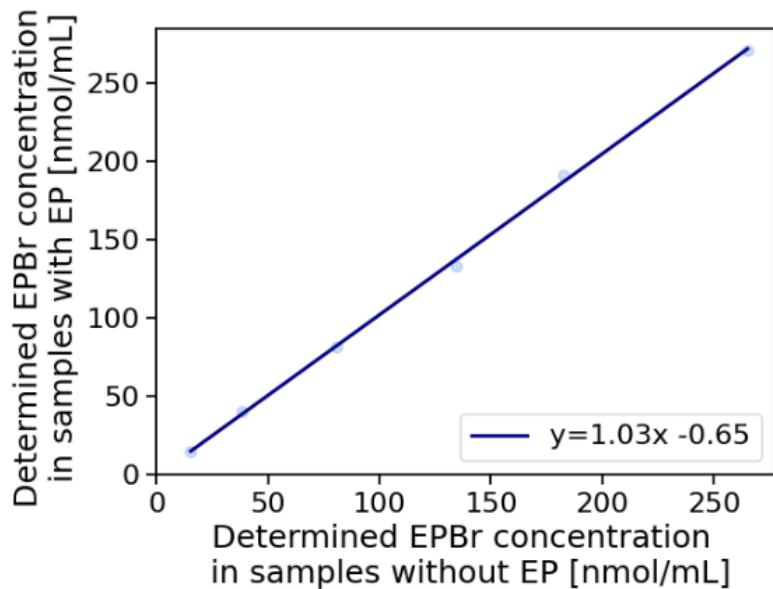


Figure S7: Analysis of matrix effects comparing Samples containing EPBr concentrations with 450 mmol/L EP (+EP) and without EP (-EP) in the sample. The orthogonal distance regression model results in (+EP) = 1.03 x (-EP) - 0.65. The relative bias between the both sample types is  $2 \pm 3\%$ .

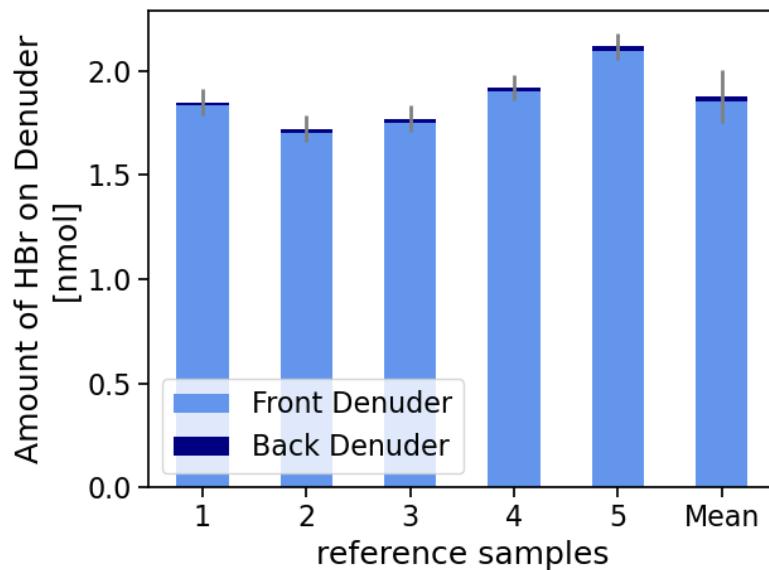


Figure S8: Precision of the method was determined by analysing five times the same test gas denuders coated with 15 mmol/L EP-solution. The experimental setup was performed as described in Fig. 1b. Resulting in a relative standard deviation of 8%.

### 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 $\mu$ l	5 $\mu$ l	3x 100 $\mu$ l
2	450	0.05	5	500 $\mu$ l	5 $\mu$ l	3x 100 $\mu$ l

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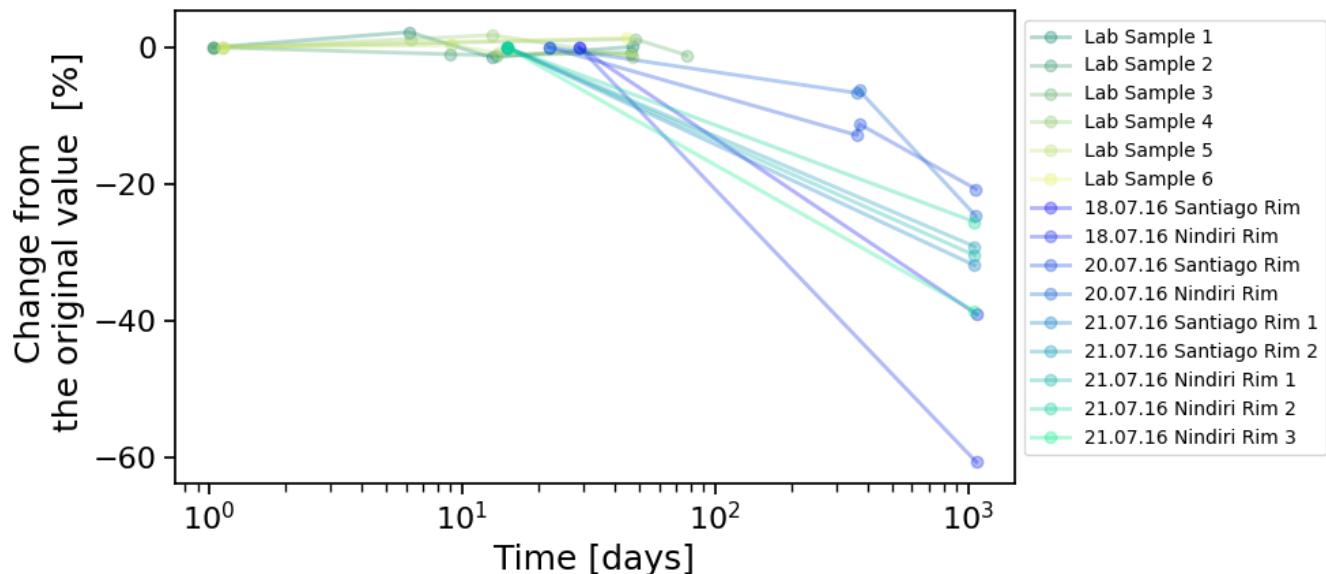


Figure S9: Stability of extracted and concentrated samples. The samples were stored in the freezer at -4°C. Stability of field-like lab samples during the first 80 days. Assignment of the samples can be seen in Table S3. The regression model indicates that a collective significant effect was not found.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

120

#### 4. References

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