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

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10
11 **ABSTRACT**

12 Earlier studies suggest that SO₂ gas reacts at the surface of mineral dust and forms sulfites or bisulfites,
13 which are then converted to sulfates. In order to monitor and quantify the amounts of both sulfites and
14 sulfates formed on the surface of mineral dusts of volcanic and desert origins an accurate and precise
15 reversed-phase liquid chromatography method was developed and validated to extract, stabilize and
16 individually analyze sulfites and sulfates initially present on the surface of dusts exposed to SO₂. The
17 method was developed on a 25 mm Restek Ultra Column C18, Particle size: 5 μm, I.D. 4.60 mm column
18 which was dynamically coated with 1.0 mM cetylpyridinium chloride in 7% acetonitrile solution to
19 produce a charged surface as recommended in the literature. Mobile phase used: 1 mM Potassium
20 Hydrogen Phthalate Buffer at pH 6.5 at a flow rate of 1.0 ml/min with negative UV-Vis detection at 255
21 nm in 15 min. The method was validated for specificity, linearity and range, injection repeatability,
22 stability, robustness, limit of detection and limit of quantitation, and sample preparation and extraction
23 reproducibility. The method was adapted for straight sulfite and sulfate quantification: (i) of

24 environmental samples, and (ii) natural samples additionally exposed to SO₂ gas in a dedicated laboratory
25 setup. The method was then successfully applied to quantify sulfites and sulfates on natural volcanic and
26 a desert dust samples both collected in the environment and additionally exposed to SO₂ gas in the
27 laboratory. The method can be efficiently used to identify sulfites and sulfates on fresh volcanic ash
28 following an eruption, on aeolian desert dust exposed to industrial pollutants, as well as for laboratory
29 investigations of sulfite and sulfate formation on the surface of minerals and natural dusts of different
30 origins.

31

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

33

34

35 1.0 INTRODUCTION

36 Sulfur dioxide (SO_2) is a noticeable component in the atmosphere, where release of SO_2 is associated with
37 the decrease in the levels of atmospheric oxidants, such as H_2O_2 , OH , and O_3 as they are involved in the
38 reactions that convert gaseous and dissolved SO_2 to sulfates [1]. Stevenson et al. estimate that, on
39 average, emissions of SO_2 gas in the atmosphere due to anthropogenic activity account for the 71.2 Tg/yr,
40 while volcanic eruptions contribute to 8.8 Tg/yr, and 1.4 Tg/yr is due to the biomass burning [1].
41 Needless to say, volcanic eruptions are a highly variable source of SO_2 gas. The 2014–2015 Holuhraun
42 eruption in Iceland, emitted ca. 11 Tg of SO_2 into the troposphere over a 6 month period, and caused one
43 of the most intense and widespread volcanogenic air pollution events in centuries [2]. It was an effusive
44 eruption with very little volcanic ash produced, yet with the amount of SO_2 that exceeded all of the
45 anthropological flux in Europe for the year 2011[2]. That is not to undermine the significance of the
46 anthropogenic contribution. The “Great smog” of 1952 in London was caused by SO_2 emitted from coal
47 burning and reached levels as high as 1.34 ppm [3].

48 Explosive volcanic eruptions have a potential to inject vast amounts of SO_2 gas into the stratosphere,
49 where conversion of SO_2 to H_2SO_4 leads to the formation of fine sulfur aerosol that can persist in the mid-
50 stratosphere for up to 2 years [1]. Sulfate aerosols are known to affect the climate by increasing the
51 reflection of radiation from the Sun back into space, thus efficiently cooling the Earth’s troposphere [1].
52 In the troposphere itself, formation of sulfur aerosols due to anthropogenic and natural emissions
53 competes with SO_2 gas deposition, and therefore sulfur aerosols formed are deposited within days or
54 weeks [1]. Important reactions of SO_2 gas in the troposphere include oxidation of SO_2 in cloud and rain
55 droplets leading to the formation of acid rain, and oxidation to sulfate on the surface of atmospheric
56 particles [4], [5], [6]. Adsorption of sulfur dioxide SO_2 gas on the surface of atmospheric samples leads to
57 the formation of sulfate coating that can affect both the dust properties and the sulfur cycle [7]. Volcanic
58 dusts acquire the sulfate coating while passing through the volcanic conduit [8], as well as further away
59 from the crater, in the colder parts of the plume, higher in the atmosphere [9], [10]. Desert dusts as well

60 are known to accumulate hygroscopic sulfate coating during their long-range transport [11]. Thus, a
61 negative correlation was observed between atmospheric concentrations of SO₂ and both Saharan and
62 Chinese desert dust loadings [12]. Once coated, these particles can act as large cloud condensation nuclei
63 (CCN) and affect cloud formation [13]. They may also affect climate forcing by forming cirrus ice clouds,
64 ice nuclei (IN), at relatively warm temperatures and low supersaturation [13].

65 The physico-chemical processes that govern transformation of SO₂ gas on the surface of dusts are poorly
66 understood and need further investigation. SO₂ shows heterogeneous reactivity towards many mineral
67 oxides such as MgO, Al₂O₃, Fe₂O₃, TiO₂, as well as volcanic ash and mineral dust [14], [4], [5], [15].
68 Reactivity of the dusts towards the uptake of SO₂ as well as influence of different atmospheric conditions
69 and various oxidants is often evaluated in terms of uptake coefficient using Knudson cell and flow-tube
70 reactors [5], [14], [15]. Quantifications of the amounts of products formed on the surface of dust could
71 provide additional information and might clarify reaction pathways.

72 While summarizing previous work on volcanic ash analysis, Witham et al. cited about 55 articles
73 reporting original volcanic ash-leaching data [16]. The ion-chromatography methods available in the
74 literature and employed to quantify the amount of SO₂ adsorbed on the surface of volcanic ash are almost
75 solely concerned with quantification of sulfates as the final oxidation product completely ignoring sulfite
76 quantification [16]. Indeed, it is widely accepted that SO₂ gas reacts at the surface of the volcanic dust and
77 forms sulfites or bisulfites, which are then converted to sulfates [17]. However, quantification of sulfites
78 along with the sulfates could provide a more comprehensive description of the SO₂ adsorption processes.
79 Sulfite to sulfate conversion on synthetic mineral dust aerosol (using α -Al₂O₃, CaO, ZnO, TiO₂, MgO,
80 and Fe₂O₃ oxides) was recently studied by He et al. using DRIFTS in order to better explain haze
81 formation mechanism in China [3]. The need to explore the effect of minerology on SO₂ adsorption using
82 authentic dust samples of various compositions in laboratory studies was expressed by Sullivan et al. [18].
83 However, employment of DRIFTS is limited on natural heterogeneous samples that are dark in color,
84 such as volcanic dust or ash. In addition, DRIFTS is a qualitative technique and does not provide

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

90 The goal of this study is to develop a method that would (i) extract both sulfites and sulfates, (ii) stop the
91 conversion of sulfites to sulfates and (iii) successfully quantify both species. The method can then be used
92 for two distinctive purposes: to quantify sulfites and sulfates on the surface of natural environmental
93 samples, such as recently erupted volcanic ash or dust passing through polluted areas, and to study the
94 kinetics of the sulfite to sulfate transformation in laboratory settings. The challenge in separating sulfites
95 from sulfates in the solution containing mineral dust comes from the nature of these dust particles, as they
96 contain various oxidizing elements, such as iron, that contribute to the oxidation of sulfites into sulfates
97 [20]. This article proposes (i) a controlled ageing of mineral samples by SO₂ gas in laboratory settings,
98 (ii) extraction and stabilization of sulfites and sulfates with a subsequent use of (iii) HPLC for quantitative
99 analysis as a technique that can be used to study the conversion of sulfites to sulfates on the surface of
100 natural samples. While in the case of taking field measurements artificial ageing is not required, it is
101 important to be able to age samples in reproducible fashion in order to study kinetics of the sulfite to
102 sulfate transformation as a part of laboratory experimental work.

103 **2.0 EXPERIMENTAL**

104 **2.1 Samples and Standards**

105 **2.1.1 Dust samples**

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

109 generation. Modal composition of Hagavatn dust (referred as Lambahraun sand by Baratoux et al.) and, in
 110 particular, the amount of crystalline material versus glassy material, was determined by Baratoux et al.
 111 using optical and scanning mode microscope [21]. Hagavatn sample contains about 80% of minerals and
 112 20 % of glassy material [21]. Mineral phases typical of basaltic rocks include olivine, pyroxene and
 113 plagioclase [21].

114 The mineral desert dust sample, used for method application only, comes from Gobi Desert, Ningxia
 115 Province, China. This area represents the second most important source of atmospheric mineral dusts after
 116 Sahara desert [22]. This is an aeolian sample that was sieved and only the fraction below 100 μm was
 117 used for further studies. The morphology of the sieved fraction of the natural Gobi dust sample was
 118 evaluated using scanning electron microscopy (SEM) carried out on a Hitachi S-4300SE/N SEM in high
 119 vacuum mode. Gobi dust particles are chunky, irregular in shape, with mean diameter ranging from a few
 120 to 50 μm . Flat particles are also observed, suggesting the presence of distinct crystalline phase structures.
 121 The relative abundance of mineral phases for Gobi dust was determined using X-ray diffraction (XRD;
 122 Bruker D2 phaser 2 theta analyzer). Gobi dust shows a low silica content typical for Asian desert dusts
 123 (33.0%). Other minerals include calcite (8.7%), albite (8.6%), muscovite (25.8%), kaolinite (8.9%), rutile
 124 (4.4%), hedenbergite (6.2%), chromian pyrope (4.1%) and beaconite (0.3%).

125 Elemental compositions of Hagavatn and Gobi dusts as determined by ICP-MS are presented in Table 1
 126 [15], [23].

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

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

129

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

133 *2.1.2 Chemicals and reagents*

134 HPLC grade acetonitrile (ACN), 99.95% and methanol (MeOH), 99.9% were obtained from Biosolve
135 Chimie, Dieuze, France. Potassium hydrogen phthalate and triethanolamine, 99% of analytical grade
136 were purchased from Acros Organics, Geel, Belgium. Cetylpyridinium chloride, 98% was purchased
137 from Alfa Aesar, Kander, Germany. Sodium sulfate was purchased from Merck, Darmstadt, Germany.
138 Sodium sulfite was purchased from Fischer Chemical, Loughborough, UK. Formalin (37% formaldehyde
139 solution by weight containing 10-15 % MeOH as stabilizer) was obtained from Sigma-Aldrich. Other
140 chemicals and solvents of analytical grade were used during research. Deionized water (DI) was used
141 throughout the investigation. A certified SO₂ cylinder, 250 ppm diluted in synthetic air (nearly 80% N₂
142 and 20% O₂) was purchased from Messer, France.

143 *2.1.3 Standards*

144 The solution of 1% Formalin was used to prepare a 1000 ppm stock solution of potassium sulfite (KSO₃)
145 and a 1000 ppm stock solution of potassium sulfate (KSO₄). Other concentrations of KSO₃ and KSO₄
146 standards were prepared from their stock solutions through serial dilution with 1% Formalin. Stock
147 solution of 1% Formalin was prepared by adding 10 ml of Formalin in a 1000 mL volumetric flask and
148 diluting to the volume with 10% methanol/water to prevent polymerization.

149 *2.2 Experimental Set-Up and Procedure*

150 *2.2.1 General Outline*

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

153 sampling”) and (ii) study kinetics of sulfite and sulfate formation on the surface of different dusts in the
154 laboratory environment by subjecting them to SO₂ ageing and analyzing the product formation (referred
155 to as “kinetics study”).

156 The developed method for “environmental sampling” protocol consists of three parts: (i) sample
157 collection, (ii) extraction and stabilization of sulfites and sulfates and (iii) HPLC analysis (Figure 1); the
158 developed method for “kinetics study” protocol includes four steps: (i) sample collection, (ii) dust
159 ageing, (iii) extraction and stabilization of sulfites and sulfates and (iv) HPLC analysis (Figure 1). Thus,
160 the difference between the two protocols is an additional step of controlled SO₂ ageing required for the
161 “kinetics study”. Sample analysis step that includes extraction and HPLC analysis is exactly the same in
162 both cases.

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

168

169 *2.2.2 Dust ageing by SO₂ gas*

170 The setup for ageing samples consists of two parts: (i) the gas mixing line and (ii) the ageing reactor. A
171 schematic representation of the setup is provided in Figure 2. A dust weighting from 100 to 200 mg is
172 spread on a 47 mm Whatman filter paper and is placed in a tightly closed reactor. The gas mixture
173 containing 175 ppm SO₂ entering the reactor is forced through the filter containing the dust at 100
174 cm³/min. The ageing of environmental samples is carried out using zero air; it is generated by a classical
175 air compressor, and then passed through a catalytic zero air generator (Claind ZeroAir 2020, Lenno, Italy)
176 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, CO₂ <
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.

181 **2.2.3 Extraction and stabilization of surface sulfites and sulfates**

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

189 **2.2.4 HPLC analysis. Instrumentation and chromatographic conditions**

190 Chromatography equipment used to develop an HPLC method consisted of Thermo Scientific Dionex
191 UltiMate 3000 UHPLC System with UV/VIS Detector (Thermo Scientific, Waltham, MA). Chromeleon
192 7.0 Data Acquisition System for LC (Thermo Scientific, Waltham, MA) was used to analyze the data.
193 Analysis was performed using Restek Ultra Column C18, 5 µm, Length 250 mm, I.D. 4.60 mm
194 dynamically coated with cetylpyridinium chloride to produce a charged surface as recommended by Zuo
195 et al. [19]. More specifically, columns were cleaned at 1 mL/min for 1.5 hour with 100% ACN before
196 being coated with 1.0 mM cetylpyridinium chloride in ACN/water (7:93, v/v) at 0.5 mL/min for 3 hours
197 [19]. The HPLC instrument was operated isocratically at 23 C° at a flow rate of 1 mL/min for 15 min.
198 Potassium hydrogen phthalate buffer, 1.0 mM was adjusted to pH 6.5 with a dilute solution of potassium
199 hydroxide (KOH), vacuum filtered and used as a mobile phase. The injection volume was 10 µL. An
200 indirect photometric detection was used for quantification of sulfates and sulfites. Detector was set at 255
201 nm as the mobile phase showed the highest absorbance at this wavelength. A 6-point linear calibration
202 curve was established daily for SO_3^{2-} and SO_4^{2-} ions in the range of 6 µg/mL to 191 µg/mL and 3 µg/mL
203 to 101 µg/mL respectively. Concentration of sulfites and sulfates in the extracts of natural samples was

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

206 **3.0 RESULTS AND DISCUSSION**

207 Chemical characterization plays a vital role in scientific representation of any process. Defined as the set
208 of techniques that allows an analyst to know qualitatively and/or quantitatively the composition of the
209 material, a method is created to reach this goal. The following sections will guide the reader through the
210 development of the method for quantitative determination of sulfites and sulfates on the surface of
211 mineral dust. As such, we've started by building an analytical HPLC method for analysis of a mixture of
212 sulfites and sulfates. We then optimized extraction procedure to ensure optimal extraction of sulfites and
213 sulfates from a dust sample. Finally, we assessed the validity of the method by going through validation
214 studies using, when possible, SO_2 -laboratory-aged dust samples in order to have a sufficient amount of
215 sulfites on the surface (unless immediately stabilized, sulfites will oxidize to sulfates).

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

227 validated for the entire “kinetics study” protocol including (i) laboratory SO₂ ageing of mineral dust, (ii)
228 extraction of sulfites and sulfates and (iii) HPLC analysis.

229 **3.1 HPLC Analytical Method Optimization**

230 The method for determination of sulfites, sulfates and hydroxymethanesulfonate (HMS) in natural and
231 atmospheric water samples developed by Zuo et al. was used as a base for development of the method for
232 determination of sulfites and sulfates on the surface of natural mineral samples discussed in this paper
233 [19]. The main drawback of the method was the lack of sulfite-stabilizing agent during sample
234 preparation and, as a consequence, inability to detect sulfites in environmental samples. The authors
235 acknowledged the problem in the “quantitative analysis” part of their study and recommended to use
236 methanol in order to stabilize sulfites. Following the suggestion, a 50/50 ppm solution of K₂SO₃/ K₂SO₄
237 was dissolved in 10% methanol used as stabilizing agent. Unfortunately, in our experiments, methanol
238 solution either did not stabilize sulfites and they were converted into sulfates, or sulfites co-eluted with
239 sulfates, as only one peak was observed. Besides, methanol would be a poor choice for the extraction of
240 sulfites in the presence of reactive ions, such as Mn or Fe, which are both known to be present in volcanic
241 dust [20]. Formalin was reported to prevent the conversion of sulfites to sulfates by converting it to
242 hydroxymethanesulfonate (HMS) and was tested as an extracting solvent [20]. Two concentrations of a
243 mixture of sulfites and sulfates of 50/50 ppm and 5/5 ppm were prepared using Formalin of the following
244 concentrations: 0.5%, 1% and 5%. A solvent peak for 5% Formalin overlapped with a sulfite peak, and
245 5% Formalin concentration was rejected for further studies. Solvent peaks of both 0.5 and 1% Formalin
246 were well separated from sulfite peak. Besides, less than 5% change was observed for sulfites and sulfates
247 in the corresponding solutions when left at ambient temperature for 2 days. Between 0.5% and 1%
248 concentrations of Formalin, a solution of 1% Formalin was chosen as an extracting solvent for further
249 studies.

250 A second concern about the method of Zuo et al. was the high pH value of the mobile phase. The diluted
 251 1.0 mM phthalate buffer mobile phase suggested by the author could not be adjusted to pH 7.9 as it was
 252 out of its buffering capacity range. An attempt to increase buffer concentration to 10 mM in order to
 253 better maintain the pH of the mobile phase overloaded the detector working in negative detection mode.
 254 Addition of triethanolamine further increased the buffer pH. Taking into consideration that pH higher
 255 than 8.0 is detrimental for the column and can easily dissolve the stationary phase, it was decided to work
 256 at pH 6.5, which was stable and easy to maintain. Addition of methanol to mobile phase didn't make any
 257 difference on formaldehyde/sulfite pair, but broadened and pushed the sulfate peak further. It was
 258 therefore decided to work with 1.0 mM Potassium phthalate buffer pH 6.5 as a mobile phase. Several
 259 other parameters, such as column type, injection volume and detection wavelength were varied to find the
 260 optimum conditions for getting a sharp peak and a good separation of sulfates and sulfites and sulfites
 261 from formaldehyde peak present in the solvent. Parameters investigated are listed in Table 2.

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

	Method by Zuo et al.	Parameters investigated	Parameters chosen
Column	150 mm C18 Column, Particle size: 5 µm, I.D. 4.60 mm	250 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm 250 mm Acclaim 120 Column C18, Particle size: 3 µm, I.D. 3 mm	250 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm
Column coating	1.0 mM cetylpyridinium chloride in 7% ACN solution		1.0 mM cetylpyridinium chloride in 7% ACN solution
Mobile phase	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
pH	7.9	6.0, 6.5, 7.0, 7.5	6.5
Flow rate	1.0 ml/min	0.5 ml/min, 1 ml/min	1.0 ml/min
Detection	negative UV-Vis detection at 265 nm	negative UV-Vis detection at 265nm, 255 nm	negative UV-Vis detection at 255 nm

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

265

266 Finally, the following chromatographic conditions were determined as optimum: 25 mm Restek Ultra
 267 Column C18, Particle size: 5 µm, I.D. 4.60 mm column which was dynamically coated with 1.0 mM
 268 cetylpyridinium chloride in 7% acetonitrile solution to produce a charged surface as recommended by
 269 Zuo et al. [19]. Mobile phase used: 1 mM potassium hydrogen phthalate buffer at pH 6.5 at a flow rate of
 270 1.0 ml/min with negative UV-Vis detection at 255 nm in 15 min.

271 Figure 3 displays three chromatograms offset for clarity: 1% Formalin, 50/50 K₂SO₃/K₂SO₄, and
 272 Hagavatn extract obtained after aging the dust for 1 hr in 175 ppm SO₂. The peak for SO₃²⁻ is observed at
 273 2.8 minutes and SO₄²⁻ peak is observed at 5.6 min. Both peaks demonstrate a high number of theoretical
 274 plates: for Hagavatn extract they are equal to 2235 for SO₃²⁻ and 884 for SO₄²⁻. Two small peaks around
 275 2.3 and 2.9 min belong to formaldehyde and are separated from the peak for SO₃²⁻ at 2.8 min. The sulfite
 276 peak present in the form of HMS eluted rather closely to the formaldehyde peak. Therefore, in order to
 277 preserve separation, it was decided to stay with a 250 mm long column.

278 3.2 Extraction Optimization

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

282 **3.2.1 Dissolution**

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

286 **3.2.2 Recovery**

287 Recovery studies were intended to prove that maximum amount of the sulfites and sulfates are extracted.
288 Three consecutive extractions with 1 mL of 1 % Formalin were evaluated for the amount of sulfites and
289 sulfates after the sample was aged by 175 ppm SO₂ for 10 min, 30 min, 1 hr, and 2hr. The criteria is less
290 than 5 % of the product can be left unaccounted. As can be observed from Table 3, all of the sulfates are
291 extracted from the surface of Hagavatn dust after the first extraction with 1 mL of 1% Formalin. As for
292 the sulfites, two extractions with 1ml of 1% Formalin are necessary. The third extraction represents from
293 0 to 3.9 % of the total amount of SO₃²⁻ extracted and therefore is not required based on the established
294 criteria. Method demonstrates efficient recovery after only two extractions. As a result, it was decided to
295 extract sulfites and sulfates with 1 mL of 1% Formalin, wash the remaining dust with another 1 mL of 1%
296 Formalin and, using the same syringe, filter and combine the solution.

297 *Table 3: Recovery results for 3 consecutive extracts of the sample of Hagavatn aged in 175 ppm SO₂ for various time periods.*
298 *Extraction with 1mL of 1% Formalin.*

Sample	Hagavatn aged with 175 ppm SO ₂			
Time	10 min	30 min	1hr	2hr
Extract 1 SO ₃ ²⁻ (ppm)	64.1	69.3	71.7	78.4
Extract 2 SO ₃ ²⁻ (ppm)	14.9	11.9	19.9	16.6
Extract 3 SO ₃ ²⁻ (ppm)	0.1	3.3	0	1.6
% SO₃²⁻ in the 3rd extract	0.1	3.9	0.00	1.2
% recovery after 3 extract	99.9	96.1	100.00	98.0

Extract 1

SO ₄ ²⁻ (ppm)	3.4	3.7	3.7	8.5
Extract 2 SO ₄ ²⁻ (ppm)	0	0	0	0
% recovery	100.00	100.00	100.00	100.00

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 SO₂ 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 SO₂ 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 SO₂ for 10 min and extracted in 1% Formalin was analyzed by Waters

320 2695 HPLC system equipped with Diode Array Detector using Empower software. Thus, specificity was
321 evaluated as spectral purity. In peak purity testing the software compares the spectrum from each data
322 point within the peak against the peak apex spectrum. Two parameters are evaluated: purity threshold,
323 which accounts for the presence of non-ideal and solvent-induced spectral changes, and purity angle.
324 When the purity angle exceeds purity threshold, a detectable impurity is present within a single
325 chromatographic peak.

326 A solution of 165 mg of Hagavatn dust aged in 175 ppm SO₂ for 10 min and extracted in 1% Formalin
327 showed no interfering peaks. All peaks were well separated from the analyte peaks. Peak purity was
328 proved by purity threshold exceeding the purity angle for both sulfite and sulfate peaks.

329 *3.3.3 Limit of detection (LOD) and limit of quantitation (LOQ)*

330 Limits of detection for sulfites and sulfates were investigated to determine the lowest concentration of
331 sulfites and sulfates that can be detected but not quantified. It was based on a signal-to-noise ratio $S/N \geq$
332 3. Limits of quantitation were studied to determine the lowest levels of the analyte concentrations that
333 can be quantified and were determined by the concentrations corresponding to signal-to-noise ratio $S/N \geq$
334 10.

335 The LOD for determination of sulfites was found to be 0.5 µg/mL of K₂SO₃ (0.32 µg/mL of SO₃²⁻ ion).
336 This value is 5 times lower than the 1.52 µg/mL of SO₃²⁻ ion reported as LOD by Zuo et al.
337 (corresponding to 19 µM of SO₃²⁻ ion), but in a good agreement with the limit of detection of
338 hydroxymethylsulfonate (HMS) reported at 0.42 µg/mL (corresponding to 3.8 µM of HMS ion). This is
339 to be expected, as the SO₃²⁻ in our case elutes as a HMS complex. The reason for improved detection limit
340 is earlier elution of SO₃²⁻ in the form of HMS at around 3 min instead of 7.5 min as a free sulfite ion using
341 the original method [19]. Earlier elution prevents peak broadening and improves LOD and LOQ. LOQ for
342 determination of SO₃²⁻ ion was found to be 1 µg/mL of K₂SO₃ (0.64 µg/mL of SO₃²⁻ ion).

343 LOD for determination of sulfates was found to be 1 $\mu\text{g/mL}$ of K_2SO_4 (0.68 $\mu\text{g/mL}$ of SO_4^{2-} ion). This
344 value is in excellent agreement with the limit of detection for SO_4 ion reported by Zuo et al. and
345 established at 6.7 μM SO_4^{2-} ion which is 0.64 $\mu\text{g/mL}$ of SO_4^{2-} . LOQ for determination of sulfates was
346 found to be 5 $\mu\text{g/mL}$ of K_2SO_4 (3.38 $\mu\text{g/mL}$ of SO_4^{2-} ion).

347 *3.3.2 Linearity and range*

348 Linearity proves that the detector response is directly proportional to the concentrations of the analyte in
349 the sample, and range provides an interval for which the procedure is linear. Calibration ranges were
350 defined as to include possible concentrations of sulfites and sulfates that can be found on the surface of
351 mineral dust. This approach was based on preliminary results used to frame the order of magnitude of
352 typical SO_3^{2-} and SO_4^{2-} surface concentrations. To investigate linearity for extracted sulfites, six different
353 concentrations of K_2SO_3 were prepared from 1000 $\mu\text{g/mL}$ stock solution of K_2SO_3 in the range 10 – 300
354 $\mu\text{g/mL}$ (corresponding to 6 $\mu\text{g/mL}$ to 191 $\mu\text{g/mL}$ of SO_3^{2-} ion). To explore linearity for sulfates, six
355 different concentrations of K_2SO_4 were prepared from 1000 $\mu\text{g/mL}$ stock solution of K_2SO_4 in the range
356 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 SO_4^{2-} ion).

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

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

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

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

373

374 *3.3.4 Injection repeatability*

375 Injection repeatability was tested to measure the sensitivity of the method towards errors coming from the
376 instrument itself: the column, the detector, the injector, the integration device. To evaluate injection
377 repeatability a solution of a mixture of 20 ppm K_2SO_3 and 10 ppm K_2SO_4 were injected into the HPLC
378 system 6 times and evaluated for area % relative standard deviation (%RSD). Injection repeatability for a
379 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
380 (Table 4).

381 *3.3.5 Robustness*

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

389 amounts of SO_3^{2-} and SO_4^{2-} ions determined in the solutions, as they fell within injection variations, where
 390 4.7 % RSD and 8.7 % RSD were reported for sulfites and sulfates respectively (Table 5). This is
 391 important, as it means that small fluctuations in pH that can come from buffer preparation will not affect
 392 quantification. Stability towards temperature changes suggests that method could be used in instruments
 393 not equipped with temperature control function. Stability of the column for at least 4 months and
 394 robustness towards change of column (different batches) assures normal use of the method.

395 *Table 5: Method robustness results. Small changes in method parameters were introduced and evaluated as percent change for*
 396 *the amounts of SO_3^{2-} and SO_4^{2-} ions in samples of Hagavatn dust as compared to their determination under original conditions*
 397 *(marked by asterisk).*

Sample	T (C°)	pH	Column Lot#	Column age (months)	Amount for SO_3^{2-} (ppm)	% Change	Amount for 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

399 3.4 Validation of the Sample Preparation and Extraction Performance. Method

400 Reproducibility

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

405 Sample preparation and extraction reproducibility studies were conducted to evaluate the sensitivity of the
406 method towards errors that may result from the combination of steps starting from ageing, extraction and
407 preparation of the samples to their subsequent analysis by HPLC instrument. To evaluate sample
408 preparation and extraction reproducibility for the “kinetics study” protocol, eight samples of Hagavatn
409 volcanic dust were aged with 175 ppm SO₂ for 1 hr and extracted in 1% Formalin. The solutions were
410 injected into HPLC system and %RSD for mass of sulfites/sulfates per square meter of dust was
411 calculated. The %RSD for reproducibility (that includes ageing and extraction of sulfites/sulfates) as
412 reported in Table 6 was found to be 16.1% for sulfites and 32.0% for sulfates. It is important to stress out
413 that reproducibility for ageing and extraction of sulfites/sulfates in a dust sample depends on
414 heterogeneity of the sample. Like most of the natural mineral dusts, Hagavatn volcanic dust represents a
415 highly heterogeneous sample and variations in adsorption/transformation of SO₂ gas by its different
416 components are expected. Many studies use a combination of different oxides as proxies for natural
417 samples. In this case %RSD for reproducibility would be expected to be lower as the sample composition
418 is well-defined and ageing process more reproducible. Nevertheless, the importance of using natural
419 samples cannot be undermined, as they often demonstrate different adsorption patterns when compared to
420 the mixture of mineral oxides used as proxies [26], [27], [22]. For example, when studying adsorption of
421 SO₂ on individual oxides and comparing them to their mixture Zhang et al. observed that the reactivity of
422 the mixture is twice as high as the reactivity of individual components [3]. In addition, using simple

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

425 *Table 6: Sample preparation and extraction reproducibility study for samples of Hagavtm aged in 175 ppm SO₂ for 1 hr.*
426 *Extraction with 1mL of 1% Formalin.*

Preparation	Date of sample preparation	Sample mass (mg)	Concentration	Concentration
			SO ₃ ²⁻ (µg/m ²)	SO ₄ ²⁻ (µg/m ²)
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
Average			65.1	29.0
Standard Deviation			10	9
%RSD			16.1	32.0

427

428 3.5 Method Summary

429 The validated method is summarized in Table 7. If “environmental sampling” is the desired purpose of the
430 method, ageing is not required and one can start the protocol from the extraction section. For “kinetics
431 study”, ageing is followed by extraction and HPLC analysis. Mass of the sample introduced into the
432 reactor will depend on the specific surface area of the dust. In case of high specific surface area a higher
433 SO₂ adsorption might be expected and therefore a smaller sample mass can be used for extraction.
434 Likewise, if the specific surface area of the dust is low an increased mass might be necessary in order to
435 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 SO₂ gas.*

Ageing		Extraction		Chromatographic conditions	
Dust sample mass	100.0-200.0 mg	Extracting solution	1% Formalin in 10% MeOH/water	Column	250 mm Restek Ultra Column C18, Particle size: 5 µm, I.D. 4.60 mm
SO₂ concentration	175 ppm	Mode of dissolution	sonication	Column modification	coated with 1.0 mM cetylpyridinium chloride in 7% ACN solution
SO₂ flow	100 cm ³ /min	Time of dissolution	10 min	Mobile phase	1 mM potassium hydrogen phthalate buffer at pH 6.5
RH	30%	Filter	0.45 µm pore size 30 mm diameter Whatman filter	Flow rate	1.0 ml/min
Time	10 min - 1 hr	Total volume of extracting solution	2 mL	Detection	negative UV-Vis detection at 255 nm
				Time	15 min

438

439 3.6 Method Application

440 3.6.1 Application of the method to natural samples

441 Samples of Hagavatl 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 SO₂ gas. In case of
 444 Hagavatl, the samples were certainly exposed to SO₂ 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 SO₂ [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 SO_3^{2-} and 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 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 SO_4^{2-} for five out of seven samples, they remained under the LOQ level of $3.38 \mu\text{g/mL}$ of 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 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 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

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

474 *Table 8: Results of method reproducibility study for determination of SO₃²⁻ and SO₄²⁻ ions in Hagavatn and Gobi natural*
 475 *samples. Note, that samples were not subjected to laboratory ageing. LOD and LOQ for sulfites and sulfates for each sample*
 476 *mass expressed in µg/m² were calculated from corresponding sample’s mass, specific surface area, extraction volume (2ml) and*
 477 *the values for LOQ and LOD expressed in µg/mL measured earlier (LOD for SO₃²⁻=0.32 µg/mL, LOQ for SO₃²⁻=0.64 µg/mL; LOD for*
 478 *SO₄²⁻=0.68 µg/mL, LOQ for SO₄²⁻=3.38 µg/mL). Determination of the absolute amounts of SO₃²⁻ and SO₄²⁻ requires the observed*
 479 *concentrations of corresponding ions to be equal or more than LOQ.*

Sample	mass (mg)	SSA _{BET} (m ² /g)	LOD for SO ₃ ²⁻ (µg/m ²)	LOQ for SO ₃ ²⁻ (µg/m ²)	Amount of SO ₃ ²⁻ (µg/m ²)	LOD for SO ₄ ²⁻ (µg/m ²)	LOQ for SO ₄ ²⁻ (µg/m ²)	Amount of SO ₄ ²⁻ (µg/m ²)
Gobi	136.2	10.5 ± 2.0	0.45	0.90	< LOD	0.95	4.73	14.1
Gobi	138.5	10.5 ± 2.0	0.44	0.88	< LOD	0.94	4.65	14.8
Gobi	139.5	10.5 ± 2.0	0.44	0.87	< LOD	0.93	4.62	16.5
Gobi	126.2	10.5 ± 2.0	0.48	0.97	< LOD	1.03	5.10	14.4
Gobi	144.5	10.5 ± 2.0	0.42	0.84	< LOD	0.90	4.46	15.5
Gobi	124.2	10.5 ± 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 ± 1.1	1.22	2.44	< LOD	2.59	12.86	< LOD
Hagavatn	113.0	4.5 ± 1.1	1.26	2.52	< LOD	2.67	13.26	< LOQ
Hagavatn	125.4	4.5 ± 1.1	1.13	2.27	< LOD	2.41	11.98	< LOQ
Hagavatn	113.5	4.5 ± 1.1	1.25	2.51	< LOD	2.66	13.24	< LOQ
Hagavatn	190.0	4.5 ± 1.1	0.75	1.50	< LOD	1.59	7.91	< LOD
Hagavatn	110.6	4.5 ± 1.1	1.29	2.57	< LOD	2.73	13.58	< LOQ
Hagavatn	505.4	4.5 ± 1.1	0.28	0.56	< LOD	0.60	2.97	< LOQ
Average								NA
STD								NA
%RSD								NA

480

481 *3.6.2 Application of the method to aged samples*

482 In the next step, following “kinetics study” protocol samples of 134.0 mg of Hagavatn and 115.0
483 mg of Gobi dusts were exposed to 175 ppm of gaseous SO₂ for 1 hour at room temperature and under 30
484 % RH. After extraction, the amount of sulfites formed on the surface was calculated at 54.4±8.6 µg/m²
485 (µg of sulfites per m² specific surface area) for Hagavatn and 27.0±4.3 µg/m² for Gobi desert dust (Figure
486 7). The amount of sulfates formed after 1 hr ageing was estimated at 25.2±8.1 µg/m² (µg of sulfate per m²
487 specific surface area) for Hagavatn and 53.4±17.0 µg/m² for Gobi desert dust. Note, that blank subtraction
488 of 15.4±1.3 µg/m² (µg of sulfates per m² specific surface area) was applied to quantify the amount of
489 sulfates formed on Gobi dust during laboratory ageing. From this experiment it is evident that after 1 hr of
490 SO₂ exposure volcanic dust accumulate a higher amount of sulfites than desert dust and a lower amount
491 of sulfates. From earlier studies it was proposed that SO₂ gas reacts on the surface of the volcanic dust and
492 forms sulfites or bisulfites, which are then converted to sulfates [17], [15]. It is possible that certain
493 mineralogical compounds on the surface of Gobi desert dust are contributing to a more efficient
494 conversion of sulfites to sulfates. A larger sample distribution would be required to confirm the trend and
495 elucidate how the surface chemical composition may influence the respective kinetics of sulfites and
496 sulfates.

497 To evaluate how relevant the artificial ageing is to the processes encountered in real atmosphere,
498 results obtained after a one-hour laboratory ageing of Gobi dust with 175 ppm SO₂ were compared to the
499 field measurements of sulfates performed during a severe dust storm in China. Similarly, results from
500 Hagavatn ageing were compared to leachate measurements of ashes coming from Stromboli volcano in
501 Italy and Soufriere Hills Volcano, Montserrat.

502 In spring of 2002 a dust storm originating from Gobi desert in Mongolia and Taklimakan desert
503 in western China spread over China, Korea and Japan [29]. On March 20 2002, the dust peak
504 concentrations over Beijing reached 10.9 mg/m³ (mg of dust per m³ of air) [29]. Using the same particle
505 matter concentrations as the ones reported over Beijing and the specific surface area of Gobi dust

506 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
507 Gobi dust corresponds to $6.07 \pm 1.9 \text{ } \mu\text{g}/\text{m}^3$ (μg of sulfates present in 1 m^3 of gas), considering a dust
508 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
509 concentration of sulfates determined by [25] from Ion Chromatography analysis of airborne samples:
510 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
511 sulfates on the surface of ash coming from Stromboli volcano, Italy. The results showed a vast variability
512 from 7 to $55,000 \text{ } \mu\text{g}/\text{g}$ (μg of sulfates per g of volcanic sample) [30]. High variability in the amount of
513 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,
514 Montserrat [31]. The amount of sulfate per specific surface determined on Hagavtn volcanic dust
515 ($25.2 \pm 8.1 \text{ } \mu\text{g}/\text{m}^2$), after 1 hr ageing, corresponds to $115 \pm 36 \text{ } \mu\text{g}/\text{g}$. (μg of sulfates per g of dust). Results
516 retrieved from our study fall within the range of concentrations determined by Bagnato et al. and
517 Edmonds et al [30], [31]. Note that for elevated concentrations of sulfates on the surface of volcanic dust,
518 samples can be easily diluted in higher volumes of extraction solution, in our case 1% Formalin.

519 4.0 CONCLUSIONS

520 A reversed-phase HPLC method was successfully developed for the assay of sulfites and sulfates on the
521 surface of dust. A method was developed on a 25 mm Restek Ultra Column C18, Particle size: $5 \text{ } \mu\text{m}$, I.D.
522 4.60 mm column which was dynamically coated with 1.0 mM cetylpyridinium chloride in 7% acetonitrile
523 solution to produce a charged surface as recommended by Zuo et al [19]. Mobile phase used: 1 mM
524 potassium hydrogen phthalate buffer at pH 6.5 at a flow rate of 1.0 ml/min with negative UV-Vis
525 detection at 255 nm in 15 min. The developed method was validated for the specificity, LOD and LOQ,
526 linearity and range, robustness, injection repeatability and reproducibility for sample preparation and
527 extraction. In addition, the sampling method is easy and fast, and does not require expensive or
528 particularly dangerous solvents. Besides, the extracted solution displays excellent stability, which is very
529 important in remote sampling during geological expeditions. Samples can be extracted on site and
530 analyzed days after sampling, provided they are kept in cool temperature conditions. We would like to

531 stress out that in case of “environmental sampling” the method should only be applied if the sample is
532 believed to be recently subjected to SO₂ gas and if quantification of sulfites is desired. Due to the
533 conversion of sulfites to sulfates, the former are not expected to stay on the surface of dust for a long time
534 [20]. An examples of missions that could use the method developed could be: identification of sulfites
535 and sulfates on fresh volcanic ash samples following an eruption, identification of sulfates and sulfites in
536 desert dust samples that pass through industrially polluted areas, as well as laboratory investigation of
537 sulfite and sulfate formation on the surface of natural dusts of different origins. Validity of ageing
538 procedure in the reference to natural gas-particle interactions was discussed. The developed method was
539 successfully applied to assay the amount of sulfites and sulfates formed on the surface of Hagavatn and
540 Gobi dusts both in natural environmental settings and after artificial ageing. Sulfates in the amount of
541 15.4±1.3 µg/m² were detected on the surface of unexposed Gobi dust. As for the laboratory-aged samples,
542 both sulfites and sulfates were detected on the surface of the two dusts. Sulfates were found to be formed
543 in higher quantities on the surface of Hagavatn volcanic dust in comparison with Gobi desert dust sample
544 (54.4±8.6 µg/m² of SO₃²⁻ ion for Hagavatn versus 27.0±4.3 µg/m² of SO₃²⁻ ion for Gobi desert dust),
545 while the opposite trend was observed for sulfates (25.2±8.1 µg/m² of SO₄²⁻ for Hagavatn and 53.4±17
546 µg/m² of SO₄²⁻ for Gobi desert dust).

547

548

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652 **Figure captions**

653

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

659 Figure 2: Left: schematic representation of the setup used to age samples of dust with SO₂ gas. Right:
660 reactor 1 and 2 with deposited dust, zoomed for clarity.

661 Figure 3: Representative chromatograms of: upper blue) Formalin, offset 60 units for clarity; middle
662 black) Hagavatn dust aged in 175 ppm SO₂ for 1 hr and extracted in 1% Formalin, offset 30 units for
663 clarity; lower red) 50/50 K₂SO₃/K₂SO₄ in 1% Formalin.

664 Figure 4: Dissolution studies for Hagavatn dust aged in 175 ppm SO₂ for 1 hr and extracted in 1%
665 Formalin. % RSD for sulfites and sulfates is equal to 16.1% and 32.0% respectfully (see section 3.4).

666 Figure 5: Stability study results for 158.2 mg sample of Hagavatn aged in 175 ppm SO₂ for 10 min.
667 Extraction with 1ml of 1% Formalin. Samples are stored at 4°C. % RSD for sulfites and sulfates is equal to
668 4.7% and 8.7% respectfully (see 3.3.4).

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

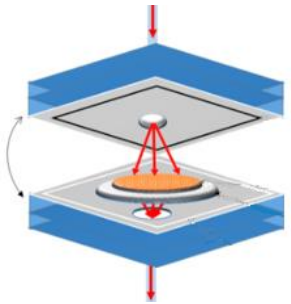
672 Figure 7: Amount of sulfites and sulfates on the surface of Hagavatn volcanic dust and Gobi desert dust
673 formed after ageing with 175 ppm SO₂ gas.

674

Collection of natural mineral dust samples



Dust sample ageing

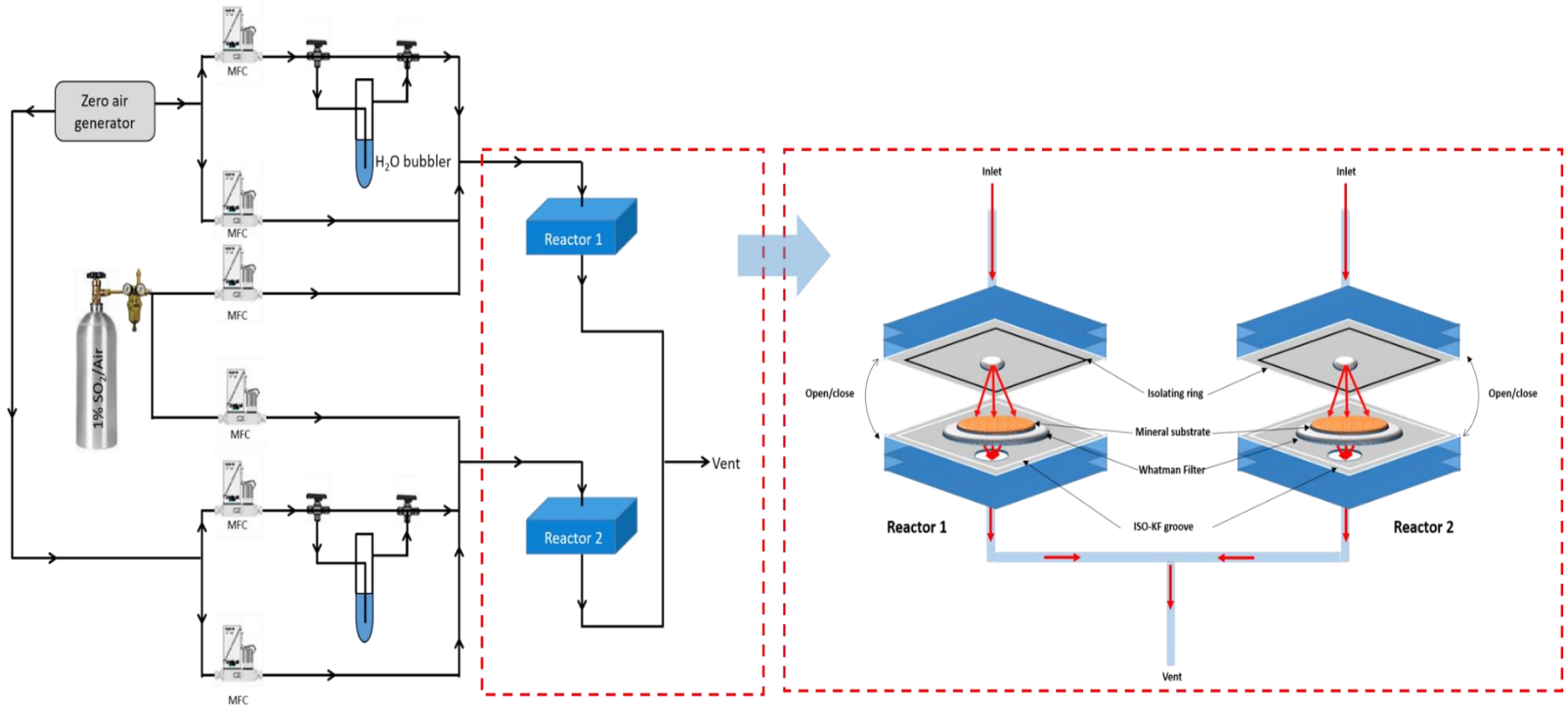


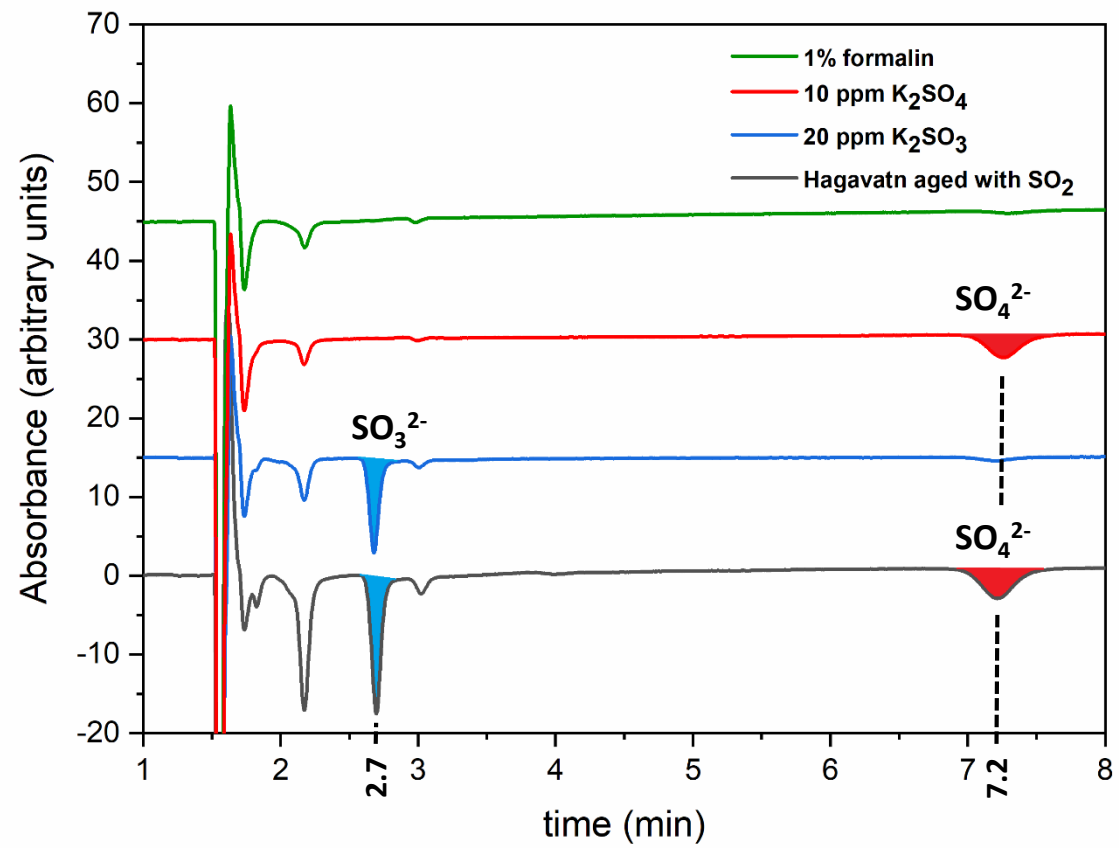
Extraction & stabilization of SO_3^{2-} & SO_4^{2-}

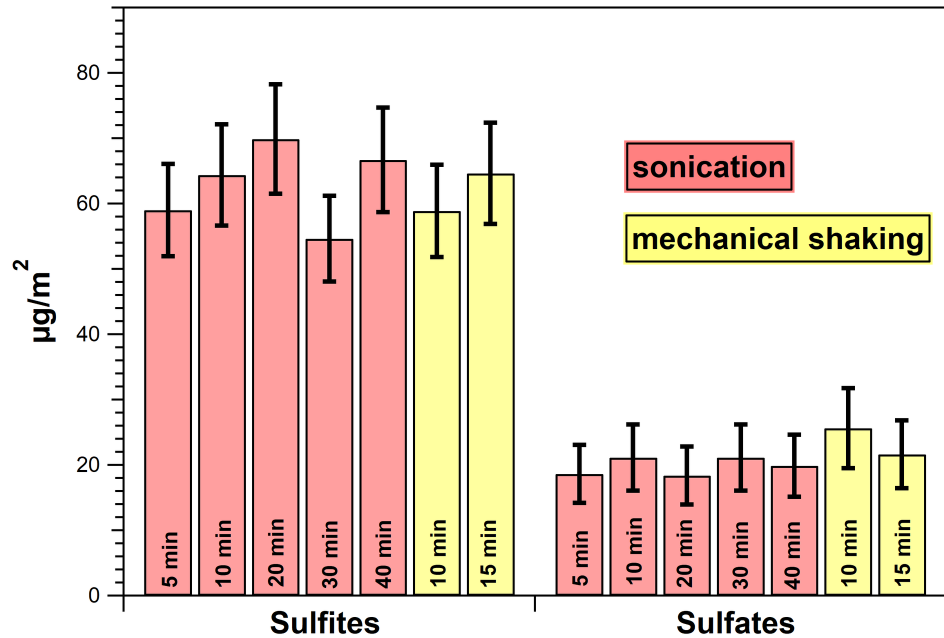


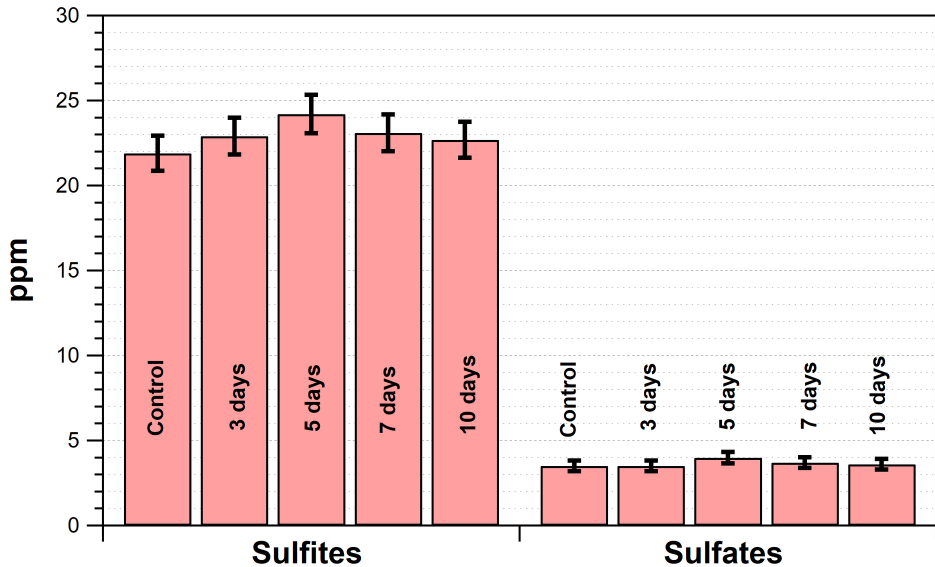
HPLC method run



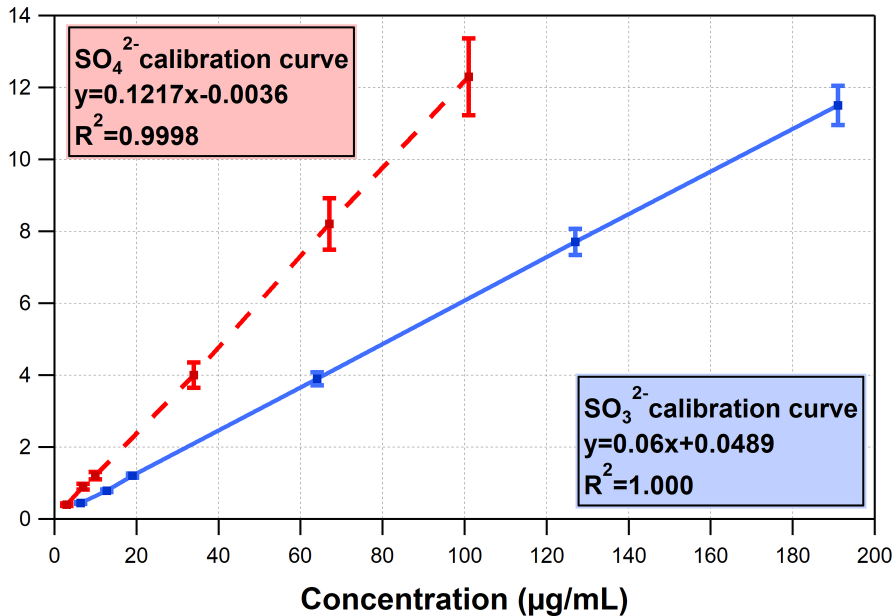


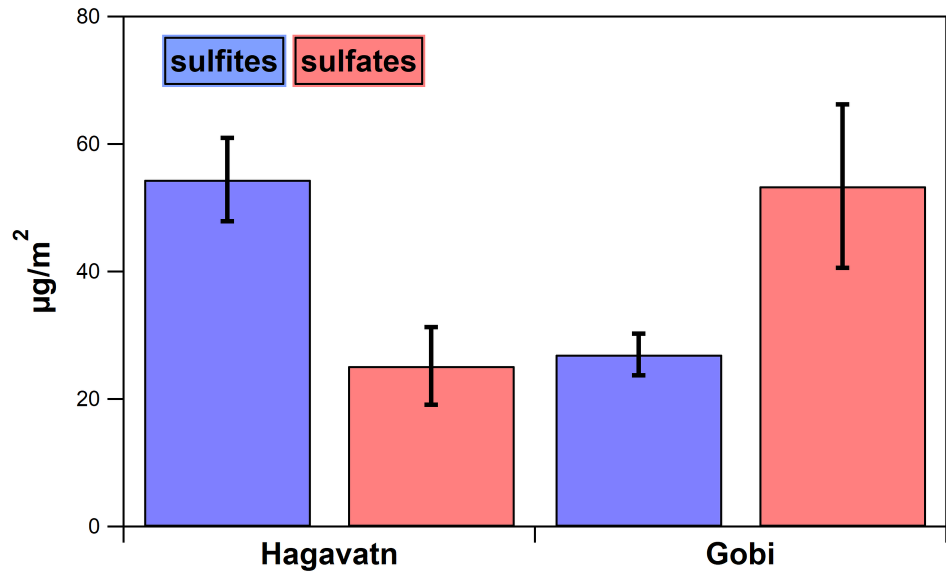






Peak area (mAU*min)

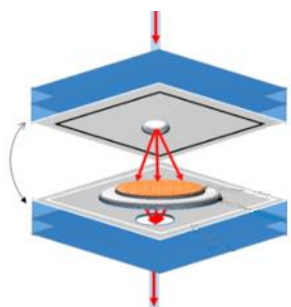




Collection of natural mineral dust samples



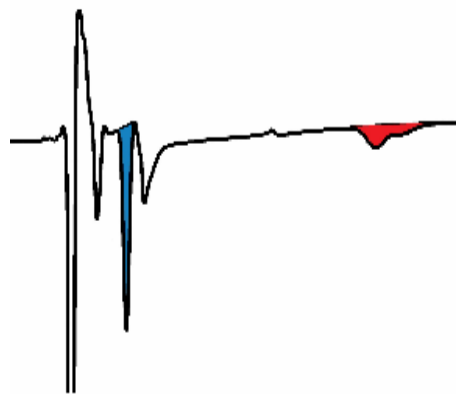
Dust sample ageing



Extraction & stabilization of SO_3^{2-} & SO_4^{2-}



HPLC method run



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

Selective quantification of adsorbed SO_3^{2-} & SO_4^{2-}

