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**METHOD DEVELOPMENT AND VALIDATION FOR THE DETERMINATION OF SULFITES  
AND SULFATES ON THE SURFACE OF MINERAL ATMOSPHERIC SAMPLES USING  
REVERSE-PHASE LIQUID CHROMATOGRAPHY**

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**ABSTRACT**

Earlier studies suggest that SO<sub>2</sub> gas reacts at the surface of mineral dust and forms sulfites or bisulfites, which are then converted to sulfates. In order to monitor and quantify the amounts of both sulfites and sulfates formed on the surface of mineral dusts of volcanic and desert origins an accurate and precise reversed-phase liquid chromatography method was developed and validated to extract, stabilize and individually analyze sulfites and sulfates initially present on the surface of dusts exposed to SO<sub>2</sub>. The method was developed on a 25 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm column which was dynamically coated with 1.0 mM cetylpyridinium chloride in 7% acetonitrile solution to produce a charged surface as recommended in the literature. Mobile phase used: 1 mM Potassium Hydrogen Phthalate Buffer at pH 6.5 at a flow rate of 1.0 ml/min with negative UV-Vis detection at 255 nm in 15 min. The method was validated for specificity, linearity and range, injection repeatability, stability, robustness, limit of detection and limit of quantitation, and sample preparation and extraction reproducibility. The method was adapted for straight sulfite and sulfate quantification: (i) of

environmental samples, and (ii) natural samples additionally exposed to SO<sub>2</sub> gas in a dedicated laboratory setup. The method was then successfully applied to quantify sulfites and sulfates on natural volcanic and a desert dust samples both collected in the environment and additionally exposed to SO<sub>2</sub> gas in the laboratory. The method can be efficiently used to identify sulfites and sulfates on fresh volcanic ash following an eruption, on aeolian desert dust exposed to industrial pollutants, as well as for laboratory investigations of sulfite and sulfate formation on the surface of minerals and natural dusts of different origins.

**Key Words:** sulfite, sulfate, mineral dust, surface analysis, HPLC

## 1.0 INTRODUCTION

Sulfur dioxide ( $\text{SO}_2$ ) is a noticeable component in the atmosphere, where release of  $\text{SO}_2$  is associated with the decrease in the levels of atmospheric oxidants, such as  $\text{H}_2\text{O}_2$ ,  $\text{OH}$ , and  $\text{O}_3$  as they are involved in the reactions that convert gaseous and dissolved  $\text{SO}_2$  to sulfates [1]. Stevenson et al. estimate that, on average, emissions of  $\text{SO}_2$  gas in the atmosphere due to anthropogenic activity account for the 71.2 Tg/yr, while volcanic eruptions contribute to 8.8 Tg/yr, and 1.4 Tg/yr is due to the biomass burning [1]. Needless to say, volcanic eruptions are a highly variable source of  $\text{SO}_2$  gas. The 2014–2015 Holuhraun eruption in Iceland, emitted ca. 11 Tg of  $\text{SO}_2$  into the troposphere over a 6 month period, and caused one of the most intense and widespread volcanogenic air pollution events in centuries [2]. It was an effusive eruption with very little volcanic ash produced, yet with the amount of  $\text{SO}_2$  that exceeded all of the anthropological flux in Europe for the year 2011[2]. That is not to undermine the significance of the anthropogenic contribution. The “Great smog” of 1952 in London was caused by  $\text{SO}_2$  emitted from coal burning and reached levels as high as 1.34 ppm [3].

Explosive volcanic eruptions have a potential to inject vast amounts of  $\text{SO}_2$  gas into the stratosphere, where conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  leads to the formation of fine sulfur aerosol that can persist in the mid-stratosphere for up to 2 years [1]. Sulfate aerosols are known to affect the climate by increasing the reflection of radiation from the Sun back into space, thus efficiently cooling the Earth’s troposphere [1]. In the troposphere itself, formation of sulfur aerosols due to anthropogenic and natural emissions competes with  $\text{SO}_2$  gas deposition, and therefore sulfur aerosols formed are deposited within days or weeks [1]. Important reactions of  $\text{SO}_2$  gas in the troposphere include oxidation of  $\text{SO}_2$  in cloud and rain droplets leading to the formation of acid rain, and oxidation to sulfate on the surface of atmospheric particles [4], [5], [6]. Adsorption of sulfur dioxide  $\text{SO}_2$  gas on the surface of atmospheric samples leads to the formation of sulfate coating that can affect both the dust properties and the sulfur cycle [7]. Volcanic dusts acquire the sulfate coating while passing through the volcanic conduit [8], as well as further away from the crater, in the colder parts of the plume, higher in the atmosphere [9], [10]. Desert dusts as well

are known to accumulate hygroscopic sulfate coating during their long-range transport [11]. Thus, a negative correlation was observed between atmospheric concentrations of SO<sub>2</sub> and both Saharan and Chinese desert dust loadings [12]. Once coated, these particles can act as large cloud condensation nuclei (CCN) and affect cloud formation [13]. They may also affect climate forcing by forming cirrus ice clouds, ice nuclei (IN), at relatively warm temperatures and low supersaturation [13].

The physico-chemical processes that govern transformation of SO<sub>2</sub> gas on the surface of dusts are poorly understood and need further investigation. SO<sub>2</sub> shows heterogeneous reactivity towards many mineral oxides such as MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, as well as volcanic ash and mineral dust [14], [4], [5], [15]. Reactivity of the dusts towards the uptake of SO<sub>2</sub> as well as influence of different atmospheric conditions and various oxidants is often evaluated in terms of uptake coefficient using Knudson cell and flow-tube reactors [5], [14], [15]. Quantifications of the amounts of products formed on the surface of dust could provide additional information and might clarify reaction pathways.

While summarizing previous work on volcanic ash analysis, Witham et al. cited about 55 articles reporting original volcanic ash-leaching data [16]. The ion-chromatography methods available in the literature and employed to quantify the amount of SO<sub>2</sub> adsorbed on the surface of volcanic ash are almost solely concerned with quantification of sulfates as the final oxidation product completely ignoring sulfite quantification [16]. Indeed, it is widely accepted that SO<sub>2</sub> gas reacts at the surface of the volcanic dust and forms sulfites or bisulfites, which are then converted to sulfates [17]. However, quantification of sulfites along with the sulfates could provide a more comprehensive description of the SO<sub>2</sub> adsorption processes. Sulfite to sulfate conversion on synthetic mineral dust aerosol (using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, CaO, ZnO, TiO<sub>2</sub>, MgO, and Fe<sub>2</sub>O<sub>3</sub> oxides) was recently studied by He et al. using DRIFTS in order to better explain haze formation mechanism in China [3]. The need to explore the effect of minerology on SO<sub>2</sub> adsorption using authentic dust samples of various compositions in laboratory studies was expressed by Sullivan et al. [18]. However, employment of DRIFTS is limited on natural heterogeneous samples that are dark in color, such as volcanic dust or ash. In addition, DRIFTS is a qualitative technique and does not provide

quantitative data. Simultaneous determination of sulfites and sulfates by reversed-phase ion-pair HPLC technique in atmospheric waters was proposed by Zuo et al. [19]. When applied to environmental samples though, the method failed to determine sulfites due to their fast conversion to sulfates [19]. Nevertheless, ion-pairing technique is a good tool to separate polar compounds by means of user-friendly widely-used HPLC technique.

The goal of this study is to develop a method that would (i) extract both sulfites and sulfates, (ii) stop the conversion of sulfites to sulfates and (iii) successfully quantify both species. The method can then be used for two distinctive purposes: to quantify sulfites and sulfates on the surface of natural environmental samples, such as recently erupted volcanic ash or dust passing through polluted areas, and to study the kinetics of the sulfite to sulfate transformation in laboratory settings. The challenge in separating sulfites from sulfates in the solution containing mineral dust comes from the nature of these dust particles, as they contain various oxidizing elements, such as iron, that contribute to the oxidation of sulfites into sulfates [20]. This article proposes (i) a controlled ageing of mineral samples by SO<sub>2</sub> gas in laboratory settings, (ii) extraction and stabilization of sulfites and sulfates with a subsequent use of (iii) HPLC for quantitative analysis as a technique that can be used to study the conversion of sulfites to sulfates on the surface of natural samples. While in the case of taking field measurements artificial ageing is not required, it is important to be able to age samples in reproducible fashion in order to study kinetics of the sulfite to sulfate transformation as a part of laboratory experimental work.

## 2.0 EXPERIMENTAL

### 2.1 Samples and Standards

#### 2.1.1 Dust samples

A sample of volcanic dust of basaltic origin, used for method development and method application, comes from Hagavatn - an active desert area of Iceland. It was collected dry from the top surface layer. Particles are small, ranging from 10 to 50 µm in diameter due to glaciofluvial processes leading to their

generation. Modal composition of Hagavatn dust (referred as Lambahraun sand by Baratoux et al.) and, in particular, the amount of crystalline material versus glassy material, was determined by Baratoux et al. using optical and scanning mode microscope [21]. Hagavatn sample contains about 80% of minerals and 20 % of glassy material [21]. Mineral phases typical of basaltic rocks include olivine, pyroxene and plagioclase [21].

The mineral desert dust sample, used for method application only, comes from Gobi Desert, Ningxia Province, China. This area represents the second most important source of atmospheric mineral dusts after Sahara desert [22]. This is an aeolian sample that was sieved and only the fraction below 100  $\mu\text{m}$  was used for further studies. The morphology of the sieved fraction of the natural Gobi dust sample was evaluated using scanning electron microscopy (SEM) carried out on a Hitachi S-4300SE/N SEM in high vacuum mode. Gobi dust particles are chunky, irregular in shape, with mean diameter ranging from a few to 50  $\mu\text{m}$ . Flat particles are also observed, suggesting the presence of distinct crystalline phase structures. The relative abundance of mineral phases for Gobi dust was determined using X-ray diffraction (XRD; Bruker D2 phaser 2 theta analyzer). Gobi dust shows a low silica content typical for Asian desert dusts (33.0%). Other minerals include calcite (8.7%), albite (8.6%), muscovite (25.8%), kaolinite (8.9%), rutile (4.4%), hedenbergite (6.2%), chromian pyrope (4.1%) and beaconite (0.3%).

Elemental compositions of Hagavatn and Gobi dusts as determined by ICP-MS are presented in Table 1 [15], [23].

*Table 1: % elemental composition of mineral dust samples used in this study adapted from [23], [15] as determined by ICP-MS experiments.*

	Si	Al	Ca	Na	Mg	Ti	K	Fe	other
<b>Hagavatn</b>	27.5	16.7	19.5	3.1	10.4	2.4	0.2	19.6	0.6
<b>Gobi</b>	57.6	11	16.1	2.5	2.3	0.8	3.5	5.5	0.7

Specific surface area (SSA) for Hagavtn and Gobi dusts was determined in previous studies using the Brunauer–Emmett–Teller (BET) method, and the values obtained are as follows:  $4.5 \pm 1.1 \text{ m}^2/\text{g}$  for Hagavtn and  $10.5 \pm 2.0 \text{ m}^2/\text{g}$  for Gobi dust [15], [24].

### 2.1.2 Chemicals and reagents

HPLC grade acetonitrile (ACN), 99.95% and methanol (MeOH), 99.9% were obtained from Biosolve Chimie, Dieuze, France. Potassium hydrogen phthalate and triethanolamine, 99% of analytical grade were purchased from Acros Organics, Geel, Belgium. Cetylpyridinium chloride, 98% was purchased from Alfa Aesar, Kandel, Germany. Sodium sulfate was purchased from Merck, Darmstadt, Germany. Sodium sulfite was purchased from Fischer Chemical, Loughborough, UK. Formalin (37% formaldehyde solution by weight containing 10-15 % MeOH as stabilizer) was obtained from Sigma-Aldrich. Other chemicals and solvents of analytical grade were used during research. Deionized water (DI) was used throughout the investigation. A certified SO<sub>2</sub> cylinder, 250 ppm diluted in synthetic air (nearly 80% N<sub>2</sub> and 20% O<sub>2</sub>) was purchased from Messer, France.

### 2.1.3 Standards

The solution of 1% Formalin was used to prepare a 1000 ppm stock solution of potassium sulfite (KSO<sub>3</sub>) and a 1000 ppm stock solution of potassium sulfate (KSO<sub>4</sub>). Other concentrations of KSO<sub>3</sub> and KSO<sub>4</sub> standards were prepared from their stock solutions through serial dilution with 1% Formalin. Stock solution of 1% Formalin was prepared by adding 10 ml of Formalin in a 1000 mL volumetric flask and diluting to the volume with 10% methanol/water to prevent polymerization.

## 2.2 Experimental Set-Up and Procedure

### 2.2.1 General Outline

This work serves two distinctive purposes: (i) analyze sulfites and sulfates on the surface of environmental dust samples during field campaign measurements (referred to as “environmental



sampling”) and (ii) study kinetics of sulfite and sulfate formation on the surface of different dusts in the laboratory environment by subjecting them to SO<sub>2</sub> ageing and analyzing the product formation (referred to as “kinetics study”).

The developed method for “environmental sampling” protocol consists of three parts: (i) sample collection, (ii) extraction and stabilization of sulfites and sulfates and (iii) HPLC analysis (Figure 1); the developed method for “kinetics study” protocol includes four steps: (i) sample collection, (ii) dust ageing, (iii) extraction and stabilization of sulfites and sulfates and (iv) HPLC analysis (Figure 1). Thus, the difference between the two protocols is an additional step of controlled SO<sub>2</sub> ageing required for the “kinetics study”. Sample analysis step that includes extraction and HPLC analysis is exactly the same in both cases.

Method for HPLC analysis was validated for specificity, limit of detection and quantitation, linearity and range, injection repeatability, and robustness. Sample preparation and extraction reproducibility was validated for the entire “kinetics study” protocol. Note that reproducibility for “environmental sampling” is expected to be superior to reproducibility for “kinetics study” due to the lack of ageing that introduces additional uncertainties.

### *2.2.2 Dust ageing by SO<sub>2</sub> gas*

The setup for ageing samples consists of two parts: (i) the gas mixing line and (ii) the ageing reactor. A schematic representation of the setup is provided in Figure 2. A dust weighting from 100 to 200 mg is spread on a 47 mm Whatman filter paper and is placed in a tightly closed reactor. The gas mixture containing 175 ppm SO<sub>2</sub> entering the reactor is forced through the filter containing the dust at 100 cm<sup>3</sup>/min. The ageing of environmental samples is carried out using zero air; it is generated by a classical air compressor, and then passed through a catalytic zero air generator (Claind ZeroAir 2020, Lenno, Italy) coupled to a pressure swing adsorption (PSA) device. The remaining impurity levels in the air stream

177 before entering the reactor are lower than the analytical system detection limits: VOCs < 0.1 ppb, CO<sub>2</sub> <  
178 10 ppb, and CO < 80 ppb. Moisture level is ca. 2 ppm. In experiments requiring humid air, a second flow  
179 of zero air going through a bubbler of ultrapure water (milli-Q, resistivity 18.2 MΩ cm) is mixed with the  
180 dry air flow, in proportions necessary to reach the relative humidity (*RH*) targeted.

### 2.2.3 Extraction and stabilization of surface sulfites and sulfates

After a defined period of ageing in the laboratory or in the absence of controlled ageing, such as in the case of samples collected in the environment, a sample weighting from 100 to 200 mg was transferred to a 10 mL glass container and stabilized with 1 mL of 1% Formalin. This step was followed by 10 min sonication in the ultrasound bath. The solution was then filtered through a 0.45  $\mu\text{m}$  pore size 30 mm diameter filter using a syringe. The remaining dust was washed with 1 mL of 1% Formalin and filtered through the same filter that was used to filter the first solution. The final solution was analyzed by HPLC system.

### 2.2.4 HPLC analysis. Instrumentation and chromatographic conditions

Chromatography equipment used to develop an HPLC method consisted of Thermo Scientific Dionex UltiMate 3000 UHPLC System with UV/VIS Detector (Thermo Scientific, Waltham, MA). Chromeleon 7.0 Data Acquisition System for LC (Thermo Scientific, Waltham, MA) was used to analyze the data. Analysis was performed using Restek Ultra Column C18, 5  $\mu\text{m}$ , Length 250 mm, I.D. 4.60 mm dynamically coated with cetylpyridinium chloride to produce a charged surface as recommended by Zuo et al. [19]. More specifically, columns were cleaned at 1 mL/min for 1.5 hour with 100% ACN before being coated with 1.0 mM cetylpyridinium chloride in ACN/water (7:93, v/v) at 0.5 mL/min for 3 hours [19]. The HPLC instrument was operated isocratically at 23 C° at a flow rate of 1 mL/min for 15 min. Potassium hydrogen phthalate buffer, 1.0 mM was adjusted to pH 6.5 with a dilute solution of potassium hydroxide (KOH), vacuum filtered and used as a mobile phase. The injection volume was 10  $\mu\text{L}$ . An indirect photometric detection was used for quantification of sulfates and sulfites. Detector was set at 255 nm as the mobile phase showed the highest absorbance at this wavelength. A 6-point linear calibration curve was established daily for  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions in the range of 6  $\mu\text{g/mL}$  to 191  $\mu\text{g/mL}$  and 3  $\mu\text{g/mL}$  to 101  $\mu\text{g/mL}$  respectively. Concentration of sulfites and sulfates in the extracts of natural samples was

determined using the slope of the calibration curve and converted to micrograms per gram ( $\mu\text{g/g}$ ) of dust using the mass of the sample.

### 3.0 RESULTS AND DISCUSSION

Chemical characterization plays a vital role in scientific representation of any process. Defined as the set of techniques that allows an analyst to know qualitatively and/or quantitatively the composition of the material, a method is created to reach this goal. The following sections will guide the reader through the development of the method for quantitative determination of sulfites and sulfates on the surface of mineral dust. As such, we've started by building an analytical HPLC method for analysis of a mixture of sulfites and sulfates. We then optimized extraction procedure to ensure optimal extraction of sulfites and sulfates from a dust sample. Finally, we assessed the validity of the method by going through validation studies using, when possible,  $\text{SO}_2$ -laboratory-aged dust samples in order to have a sufficient amount of sulfites on the surface (unless immediately stabilized, sulfites will oxidize to sulfates).

The global objective of validation of the method is to demonstrate its suitability for the intended use [25]. In the case of this study the method is expected to be used for research purposes. More specifically, method validation is a process that uses a defined set of experiments to establish the performance criteria that should be achieved by an analyst using the method and that provides a means to assess the reliability of results obtained. Method validation is commonly used to prove compliance with certain established criteria. In the case of this study though, method validation is solemnly used to establish performance criteria, as, to the best of our knowledge, no regulatory body is concerned with determination of sulfites and sulfates on the surface of natural mineral samples and no reference method exists for extraction, stabilization, and determination of both sulfites and sulfates on the surface of mineral dusts. Hence, analytical HPLC method was validated for specificity, limit of detection and limit of quantitation, linearity and range, injection repeatability, and robustness. Additionally, method reproducibility was

validated for the entire “kinetics study” protocol including (i) laboratory SO<sub>2</sub> ageing of mineral dust, (ii) extraction of sulfites and sulfates and (iii) HPLC analysis.

### 3.1 HPLC Analytical Method Optimization

The method for determination of sulfites, sulfates and hydroxymethanesulfonate (HMS) in natural and atmospheric water samples developed by Zuo et al. was used as a base for development of the method for determination of sulfites and sulfates on the surface of natural mineral samples discussed in this paper [19]. The main drawback of the method was the lack of sulfite-stabilizing agent during sample preparation and, as a consequence, inability to detect sulfites in environmental samples. The authors acknowledged the problem in the “quantitative analysis” part of their study and recommended to use methanol in order to stabilize sulfites. Following the suggestion, a 50/50 ppm solution of K<sub>2</sub>SO<sub>3</sub>/ K<sub>2</sub>SO<sub>4</sub> was dissolved in 10% methanol used as stabilizing agent. Unfortunately, in our experiments, methanol solution either did not stabilize sulfites and they were converted into sulfates, or sulfites co-eluted with sulfates, as only one peak was observed. Besides, methanol would be a poor choice for the extraction of sulfites in the presence of reactive ions, such as Mn or Fe, which are both known to be present in volcanic dust [20]. Formalin was reported to prevent the conversion of sulfites to sulfates by converting it to hydroxymethanesulfonate (HMS) and was tested as an extracting solvent [20]. Two concentrations of a mixture of sulfites and sulfates of 50/50 ppm and 5/5 ppm were prepared using Formalin of the following concentrations: 0.5%, 1% and 5%. A solvent peak for 5% Formalin overlapped with a sulfite peak, and 5% Formalin concentration was rejected for further studies. Solvent peaks of both 0.5 and 1% Formalin were well separated from sulfite peak. Besides, less than 5% change was observed for sulfites and sulfates in the corresponding solutions when left at ambient temperature for 2 days. Between 0.5% and 1% concentrations of Formalin, a solution of 1% Formalin was chosen as an extracting solvent for further studies.

A second concern about the method of Zuo et al. was the high pH value of the mobile phase. The diluted 1.0 mM phthalate buffer mobile phase suggested by the author could not be adjusted to pH 7.9 as it was out of its buffering capacity range. An attempt to increase buffer concentration to 10 mM in order to better maintain the pH of the mobile phase overloaded the detector working in negative detection mode. Addition of triethanolamine further increased the buffer pH. Taking into consideration that pH higher than 8.0 is detrimental for the column and can easily dissolve the stationary phase, it was decided to work at pH 6.5, which was stable and easy to maintain. Addition of methanol to mobile phase didn't make any difference on formaldehyde/sulfite pair, but broadened and pushed the sulfate peak further. It was therefore decided to work with 1.0 mM Potassium phthalate buffer pH 6.5 as a mobile phase. Several other parameters, such as column type, injection volume and detection wavelength were varied to find the optimum conditions for getting a sharp peak and a good separation of sulfates and sulfites and sulfites from formaldehyde peak present in the solvent. Parameters investigated are listed in Table 2.

*Table 2: Parameters investigated and changed in order to adapt a method for “Simultaneous determination of sulfite, sulfate, and hydroxymethanesulfonate in atmospheric waters by ion-pair HPLC technique” by Zuo et al. to determination of sulfites and sulfates on the surface of environmental samples investigated in this work [19].*

	Method by Zuo et al.	Parameters investigated	Parameters chosen
<b>Column</b>	150 mm C18 Column, Particle size: 5 $\mu$ m, I.D. 4.60 mm	250 mm Restek Ultra Column C18, Particle size: 5 $\mu$ m, I.D. 4.60 mm  250 mm Acclaim 120 Column C18, Particle size: 3 $\mu$ m, I.D. 3 mm	250 mm Restek Ultra Column C18, Particle size: 5 $\mu$ m, I.D. 4.60 mm
<b>Column coating</b>	1.0 mM cetylpyridinium chloride in 7% ACN solution		1.0 mM cetylpyridinium chloride in 7% ACN solution
<b>Mobile phase</b>	potassium hydrogen phthalate buffer 0.5 mM-0.015% triethanolamine-3% methanol	triethanolamine: 0%, 0.015%  potassium hydrogen phthalate buffer: 0.5 mM, 1mM, 10 mM  % Methanol: 0%, 1%, 3% 5%	1 mM potassium hydrogen phthalate buffer
<b>pH</b>	7.9	6.0, 6.5, 7.0, 7.5	6.5
<b>Flow rate</b>	1.0 ml/min	0.5 ml/min, 1 ml/min	1.0 ml/min
<b>Detection</b>	negative UV-Vis detection at 265 nm	negative UV-Vis detection at 265nm, 255 nm	negative UV-Vis detection at 255 nm

<b>Time</b>	15 min	10 min, 15 min	15 min
<b>HPLC mode</b>	isocratic elution		isocratic elution
<b>Temperature</b>	23 °C	20 °C, 23 °C, 26 °C, 30°C, 35°C	23 °C
<b>Injection volume</b>	10 µL	10, 15, 20 µL	10 µL
<b>Sulfite-stabilizing reagent</b>	none	methanol 10 % Formalin: 0.5%, 1%, 5%	1% Formalin

Finally, the following chromatographic conditions were determined as optimum: 25 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm column which was dynamically coated with 1.0 mM cetylpyridinium chloride in 7% acetonitrile solution to produce a charged surface as recommended by Zuo et al. [19]. Mobile phase used: 1 mM potassium hydrogen phthalate buffer at pH 6.5 at a flow rate of 1.0 ml/min with negative UV-Vis detection at 255 nm in 15 min.

Figure 3 displays three chromatograms offset for clarity: 1% Formalin, 50/50 K<sub>2</sub>SO<sub>3</sub>/K<sub>2</sub>SO<sub>4</sub>, and Hagavatn extract obtained after aging the dust for 1 hr in 175 ppm SO<sub>2</sub>. The peak for SO<sub>3</sub><sup>2-</sup> is observed at 2.8 minutes and SO<sub>4</sub><sup>2-</sup> peak is observed at 5.6 min. Both peaks demonstrate a high number of theoretical plates: for Hagavatn extract they are equal to 2235 for SO<sub>3</sub><sup>2-</sup> and 884 for SO<sub>4</sub><sup>2-</sup>. Two small peaks around 2.3 and 2.9 min belong to formaldehyde and are separated from the peak for SO<sub>3</sub><sup>2-</sup> at 2.8 min. The sulfite peak present in the form of HMS eluted rather closely to the formaldehyde peak. Therefore, in order to preserve separation, it was decided to stay with a 250 mm long column.

### 3.2 Extraction Optimization

Different parameters, such as extraction time and extraction techniques (shaking vs sonication), as well as volume of the extracting solution, were studied to insure maximum extraction of sulfites and sulfates. Solution stability was investigated to assess the time window during which the analysis can be performed.

### 3.2.1 Dissolution

The dissolution time of up to 40 min of Hagavatn extract was investigated using sonication. Sulfites and sulfates immediately dissolved as shown in Figure 4. Similar results were obtained with mechanical shaking, and 10 minutes sonication was found to be an appropriate dissolution technique.

### 3.2.2 Recovery

Recovery studies were intended to prove that maximum amount of the sulfites and sulfates are extracted. Three consecutive extractions with 1 mL of 1 % Formalin were evaluated for the amount of sulfites and sulfates after the sample was aged by 175 ppm SO<sub>2</sub> for 10 min, 30 min, 1 hr, and 2hr. The criteria is less than 5 % of the product can be left unaccounted. As can be observed from Table 3, all of the sulfates are extracted from the surface of Hagavatn dust after the first extraction with 1 mL of 1% Formalin. As for the sulfites, two extractions with 1ml of 1% Formalin are necessary. The third extraction represents from 0 to 3.9 % of the total amount of SO<sub>3</sub><sup>2-</sup> extracted and therefore is not required based on the established criteria. Method demonstrates efficient recovery after only two extractions. As a result, it was decided to extract sulfites and sulfates with 1 mL of 1% Formalin, wash the remaining dust with another 1 mL of 1% Formalin and, using the same syringe, filter and combine the solution.

Table 3: Recovery results for 3 consecutive extracts of the sample of Hagavatn aged in 175 ppm SO<sub>2</sub> for various time periods. Extraction with 1mL of 1% Formalin.

Sample	Hagavatn aged with 175 ppm SO <sub>2</sub>			
Time	10 min	30 min	1hr	2hr
<b>Extract 1</b> SO <sub>3</sub> <sup>2-</sup> (ppm)	64.1	69.3	71.7	78.4
<b>Extract 2</b> SO <sub>3</sub> <sup>2-</sup> (ppm)	14.9	11.9	19.9	16.6
<b>Extract 3</b> SO <sub>3</sub> <sup>2-</sup> (ppm)	0.1	3.3	0	1.6
% SO <sub>3</sub> <sup>2-</sup> in the 3 <sup>rd</sup> extract	0.1	3.9	0.00	1.2
% recovery after 3 extract	99.9	96.1	100.00	98.0
<b>Extract 1</b>				



SO <sub>4</sub> <sup>2-</sup> (ppm)	3.4	3.7	3.7	8.5
<b>Extract 2</b> SO <sub>4</sub> <sup>2-</sup> (ppm)	0	0	0	0
<b>% recovery</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>	<b>100.00</b>

299

### 300 3.2.3 Solution stability

301 In order to observe how analytes of interest changes over time, Hagavatn extract was prepared and  
302 injected into the HPLC system. The same solution was injected after 3, 5, 7, and 10 days. Solution  
303 stability results obtained from injecting a sample of 158.2 mg of Hagavatn aged for 10 min are shown in  
304 Figure 5. Solution stability studies indicate that both sulfites and sulfates remain stable up to 10 days,  
305 which means that a sample can be easily collected and extracted to be kept for later analysis, which is  
306 indispensable during geological sampling when the analyzing facility might be far away from the  
307 sampling location. Moreover, in separate experiments a 165 mg sample of Hagavatn aged with SO<sub>2</sub> for  
308 1hr was checked for stability after 10 days and 3 months. Percent change in ppm concentration for  
309 sulfites was established at 4.5% after 10 days and 3.2% in 3 months; as for sulfates 5.4 % change was  
310 observed after both 10 days and 3 months. Thus, the results indicate that dust samples aged with SO<sub>2</sub> and  
311 stabilized with 1% Formalin are stable for long periods (at least up to 3 months). Exceptional stability of  
312 solutions is very important in field campaigns as it makes it possible to collect and stabilize a sample on  
313 the go but analyze it later in the laboratory.

### 314 3.3 Validation of Analytical Performance

315 The developed method was validated for specificity, limit of detection and limit of quantitation, linearity  
316 and range, injection repeatability, and robustness.

#### 317 3.3.1 Specificity

318 To ensure that the peak response is due to only one component and no co-elution occurs, a solution of  
319 Hagavatn dust aged in 175 ppm SO<sub>2</sub> for 10 min and extracted in 1% Formalin was analyzed by Waters

2695 HPLC system equipped with Diode Array Detector using Empower software. Thus, specificity was evaluated as spectral purity. In peak purity testing the software compares the spectrum from each data point within the peak against the peak apex spectrum. Two parameters are evaluated: purity threshold, which accounts for the presence of non-ideal and solvent-induced spectral changes, and purity angle. When the purity angle exceeds purity threshold, a detectable impurity is present within a single chromatographic peak.

A solution of 165 mg of Hagavatr dust aged in 175 ppm SO<sub>2</sub> for 10 min and extracted in 1% Formalin showed no interfering peaks. All peaks were well separated from the analyte peaks. Peak purity was proved by purity threshold exceeding the purity angle for both sulfite and sulfate peaks.

### *3.3.3 Limit of detection (LOD) and limit of quantitation (LOQ)*

Limits of detection for sulfites and sulfates were investigated to determine the lowest concentration of sulfites and sulfates that can be detected but not quantified. It was based on a signal-to-noise ratio  $S/N \geq 3$ . Limits of quantitation were studied to determine the lowest levels of the analyte concentrations that can be quantified and were determined by the concentrations corresponding to signal-to-noise ratio  $S/N \geq 10$ .

The LOD for determination of sulfites was found to be 0.5 µg/mL of K<sub>2</sub>SO<sub>3</sub> (0.32 µg/mL of SO<sub>3</sub><sup>2-</sup> ion). This value is 5 times lower than the 1.52 µg/mL of SO<sub>3</sub><sup>2-</sup> ion reported as LOD by Zuo et al. (corresponding to 19 µM of SO<sub>3</sub><sup>2-</sup> ion), but in a good agreement with the limit of detection of hydroxymethylsulfonate (HMS) reported at 0.42 µg/mL (corresponding to 3.8 µM of HMS ion). This is to be expected, as the SO<sub>3</sub><sup>2-</sup> in our case elutes as a HMS complex. The reason for improved detection limit is earlier elution of SO<sub>3</sub><sup>2-</sup> in the form of HMS at around 3 min instead of 7.5 min as a free sulfite ion using the original method [19]. Earlier elution prevents peak broadening and improves LOD and LOQ. LOQ for determination of SO<sub>3</sub><sup>2-</sup> ion was found to be 1 µg/mL of K<sub>2</sub>SO<sub>3</sub> (0.64 µg/mL of SO<sub>3</sub><sup>2-</sup> ion).

LOD for determination of sulfates was found to be 1  $\mu\text{g/mL}$  of  $\text{K}_2\text{SO}_4$  (0.68  $\mu\text{g/mL}$  of  $\text{SO}_4^{2-}$  ion). This value is in excellent agreement with the limit of detection for  $\text{SO}_4$  ion reported by Zuo et al. and established at 6.7  $\mu\text{M}$   $\text{SO}_4^{2-}$  ion which is 0.64  $\mu\text{g/mL}$  of  $\text{SO}_4^{2-}$ . LOQ for determination of sulfates was found to be 5  $\mu\text{g/mL}$  of  $\text{K}_2\text{SO}_4$  (3.38  $\mu\text{g/mL}$  of  $\text{SO}_4^{2-}$  ion).

### 3.3.2 Linearity and range

Linearity proves that the detector response is directly proportional to the concentrations of the analyte in the sample, and range provides an interval for which the procedure is linear. Calibration ranges were defined as to include possible concentrations of sulfites and sulfates that can be found on the surface of mineral dust. This approach was based on preliminary results used to frame the order of magnitude of typical  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  surface concentrations. To investigate linearity for extracted sulfites, six different concentrations of  $\text{K}_2\text{SO}_3$  were prepared from 1000  $\mu\text{g/mL}$  stock solution of  $\text{K}_2\text{SO}_3$  in the range 10 – 300  $\mu\text{g/mL}$  (corresponding to 6  $\mu\text{g/mL}$  to 191  $\mu\text{g/mL}$  of  $\text{SO}_3^{2-}$  ion). To explore linearity for sulfates, six different concentrations of  $\text{K}_2\text{SO}_4$  were prepared from 1000  $\mu\text{g/mL}$  stock solution of  $\text{K}_2\text{SO}_4$  in the range 5-150  $\mu\text{g/mL}$  and injected into the HPLC system (corresponding to 3  $\mu\text{g/mL}$  to 101  $\mu\text{g/mL}$  of  $\text{SO}_4^{2-}$  ion).

Calibration plots were constructed every day in order to insure accurate identification of sulfates and sulfites in dust. Moreover, since the detection is achieved in negative mode (i.e. the mobile phase absorbs UV light and the peaks are “observed” when a compound lacking chromophore is passing through the column) the absorbance of the mobile phase depends on the concentration of the UV absorbing buffer. Even slightest variations in buffer concentration can change the slope of the calibration plot. Therefore, it is crucial to construct a new calibration curve every time a freshly-made buffer is introduced into the system. Nevertheless, it is important to keep in mind that even though the slope of the calibration curve may change the curve remains linear within the range. Therefore, the daily-constructed curve can be used for quantitation purposes as long as the same batch of buffer is used. Calibration curves from a typical experimental day are represented in Figure 6; calibration curve equations, coefficients of determination

( $R^2$ ) and root mean square errors are provided in Table 4. While  $R^2$  shows how close the data are to the fitted regression line, root mean square error can be interpreted as the average distance of a data point from the fitted line, measured along a vertical line.

*Table 4: Analytical Performance: Range, Linearity (calibration curve equation, coefficient of determination, root mean square error) and Injection Repeatability (expressed as %RSD for 6 consecutive injections of a solution of 20 ppm  $K_2SO_3$  and 10 ppm  $K_2SO_4$ ).*

	Test range ( $\mu\text{g/mL}$ )	Calibration curve	$R^2$	Root Mean Square Error	% RSD n=6
<b>Sulfites</b>	6-191	$y = 0,06x + 0,0489$	1.0000	0.024	4.7
<b>Sulfates</b>	3-101	$y = 0,1217x - 0,0036$	0.9998	0.079	8.7

#### 3.3.4 Injection repeatability

Injection repeatability was tested to measure the sensitivity of the method towards errors coming from the instrument itself: the column, the detector, the injector, the integration device. To evaluate injection repeatability a solution of a mixture of 20 ppm  $K_2SO_3$  and 10 ppm  $K_2SO_4$  were injected into the HPLC system 6 times and evaluated for area % relative standard deviation (%RSD). Injection repeatability for a solution of 20 ppm  $K_2SO_3$  and 10 ppm  $K_2SO_4$  was calculated to be 4.7 % for sulfites and 8.7% for sulfates (Table 4).

#### 3.3.5 Robustness

Robustness of an analytical procedure is a measure of its capacity to remain unaffected by small but deliberate variations in parameters listed in the procedure. In this study “remain unaffected” was defined as no change of the detected amount of the analyte in a sample in spite of the variation of the method parameter. Stability of the method was evaluated with respect to variations of the internal factors of the method such as pH of the mobile phase pH ( $6.5 \pm 0.5$ ), column temperature ( $23 \pm 3$ ), different column lots (Lot #160210E and Lot #130505R) and 1 month old vs 4 months column. Changes in temperature, pH, column age (up to 4 months) and lot number (Lot #160210E and Lot #130505R) did not affect the

amounts of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions determined in the solutions, as they fell within injection variations, where 4.7 % RSD and 8.7 % RSD were reported for sulfites and sulfates respectively (Table 5). This is important, as it means that small fluctuations in pH that can come from buffer preparation will not affect quantification. Stability towards temperature changes suggests that method could be used in instruments not equipped with temperature control function. Stability of the column for at least 4 months and robustness towards change of column (different batches) assures normal use of the method.

*Table 5: Method robustness results. Small changes in method parameters were introduced and evaluated as percent change for the amounts of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions in samples of Hagavatn dust as compared to their determination under original conditions (marked by asterisk).*

Sample	T (C°)	pH	Column Lot#	Column age (months)	Amount for $\text{SO}_3^{2-}$ (ppm)	% Change	Amount for $\text{SO}_4^{2-}$ (ppm)	% Change
Hagavatn 194 mg aged for 1hr*	23	6.5	160210E	1	27.5		10.45	
Hagavatn 194 mg aged for 1hr	20	6.5	160210E	1	26.7	-2.9	10.82	3.5
Hagavatn 194 mg aged for 1hr	26	6.5	160210E	1	27.2	-1.1	10.45	0.0
Hagavatn 158 mg aged for 10 min*	23	7.0	160210E	1	22.7		3.6	
Hagavatn 158 mg aged for 10 min	23	6.5	160210E	1	23.09	1.7	3.7	2.8
Hagavatn 158 mg aged for 10 min	23	6.0	160210E	1	21.7	-4.4	3.4	-5.6
Hagavatn 165 mg aged for 1hr*	23	6.5	160210E	1	27.8		8.2	
Hagavatn 165 mg aged for 1hr	23	6.5	130505R	1	26.6	-4.5	8.6	5.4
Hagavatn 165 mg aged for 1hr*	23	6.5	160210E	1	27.8		8.2	
Hagavatn 165 mg aged for 1hr	23	6.5	160210E	4	26.9	-3.2	8.6	5.4

### 3.4 Validation of the Sample Preparation and Extraction Performance. Method

#### Reproducibility

The developed method was further validated for sample preparation and extraction reproducibility. It was decided to use the protocol for “kinetics study” to evaluate reproducibility because in comparison with “environmental sampling” protocol it has a supplementary step of dust ageing that can introduce additional errors.

Sample preparation and extraction reproducibility studies were conducted to evaluate the sensitivity of the method towards errors that may result from the combination of steps starting from ageing, extraction and preparation of the samples to their subsequent analysis by HPLC instrument. To evaluate sample preparation and extraction reproducibility for the “kinetics study” protocol, eight samples of Hagavtn volcanic dust were aged with 175 ppm SO<sub>2</sub> for 1 hr and extracted in 1% Formalin. The solutions were injected into HPLC system and %RSD for mass of sulfites/sulfates per square meter of dust was calculated. The %RSD for reproducibility (that includes ageing and extraction of sulfites/sulfates) as reported in Table 6 was found to be 16.1% for sulfites and 32.0% for sulfates. It is important to stress out that reproducibility for ageing and extraction of sulfites/sulfates in a dust sample depends on heterogeneity of the sample. Like most of the natural mineral dusts, Hagavtn volcanic dust represents a highly heterogeneous sample and variations in adsorption/transformation of SO<sub>2</sub> gas by its different components are expected. Many studies use a combination of different oxides as proxies for natural samples. In this case %RSD for reproducibility would be expected to be lower as the sample composition is well-defined and ageing process more reproducible. Nevertheless, the importance of using natural samples cannot be undermined, as they often demonstrate different adsorption patterns when compared to the mixture of mineral oxides used as proxies [26], [27], [22]. For example, when studying adsorption of SO<sub>2</sub> on individual oxides and comparing them to their mixture Zhang et al. observed that the reactivity of the mixture is twice as high as the reactivity of individual components [3]. In addition, using simple

oxides as proxies instead of natural samples undermines the importance of complex mineralogy of natural samples.

*Table 6: Sample preparation and extraction reproducibility study for samples of Hagavatu aged in 175 ppm SO<sub>2</sub> for 1 hr. Extraction with 1mL of 1% Formalin.*

Preparation	Date of sample preparation	Sample mass (mg)	Concentration SO <sub>3</sub> <sup>2-</sup> (µg/m <sup>2</sup> )	Concentration SO <sub>4</sub> <sup>2-</sup> (µg/m <sup>2</sup> )
1	April 8	146.5	47.3	47.0
2	April 8	134.0	59.3	25.2
3	April 12	89.0	66.4	28.7
4	April 12	194.0	67.1	20.5
5	April 15	137.3	69.6	22.7
6	April 15	138.6	56.2	39.1
7	April 16	158.0	75.7	26.1
8	April 16	165.4	79.3	22.5
<b>Average</b>			<b>65.1</b>	<b>29.0</b>
<b>Standard Deviation</b>			<b>10</b>	<b>9</b>
<b>%RSD</b>			<b>16.1</b>	<b>32.0</b>

### 3.5 Method Summary

The validated method is summarized in Table 7. If “environmental sampling” is the desired purpose of the method, ageing is not required and one can start the protocol from the extraction section. For “kinetics study”, ageing is followed by extraction and HPLC analysis. Mass of the sample introduced into the reactor will depend on the specific surface area of the dust. In case of high specific surface area a higher SO<sub>2</sub> adsorption might be expected and therefore a smaller sample mass can be used for extraction. Likewise, if the specific surface area of the dust is low an increased mass might be necessary in order to detect sulfites/sulfates on the surface. Thus, the method can be easily adapted to different dust samples.

436 *Table 7: Summary of the validated conditions used to age, extract and quantify sulfites and sulfates in the sample of dust aged*  
 437 *with SO<sub>2</sub> gas.*

Ageing		Extraction		Chromatographic conditions	
<b>Dust sample mass</b>	100.0-200.0 mg	<b>Extracting solution</b>	1% Formalin in 10% MeOH/water	<b>Column</b>	250 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm
<b>SO<sub>2</sub> concentration</b>	175 ppm	<b>Mode of dissolution</b>	sonication	<b>Column modification</b>	coated with 1.0 mM cetylpyridinium chloride in 7% ACN solution
<b>SO<sub>2</sub> flow</b>	100 cm <sup>3</sup> /min	<b>Time of dissolution</b>	10 min	<b>Mobile phase</b>	1 mM potassium hydrogen phthalate buffer at pH 6.5
<b>RH</b>	30%	<b>Filter</b>	0.45 µm pore size 30 mm diameter Whatman filter	<b>Flow rate</b>	1.0 ml/min
<b>Time</b>	10 min - 1 hr	<b>Total volume of extracting solution</b>	2 mL	<b>Detection</b>	negative UV-Vis detection at 255 nm
				<b>Time</b>	15 min

438

## 439 3.6 Method Application

### 440 3.6.1 Application of the method to natural samples

441 Samples of Hagavatn volcanic dust and Gobi desert dust were tested for sulfites and sulfates  
 442 using the “environmental sampling” method for extraction and quantification described above. Samples  
 443 were not aged in the laboratory, but could have been previously subjected to SO<sub>2</sub> gas. In case of  
 444 Hagavatn, the samples were certainly exposed to SO<sub>2</sub> gas during volcanic eruption. As for aeolian  
 445 samples of Gobi dust, it is also likely that during its long-range transfer the dust encountered industrially  
 446 polluted areas of China known to contain high levels of SO<sub>2</sub> [11]. Six samples of natural desert dust



447 ranging from 124.2 to 144.5 mg and seven Hagavatn volcanic dusts ranging from 110.6 to 505.4 mg were  
448 tested to determine their  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ion surface concentrations. As can be seen from Table 8, the  
449 extraction of both Gobi and Hagavatn surface dust did not evidence sulfites above the limit of detection of  
450  $0.32 \mu\text{g/mL}$  for  $\text{SO}_3^{2-}$  ion. Note, that the absolute amount of sulfites and sulfates are directly dependent  
451 on the sample mass since this parameter drives the effective surface area of the considered sample. As for  
452 the sulfates, although the amounts on the surface of Hagavatn samples were above the LOD level of  $0.68$   
453  $\mu\text{g/mL}$  of  $\text{SO}_4^{2-}$  for five out of seven samples, they remained under the LOQ level of  $3.38 \mu\text{g/mL}$  of  $\text{SO}_4^{2-}$   
454 ion even when the mass of the sample was increased to 505.4 mg. Furthermore, in terms of absolute  
455 amounts of sulfates detected on Hagavatn dust, increasing the mass of the dust sample to 505.4 mg  
456 increases its total surface area and therefore decreases the minimum amount of  $\text{SO}_4^{2-}$  ion per meter square  
457 that could be detected on the surface. The fact that the amount of sulfates recorded after extraction of  
458 113.5 mg sample is the same as on the 505.4 mg sample suggests that sulfates are not coming from  
459 Hagavatn sample. A small amount of sulfates determined in Hagavatn and Gobi dust samples could have  
460 also come from 1% Formalin extracting solution that contains traces of sulfate impurities. The amount of  
461 sulfates in 1% Formalin solution was measured at  $1 \mu\text{g/mL}$ , which is under LOQ limit. The lack of  
462 sulfates on the surface of Hagavatn volcanic dust might be explained by the fact that sulfates were  
463 dissolved from the surface of the natural sample by rain or surface water, as the sample is coming from  
464 the lava field formed about 4,000 years ago and is subjected to fluctuating water levels [21], [28]. As for  
465 Gobi dust, it displayed a considerable amount of sulfates averaging at  $15.4 \pm 1.3 \mu\text{g/m}^2$ . Interestingly,  
466 method reproducibility for extraction and quantification of sulfates on the surface of Gobi dust was  
467 evaluated at 8.4 %RSD for 6 samples, which is three times lower than 32.0% RSD for sample preparation  
468 and extraction reproducibility determined earlier for 8 Hagavatn samples used for validation of “kinetics  
469 study” protocol (see section 3.4, Table 6). In addition, one should keep in mind that 8.4% RSD for Gobi  
470 samples was calculated based on average amount of  $\text{SO}_4^{2-}$  of  $15.4 \mu\text{g/m}^2$ , while higher average of  $29.0$   
471  $\mu\text{g/m}^2$  was used for calculation of 32.0% RSD for Hagavatn samples. The improvement in method

reproducibility for “environmental sampling” most certainly comes from the fact that no artificial ageing was performed.

*Table 8: Results of method reproducibility study for determination of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  ions in Hagavatn and Gobi natural samples. Note, that samples were not subjected to laboratory ageing. LOD and LOQ for sulfites and sulfates for each sample mass expressed in  $\mu\text{g}/\text{m}^2$  were calculated from corresponding sample's mass, specific surface area, extraction volume (2ml) and the values for LOQ and LOD expressed in  $\mu\text{g}/\text{mL}$  measured earlier (LOD for  $\text{SO}_3^{2-}=0.32 \mu\text{g}/\text{mL}$ , LOQ for  $\text{SO}_3^{2-}=0.64 \mu\text{g}/\text{mL}$ ; LOD for  $\text{SO}_4^{2-}=0.68 \mu\text{g}/\text{mL}$ , LOQ for  $\text{SO}_4^{2-}=3.38 \mu\text{g}/\text{mL}$ ). Determination of the absolute amounts of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  requires the observed concentrations of corresponding ions to be equal or more than LOQ.*

Sample	mass (mg)	SSA <sub>BET</sub> ( $\text{m}^2/\text{g}$ )	LOD for $\text{SO}_3^{2-}$ ( $\mu\text{g}/\text{m}^2$ )	LOQ for $\text{SO}_3^{2-}$ ( $\mu\text{g}/\text{m}^2$ )	Amount of $\text{SO}_3^{2-}$ ( $\mu\text{g}/\text{m}^2$ )	LOD for $\text{SO}_4^{2-}$ ( $\mu\text{g}/\text{m}^2$ )	LOQ for $\text{SO}_4^{2-}$ ( $\mu\text{g}/\text{m}^2$ )	Amount of $\text{SO}_4^{2-}$ ( $\mu\text{g}/\text{m}^2$ )
Gobi	136.2	$10.5 \pm 2.0$	0.45	0.90	< LOD	0.95	4.73	14.1
Gobi	138.5	$10.5 \pm 2.0$	0.44	0.88	< LOD	0.94	4.65	14.8
Gobi	139.5	$10.5 \pm 2.0$	0.44	0.87	< LOD	0.93	4.62	16.5
Gobi	126.2	$10.5 \pm 2.0$	0.48	0.97	< LOD	1.03	5.10	14.4
Gobi	144.5	$10.5 \pm 2.0$	0.42	0.84	< LOD	0.90	4.46	15.5
Gobi	124.2	$10.5 \pm 2.0$	0.49	0.98	< LOD	1.04	5.18	17.2
Average								15.4
STD								1.3
% RSD								8.4
Hagavatn	116.8	$4.5 \pm 1.1$	1.22	2.44	< LOD	2.59	12.86	< LOD
Hagavatn	113.0	$4.5 \pm 1.1$	1.26	2.52	< LOD	2.67	13.26	< LOQ
Hagavatn	125.4	$4.5 \pm 1.1$	1.13	2.27	< LOD	2.41	11.98	< LOQ
Hagavatn	113.5	$4.5 \pm 1.1$	1.25	2.51	< LOD	2.66	13.24	< LOQ
Hagavatn	190.0	$4.5 \pm 1.1$	0.75	1.50	< LOD	1.59	7.91	< LOD
Hagavatn	110.6	$4.5 \pm 1.1$	1.29	2.57	< LOD	2.73	13.58	< LOQ
Hagavatn	505.4	$4.5 \pm 1.1$	0.28	0.56	< LOD	0.60	2.97	< LOQ
Average								NA
STD								NA
% RSD								NA

### 3.6.2 Application of the method to aged samples

In the next step, following “kinetics study” protocol samples of 134.0 mg of Hagavatn and 115.0 mg of Gobi dusts were exposed to 175 ppm of gaseous SO<sub>2</sub> for 1 hour at room temperature and under 30 % RH. After extraction, the amount of sulfites formed on the surface was calculated at 54.4±8.6 µg/m<sup>2</sup> (µg of sulfites per m<sup>2</sup> specific surface area) for Hagavatn and 27.0±4.3 µg/m<sup>2</sup> for Gobi desert dust (Figure 7). The amount of sulfates formed after 1 hr ageing was estimated at 25.2±8.1 µg/m<sup>2</sup> (µg of sulfate per m<sup>2</sup> specific surface area) for Hagavatn and 53.4±17.0 µg/m<sup>2</sup> for Gobi desert dust. Note, that blank subtraction of 15.4±1.3 µg/m<sup>2</sup> (µg of sulfates per m<sup>2</sup> specific surface area) was applied to quantify the amount of sulfates formed on Gobi dust during laboratory ageing. From this experiment it is evident that after 1 hr of SO<sub>2</sub> exposure volcanic dust accumulate a higher amount of sulfites than desert dust and a lower amount of sulfates. From earlier studies it was proposed that SO<sub>2</sub> gas reacts on the surface of the volcanic dust and forms sulfites or bisulfites, which are then converted to sulfates [17], [15]. It is possible that certain mineralogical compounds on the surface of Gobi desert dust are contributing to a more efficient conversion of sulfites to sulfates. A larger sample distribution would be required to confirm the trend and elucidate how the surface chemical composition may influence the respective kinetics of sulfites and sulfates.

To evaluate how relevant the artificial ageing is to the processes encountered in real atmosphere, results obtained after a one-hour laboratory ageing of Gobi dust with 175 ppm SO<sub>2</sub> were compared to the field measurements of sulfates performed during a severe dust storm in China. Similarly, results from Hagavatn ageing were compared to leachate measurements of ashes coming from Stromboli volcano in Italy and Soufriere Hills Volcano, Montserrat.

In spring of 2002 a dust storm originating from Gobi desert in Mongolia and Taklimakan desert in western China spread over China, Korea and Japan [29]. On March 20 2002, the dust peak concentrations over Beijing reached 10.9 mg/m<sup>3</sup> (mg of dust per m<sup>3</sup> of air) [29]. Using the same particle matter concentrations as the ones reported over Beijing and the specific surface area of Gobi dust

determined in the current study ( $10.5 \text{ m}^2/\text{g}$ ), our results of  $53.4 \pm 17.0 \text{ } \mu\text{g}/\text{m}^2$  of sulfates on the surface of Gobi dust corresponds to  $6.07 \pm 1.9 \text{ } \mu\text{g}/\text{m}^3$  ( $\mu\text{g}$  of sulfates present in  $1 \text{ m}^3$  of gas), considering a dust density of  $10.9 \text{ mg}/\text{m}^3$  as reported by [25]. This result is in the same order of magnitude than the volume concentration of sulfates determined by [25] from Ion Chromatography analysis of airborne samples: from 18 to  $19 \text{ } \mu\text{g}/\text{m}^3$ . As for the samples of volcanic origin, Bagnato et al. measured the amount of sulfates on the surface of ash coming from Stromboli volcano, Italy. The results showed a vast variability from 7 to  $55,000 \text{ } \mu\text{g}/\text{g}$  ( $\mu\text{g}$  of sulfates per g of volcanic sample) [30]. High variability in the amount of sulfates in ash leachates was noted by Edmonds et al. (from 34 to  $9,280 \text{ } \mu\text{g}/\text{g}$ ) at Soufriere Hills Volcano, Montserrat [31]. The amount of sulfate per specific surface determined on Hagavtn volcanic dust ( $25.2 \pm 8.1 \text{ } \mu\text{g}/\text{m}^2$ ), after 1 hr ageing, corresponds to  $115 \pm 36 \text{ } \mu\text{g}/\text{g}$ . ( $\mu\text{g}$  of sulfates per g of dust). Results retrieved from our study fall within the range of concentrations determined by Bagnato et al. and Edmonds et al [30], [31]. Note that for elevated concentrations of sulfates on the surface of volcanic dust, samples can be easily diluted in higher volumes of extraction solution, in our case 1% Formalin.

## 4.0 CONCLUSIONS

A reversed-phase HPLC method was successfully developed for the assay of sulfites and sulfates on the surface of dust. A method was developed on a 25 mm Restek Ultra Column C18, Particle size:  $5 \text{ } \mu\text{m}$ , I.D.  $4.60 \text{ mm}$  column which was dynamically coated with  $1.0 \text{ mM}$  cetylpyridinium chloride in 7% acetonitrile solution to produce a charged surface as recommended by Zuo et al [19]. Mobile phase used:  $1 \text{ mM}$  potassium hydrogen phthalate buffer at pH 6.5 at a flow rate of  $1.0 \text{ ml}/\text{min}$  with negative UV-Vis detection at  $255 \text{ nm}$  in 15 min. The developed method was validated for the specificity, LOD and LOQ, linearity and range, robustness, injection repeatability and reproducibility for sample preparation and extraction. In addition, the sampling method is easy and fast, and does not require expensive or particularly dangerous solvents. Besides, the extracted solution displays excellent stability, which is very important in remote sampling during geological expeditions. Samples can be extracted on site and analyzed days after sampling, provided they are kept in cool temperature conditions. We would like to

stress out that in case of “environmental sampling” the method should only be applied if the sample is believed to be recently subjected to SO<sub>2</sub> gas and if quantification of sulfites is desired. Due to the conversion of sulfites to sulfates, the former are not expected to stay on the surface of dust for a long time [20]. An examples of missions that could use the method developed could be: identification of sulfites and sulfates on fresh volcanic ash samples following an eruption, identification of sulfates and sulfites in desert dust samples that pass through industrially polluted areas, as well as laboratory investigation of sulfite and sulfate formation on the surface of natural dusts of different origins. Validity of ageing procedure in the reference to natural gas-particle interactions was discussed. The developed method was successfully applied to assay the amount of sulfites and sulfates formed on the surface of Hagavathn and Gobi dusts both in natural environmental settings and after artificial ageing. Sulfates in the amount of 15.4±1.3 µg/m<sup>2</sup> were detected on the surface of unexposed Gobi dust. As for the laboratory-aged samples, both sulfites and sulfates were detected on the surface of the two dusts. Sulfates were found to be formed in higher quantities on the surface of Hagavathn volcanic dust in comparison with Gobi desert dust sample (54.4±8.6 µg/m<sup>2</sup> of SO<sub>3</sub><sup>2-</sup> ion for Hagavathn versus 27.0±4.3 µg/m<sup>2</sup> of SO<sub>3</sub><sup>2-</sup> ion for Gobi desert dust), while the opposite trend was observed for sulfates (25.2±8.1 µg/m<sup>2</sup> of SO<sub>4</sub><sup>2-</sup> for Hagavathn and 53.4±17 µg/m<sup>2</sup> of SO<sub>4</sub><sup>2-</sup> for Gobi desert dust).

## 5.0 ACKNOWLEDGMENTS

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- [1] D.S. Stevenson, C.E. Johnson, E.J. Highwood, V. Gauci, W.J. Collins, R.G. Derwent, Atmospheric impact of the 1783–1784 Laki eruption: Part I Chemistry modelling, *Atmos. Chem. Phys.* 3 (2003) 487–507. <https://doi.org/10.5194/acp-3-487-2003>.
- [2] E. Ilyinskaya, A. Schmidt, T.A. Mather, F.D. Pope, C. Witham, P. Baxter, T. Jóhannsson, M. Pfeffer, S. Barsotti, A. Singh, P. Sanderson, B. Bergsson, B. McCormick Kilbride, A. Donovan, N. Peters, C. Oppenheimer, M. Edmonds, Understanding the environmental impacts of large fissure eruptions: Aerosol and gas emissions from the 2014–2015 Holuhraun eruption (Iceland), *Earth and Planetary Science Letters*. 472 (2017) 309–322. <https://doi.org/10.1016/j.epsl.2017.05.025>.
- [3] H. He, Y. Wang, Q. Ma, J. Ma, B. Chu, D. Ji, G. Tang, C. Liu, H. Zhang, J. Hao, Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days, *Scientific Reports*. 4 (2014) 4172. <https://doi.org/10.1038/srep04172>.
- [4] E.C. Maters, P. Delmelle, M.J. Rossi, P.M. Ayris, Reactive Uptake of Sulfur Dioxide and Ozone on Volcanic Glass and Ash at Ambient Temperature, *J. Geophys. Res.-Atmos.* 122 (2017) 10077–10088. <https://doi.org/10.1002/2017JD026993>.
- [5] M. Ullerstam, R. Vogt, S. Langer, E. Ljungstrom, The kinetics and mechanism of SO<sub>2</sub> oxidation by O<sub>3</sub> on mineral dust, *Phys. Chem. Chem. Phys.* 4 (2002) 4694–4699. <https://doi.org/10.1039/b203529b>.
- [6] A.L. Goodman, P. Li, C.R. Usher, V.H. Grassian, Heterogeneous Uptake of Sulfur Dioxide On Aluminum and Magnesium Oxide Particles, *J. Phys. Chem. A*. 105 (2001) 6109–6120. <https://doi.org/10.1021/jp004423z>.
- [7] E. Harris, B. Sinha, S. Foley, J.N. Crowley, S. Borrmann, P. Hoppe, Sulfur isotope fractionation during heterogeneous oxidation of SO<sub>2</sub> on mineral dust, *Atmospheric Chemistry and Physics*. 12 (2012) 4867–4884. <https://doi.org/10.5194/acp-12-4867-2012>.
- [8] P.M. Ayris, A.F. Lee, K. Wilson, U. Kueppers, D.B. Dingwell, P. Delmelle, SO<sub>2</sub> sequestration in large volcanic eruptions: High-temperature scavenging by tephra, *Geochimica et Cosmochimica Acta*. 110 (2013) 58–69. <https://doi.org/10.1016/j.gca.2013.02.018>.
- [9] D. Schmauss, H. Keppler, Adsorption of sulfur dioxide on volcanic ashes, *American Mineralogist*. 99 (2014) 1085–1094. <https://doi.org/10.2138/am.2014.4656>.
- [10] E. Bagnato, A. Aiuppa, A. Bertagnini, C. Bonadonna, R. Cioni, M. Pistolesi, M. Pedone, A. Hoskuldsson, Scavenging of sulphur, halogens and trace metals by volcanic ash: The 2010 Eyjafjallajökull eruption, *Geochimica et Cosmochimica Acta*. 103 (2013) 138–160. <https://doi.org/10.1016/j.gca.2012.10.048>.
- [11] X. Zhang, G. Zhuang, J. Chen, Y. Wang, X. Wang, Z. An, P. Zhang, Heterogeneous Reactions of Sulfur Dioxide on Typical Mineral Particles, *J. Phys. Chem. B*. 110 (2006) 12588–12596. <https://doi.org/10.1021/jp0617773>.
- [12] J.W. Adams, D. Rodriguez, R.A. Cox, The uptake of SO<sub>2</sub> on Saharan dust: a flow tube study, *Atmospheric Chemistry and Physics*. 5 (2005) 2679–2689. <https://doi.org/10.5194/acp-5-2679-2005>.
- [13] T. Kojima, P.R. Buseck, Y. Iwasaka, A. Matsuki, D. Trochkin, Sulfate-coated dust particles in the free troposphere over Japan, *Atmospheric Research*. 82 (2006) 698–708. <https://doi.org/10.1016/j.atmosres.2006.02.024>.
- [14] C.R. Usher, H. Al-Hosney, S. Carlos-Cuellar, V.H. Grassian, A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles, *J.-Geophys.-Res.* 107 (2002) 4713. <https://doi.org/10.1029/2002JD002051>.
- [15] D. Urupina, J. Lasne, M.N. Romanias, V. Thiery, P. Dagsson-Waldhauserova, F. Thevenet, Uptake and surface chemistry of SO<sub>2</sub> on natural volcanic dusts, *Atmospheric Environment*. 217 (2019) 116942. <https://doi.org/10.1016/j.atmosenv.2019.116942>.

- [16] C.S. Witham, C. Oppenheimer, C.J. Horwell, Volcanic ash-leachates: a review and recommendations for sampling methods, *Journal of Volcanology and Geothermal Research*. 141 (2005) 299–326. <https://doi.org/10.1016/j.jvolgeores.2004.11.010>.
- [17] T. Wang, Y. Liu, Y. Deng, H. Fu, L. Zhang, J. Chen, Emerging investigator series: heterogeneous reactions of sulfur dioxide on mineral dust nanoparticles: from single component to mixed components, *Environ. Sci.: Nano*. 5 (2018) 1821–1833. <https://doi.org/10.1039/C8EN00376A>.
- [18] R.C. Sullivan, S.A. Guazzotti, D.A. Sodeman, K.A. Prather, Direct observations of the atmospheric processing of Asian mineral dust, *Atmospheric Chemistry and Physics*. 7 (2007) 1213–1236. <https://doi.org/10.5194/acp-7-1213-2007>.
- [19] Y. Zuo, H. Chen, Simultaneous determination of sulfite, sulfate, and hydroxymethanesulfonate in atmospheric waters by ion-pair HPLC technique, *Talanta*. 59 (2003) 875–881. [https://doi.org/10.1016/S0039-9140\(02\)00647-1](https://doi.org/10.1016/S0039-9140(02)00647-1).
- [20] Y. Michigami, K. Ueda, Sulphite stabilizer in ion chromatography, *Journal of Chromatography A*. 663 (1994) 255–258. [https://doi.org/10.1016/0021-9673\(94\)85252-9](https://doi.org/10.1016/0021-9673(94)85252-9).
- [21] D. Baratoux, N. Mangold, O. Arnalds, J.-M. Bardintzeff, B. Platevoet, M. Grégoire, P. Pinet, Volcanic Sand in Iceland: Diverse origins of aeolian sand deposits revealed at Dyngjúsandur and Lambahraun, Iceland, *Earth Surface Processes and Landforms*. 36 (2011) 1789–1808. <https://doi.org/10.1002/esp.2201>.
- [22] X. Wang, M.N. Romanias, F. Thévenet, A. Rousseau, Geocatalytic Uptake of Ozone onto Natural Mineral Dust, *Catalysts*. 8 (2018) 263. <https://doi.org/10.3390/catal8070263>.
- [23] N. Joshi, M.N. Romanias, V. Riffault, F. Thevenet, Investigating water adsorption onto natural mineral dust particles: Linking DRIFTS experiments and BET theory, *Aeolian Research*. 27 (2017) 35–45. <https://doi.org/10.1016/j.aeolia.2017.06.001>.
- [24] M.N. Zeineddine, M.N. Romanias, V. Gaudion, V. Riffault, F. Thévenet, Heterogeneous Interaction of Isoprene with Natural Gobi Dust, *ACS Earth Space Chem*. 1 (2017) 236–243. <https://doi.org/10.1021/acsearthspacechem.7b00050>.
- [25] ICH Official web site : ICH, (n.d.). <https://www.ich.org/page/quality-guidelines> (accessed March 6, 2020).
- [26] M.N. Zeineddine, M.N. Romanias, V. Riffault, F. Thévenet, Heterogeneous Interaction of Various Natural Dust Samples with Isopropyl Alcohol as a Probe VOC, *The Journal of Physical Chemistry A*. (2018). <https://doi.org/10.1021/acs.jpca.8b02034>.
- [27] J. Lasne, M.N. Romanias, F. Thevenet, Ozone Uptake by Clay Dusts under Environmental Conditions, *ACS Earth Space Chem*. 2 (2018) 904–914. <https://doi.org/10.1021/acsearthspacechem.8b00057>.
- [28] O. Arnalds, P. Dagsson-Waldhauserova, H. Olafsson, The Icelandic volcanic aeolian environment: Processes and impacts — A review, *Aeolian Research*. 20 (2016) 176–195. <https://doi.org/10.1016/j.aeolia.2016.01.004>.
- [29] Y. Sun, G. Zhuang, Y. Wang, X. Zhao, J. Li, Z. Wang, Z. An, Chemical composition of dust storms in Beijing and implications for the mixing of mineral aerosol with pollution aerosol on the pathway, *Journal of Geophysical Research: Atmospheres*. 110 (2005). <https://doi.org/10.1029/2005JD006054>.
- [30] E. Bagnato, A. Aiuppa, D. Andronico, A. Cristaldi, M. Liotta, L. Brusca, L. Miraglia, Leachate analyses of volcanic ashes from Stromboli volcano: A proxy for the volcanic gas plume composition?, *Journal of Geophysical Research: Atmospheres*. 116 (2011). <https://doi.org/10.1029/2010JD015512>.
- [31] M. Edmonds, C. Oppenheimer, D. Pyle, R. Herd, Rainwater and ash leachate analysis as proxies for plume chemistry at Soufriere Hills Volcano, Montserrat, *Geological Society Special Publication*. 213 (2003) 203–218. <https://doi.org/10.1144/GSL.SP.2003.213.01.12>.

## Figure captions

Figure 1: Diagram representing two protocols: (A) “environmental sampling” that includes (i) sample collection, (ii) extraction and stabilization of sulfites and sulfates and (iii) HPLC analysis and (B) “kinetics study” that includes (i) sample collection, (ii) dust ageing, (iii) extraction and stabilization of sulfites and sulfates and (iv) HPLC analysis. Dark blue arrows lead through “environmental sampling” protocol, while orange arrows lead through “kinetics study” protocol.

Figure 2: Left: schematic representation of the setup used to age samples of dust with SO<sub>2</sub> gas. Right: reactor 1 and 2 with deposited dust, zoomed for clarity.

Figure 3: Representative chromatograms of: upper blue) Formalin, offset 60 units for clarity; middle black) Hagavath dust aged in 175 ppm SO<sub>2</sub> for 1 hr and extracted in 1% Formalin, offset 30 units for clarity; lower red) 50/50 K<sub>2</sub>SO<sub>3</sub>/K<sub>2</sub>SO<sub>4</sub> in 1% Formalin.

Figure 4: Dissolution studies for Hagavath dust aged in 175 ppm SO<sub>2</sub> for 1 hr and extracted in 1% Formalin. % RSD for sulfites and sulfates is equal to 16.1% and 32.0% respectively (see section 3.4).

Figure 5: Stability study results for 158.2 mg sample of Hagavath aged in 175 ppm SO<sub>2</sub> for 10 min. Extraction with 1ml of 1% Formalin. Samples are stored at 4°C. % RSD for sulfites and sulfates is equal to 4.7% and 8.7% respectively (see 3.3.4).

Figure 6: The typical plot of peak area versus concentration for a) sulfite (blue solid line) and b) sulfate (red dashed line) ions. The linearity plot was created daily before conducting experiments and each time the mobile phase solution was changed.

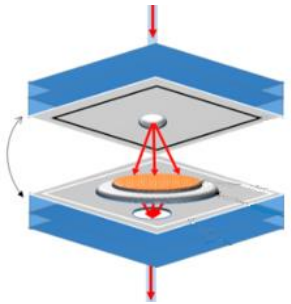
Figure 7: Amount of sulfites and sulfates on the surface of Hagavath volcanic dust and Gobi desert dust formed after ageing with 175 ppm SO<sub>2</sub> gas.



## Collection of natural mineral dust samples



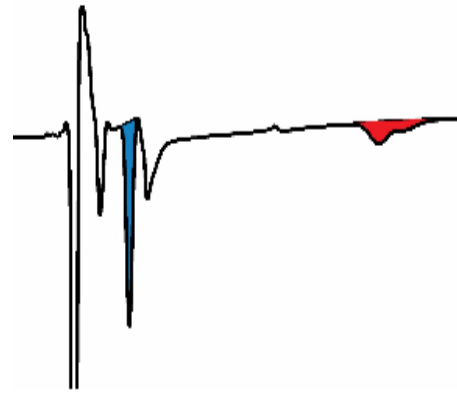
### Dust sample ageing

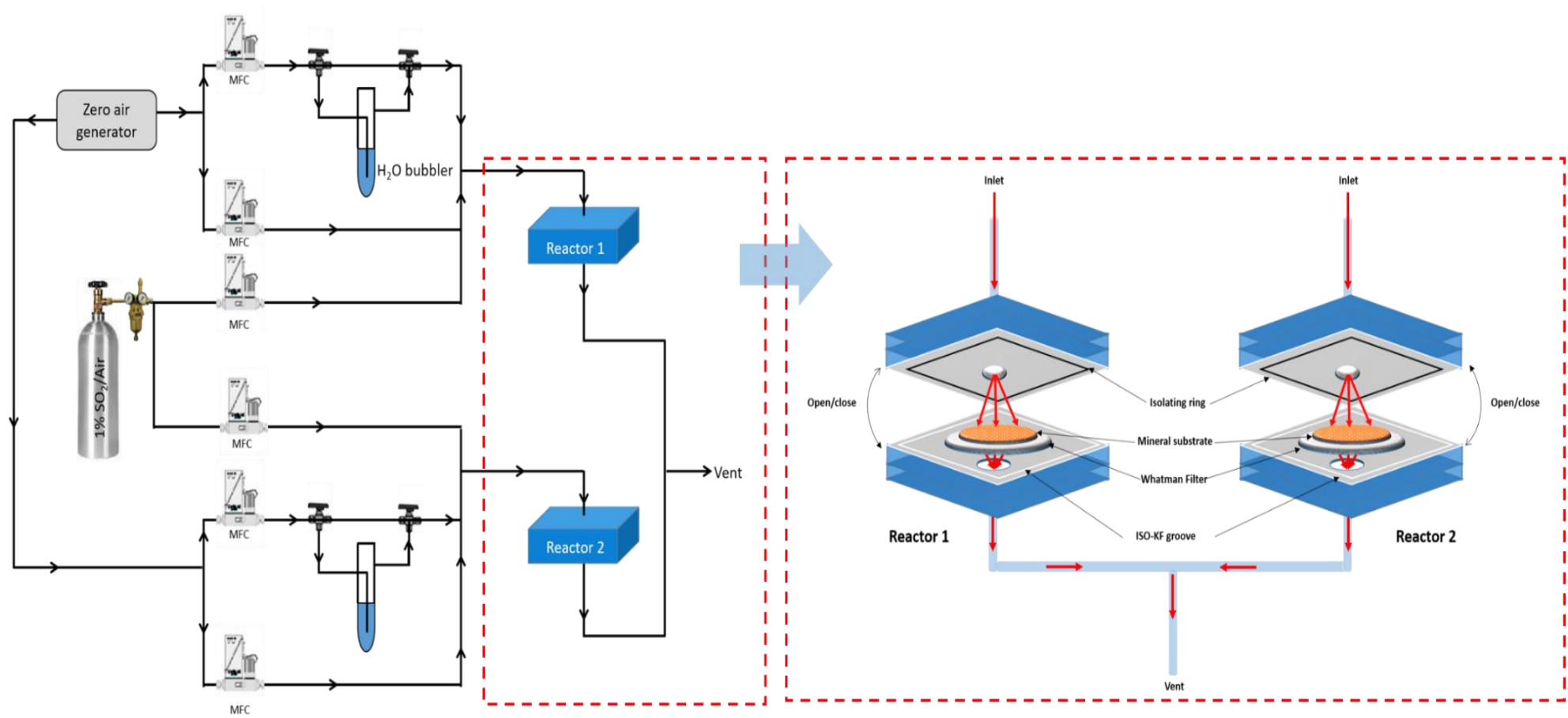


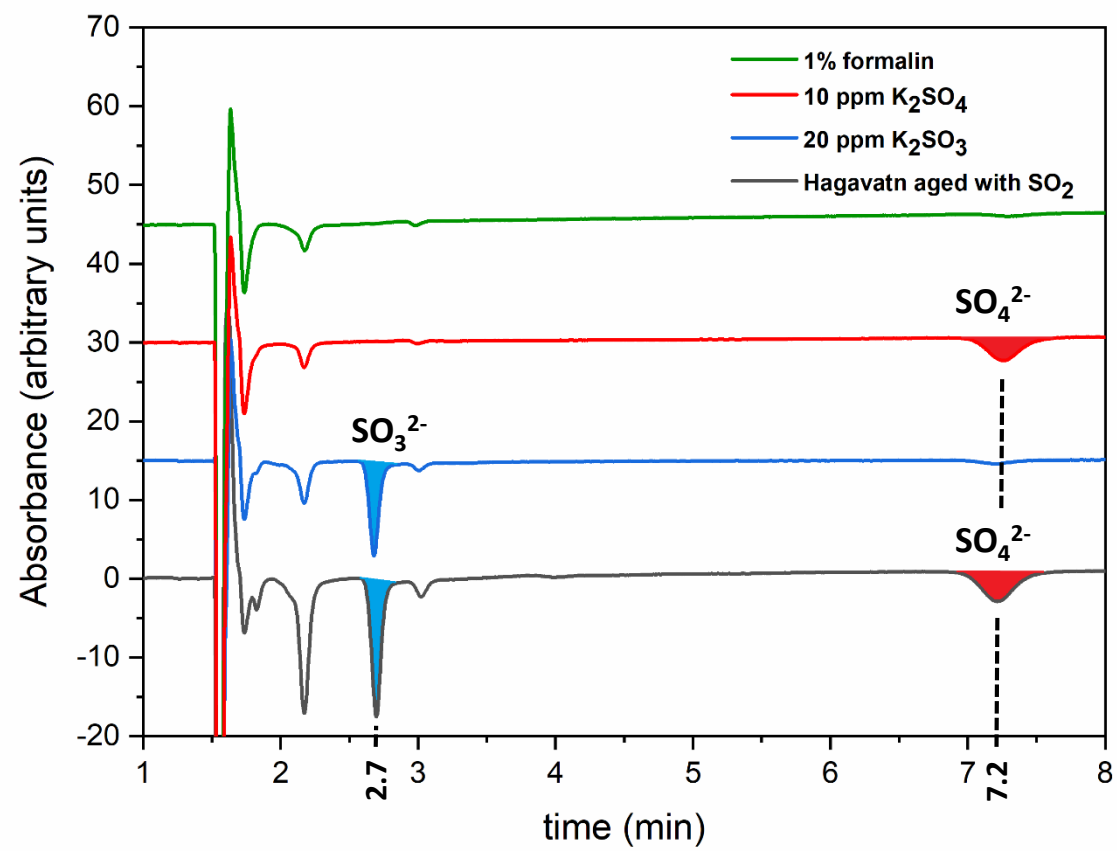
### Extraction & stabilization of $\text{SO}_3^{2-}$ & $\text{SO}_4^{2-}$

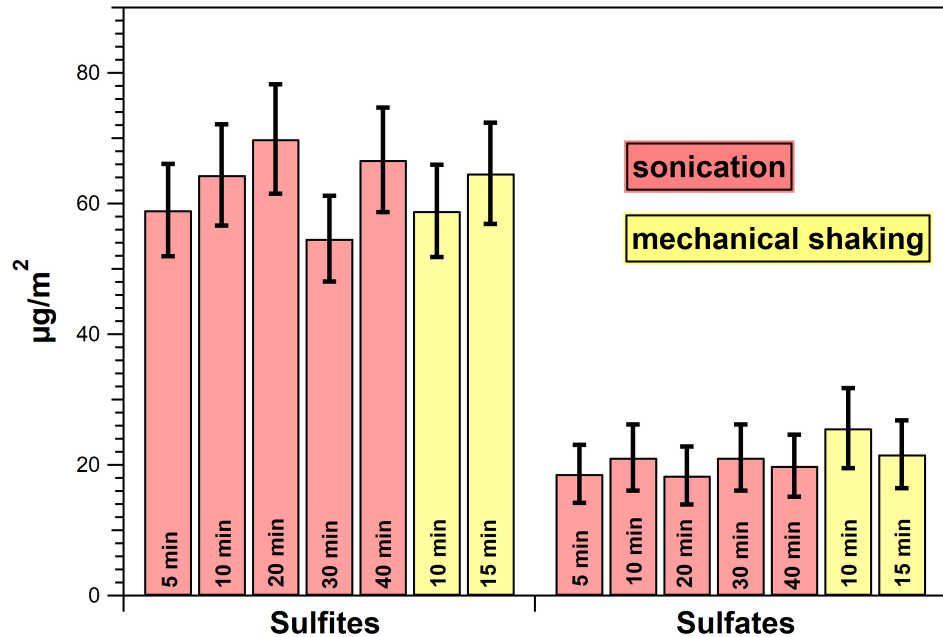


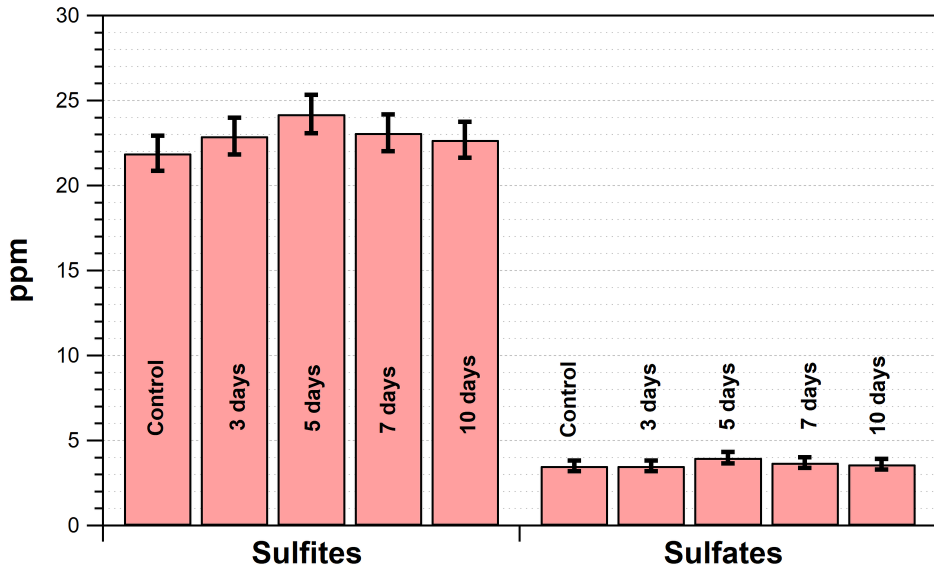
### HPLC method run



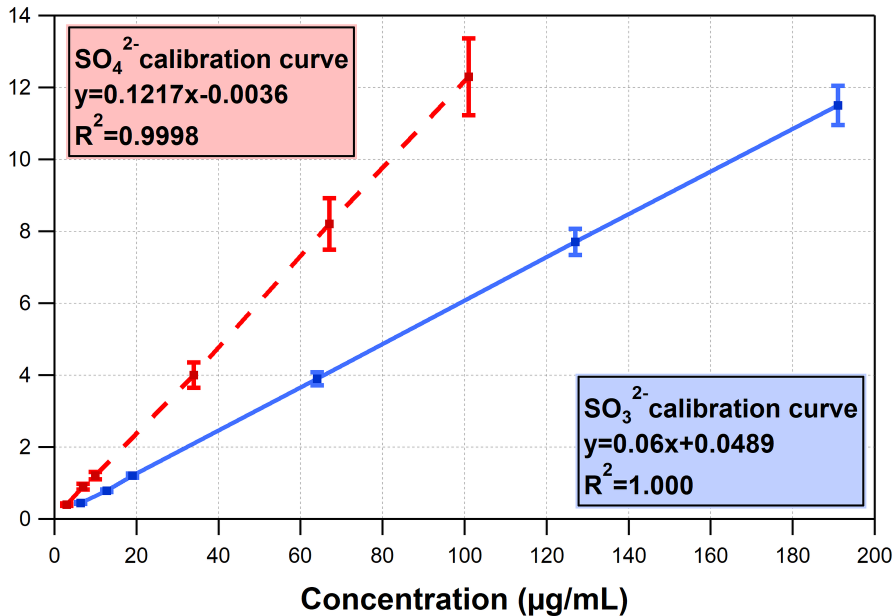


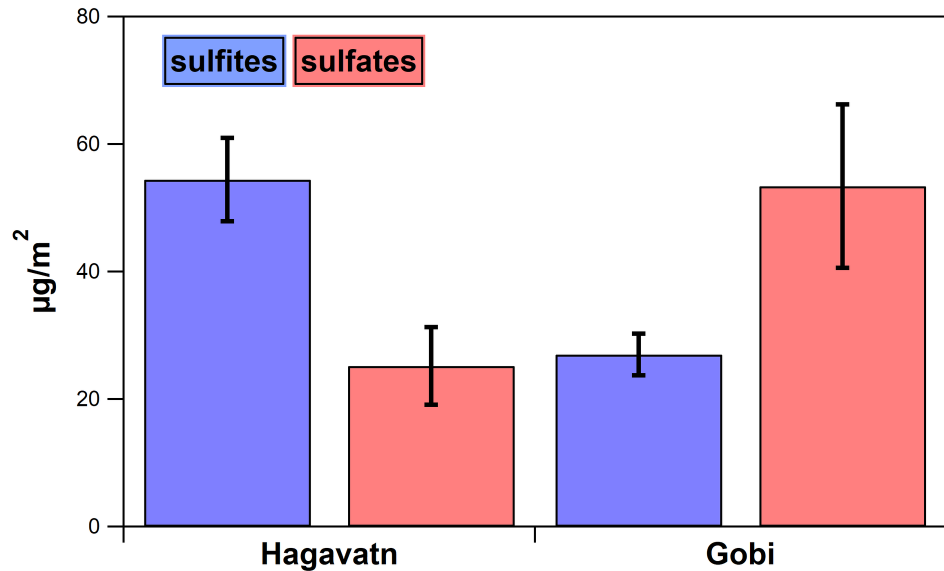






Peak area (mAU\*min)

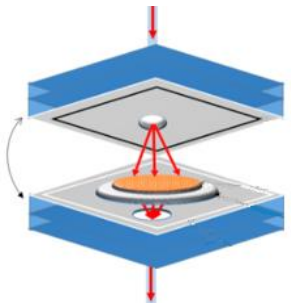




Collection of natural mineral dust samples



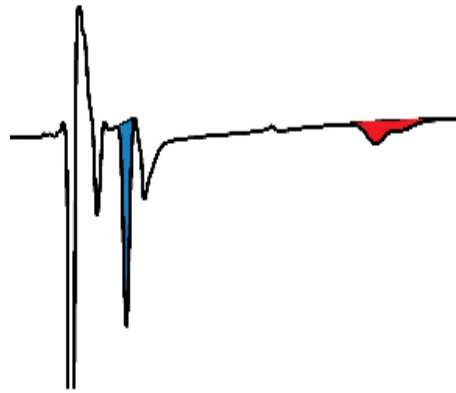
Dust sample  
ageing



Extraction &  
stabilization of  
 $\text{SO}_3^{2-}$  &  $\text{SO}_4^{2-}$



HPLC method run



To gain a better  
knowledge and  
understanding of  
the surface  
properties of  
mineral dust

Selective quantification  
of adsorbed  $\text{SO}_3^{2-}$  &  $\text{SO}_4^{2-}$

