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Laboratory Validation of a Passive Sampler for SO₂ Atmospheric Monitoring

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O desempenho de um amostrador passivo foi testado sob exposição em câmara de Teflon. O SO₂ fixado no filtro impregnado com solução de Na₂CO₃ 1,0 x 10⁻² mol L⁻¹ foi extraído com uso de banho de ultra-som e solução de H₂O₂ durante 15 min, e determinado como SO₄²⁻ por cromatografia iônica. O amostrador apresentou bom desempenho, exceto sob condições de estagnação total do ar (0 m s⁻¹), para períodos de exposição muito curtos (0,5 h), em atmosfera contendo O₃ ≥ 150 μg m⁻³ e compostos reduzidos de enxofre em altas concentrações. A umidade relativa do ar (20 - 80%) e exposição à concentração zero não afetaram o desempenho. Mostrou estabilidade por um mês quando estocado a 4 ℃ ou por uma semana à temperatura ambiente (≈25 ℃). Sua precisão variou entre 3,5 e 23% dependendo da concentração de SO₂ e a exatidão entre 91 e 100%.

The performance of a passive sampler was tested under exposure in Teflon chamber. The SO₂ trapped in impregnated filter with 1.0 x 10⁻² mol L⁻¹ Na₂CO₃ solution was extracted in ultrasound bath with H₂O₂ solution for 15 min and determined as SO₄²⁻ by ion chromatography. The sampler presented good performance except for air in total stillness condition (0 m s⁻¹), for very short exposure periods (0.5 h), for atmosphere with O₃ ≥ 150 μg m⁻³ and for high concentrations of reduced sulfur compounds. The relative humidity of the air (20 - 80%) and the exposure to zero concentration did not affect the sampler performance. It showed stability for one month at 4 ℃ or for one week at about 25 ℃. Its precision varied within 3.5 and 23% depending of the SO₂ concentration and the accuracy varied from 91 to 100%.

Keywords: passive sampling, atmospheric sulfur dioxide, air monitoring

Introduction

High amounts of SO₂, estimated as 100 - 130 millions ton a year, are released in the atmosphere by anthropogenic sources, mainly produced by burning fossil fuel for heating and energy production, and by industrial sources like non-ferrous ore fusion, besides other processes such as sulfuric acid production and paper production.[1-3] SO₂ is also released by natural sources, for instance, through volcanic eruptions, which discharges into atmosphere an amount of sulfur likely smaller than 5 Tg S per year.[3]

Several methods can be used for either indirect or direct determination of the concentration of this gas in the atmosphere,[4] such as spectrophotometric, coulometric, conductometric and chromatographic. For monitoring atmospheric SO₂ concentrations usually active sampling techniques have been applied, which comprise equipments,

sometimes sophisticated, electric power supply, and qualified staff to operate equipments, limiting the number of sites to be measured. Thus, simple alternative methods and low cost become relevant to this purpose. Passive samplers are devices able to fix either gaseous compounds or vapours from atmosphere, without involving air active movement through the sampler. The fixation rate of gases and vapours is controlled by physical processes, such as diffusion and permeation,[5-7] and its average atmospheric concentration during the exposure period is calculated by integration of Fick's first law.[8]

$$C = \frac{mL}{DAt} \qquad (1)$$

where C is the external (environmental) pollutant concentration (μg m⁻³), m is the total collected mass (μg), L is the diffusion course length (m), D is the diffusion coefficient (m² h⁻¹), A is the cross-section area of diffusion course (m²) and t is the sampling time (h).

SO₂ diffusion coefficient in air must be corrected to

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average ambient temperature T (K) and P, atmospheric pressure (Torr) during sampling period, according to equation 2:[9]

$$D = 0.004832 \frac{T^{1.75}}{P} \; ; (cm^2 s^{-1}) \qquad (2)$$

Basically there are two kinds of passive samplers. The first one, also the most used, is based on the principle of molecules diffusion through a static gas layer. Usually there is one or more diffusion barriers between collection surface and air inlet, that do not offer resistance to molecules transport. These barriers control diffusion and sampling rate, and hinder the inlet of particulate material into the diffusion area. The second kind of passive sampler is based on the absorption and further permeation of gas or vapour molecules through a membrane.[10]

Use of these samplers has spread and their theoretical bases were established in the earlier 70's, when Palmes and Gunnison[11] developed a tubular sampler for SO₂. Although passive samplers were first developed to measure individual exposure in occupational environments,[11-19] where pollutant concentrations are fairly high, recently they started to be applied to outdoor environmental monitoring,[20-25] where concentrations usually are much lower than those ones in occupational environments and undergo influence of meteorological conditions.

These samplers present several advantages compared to conventional active techniques: simplicity, low cost, portability, no need for air flux calibration and electricity. Results from passive measurements are derived in form of time-weighted average concentration, and there is no need to know the sampled air volume. These features make this kind of sampler suitable not only to monitor individual exposure, but also for application to environmental atmosphere, including remote areas, where generally there is no available electric power and other techniques cannot be used.[10,26-30] On the other hand, these samplers show some disadvantages, as they do not provide instantaneous concentrations, are not commercially available for several atmospheric compounds, do not allow sampling rate to vary - thus hindering concentration or dilution during sampling -, and do not have suitable sensitivity when exposed for short periods.[28,29] However accuracy of passive samplers have been tested in comparison with active methods, and usually good agreement has been derived for average concentrations in measured periods.[30-33]

This work validated a SO₂ passive sampler, built in the authors' laboratory in order to apply it to atmospheric monitoring networks, making possible spacial resolution for larger areas and improving cost-benefit ratio in the development of environmental activities management.

Experimental

Model of passive sampler used

The passive sampler used in this paper has a configuration suggested by Ferm and Svanberg,[30] and comprises a cylindrical polyethylene tube (21 mm internal diameter and 12 mm length), sealed at the bottom to avoid convective transport thus producing positive errors in determined pollutant concentration. A stainless steel screen (thread diameter 0.08 mm and a aperture of 0.125 mm) followed by a Teflon membrane (pore 0.5 μm, diameter 25 mm) is adapted in the air inlet. After diffusion layer, SO₂ is trapped in cellulose filter impregnated with a suitable reagent (Figure 1).

This model was chosen considering some advantages when compared to other kinds of samplers: possibility of reuse all parts (except filters and membranes), use of different filter loading reagents, minimization of turbulence and penetration of particles at the air inlet by the presence of a Teflon membrane, simplicity of sampler model, as well as possibility of increasing of length and introduction of a second absorbing medium, thus minimizing operational problems and increasing device capacity.
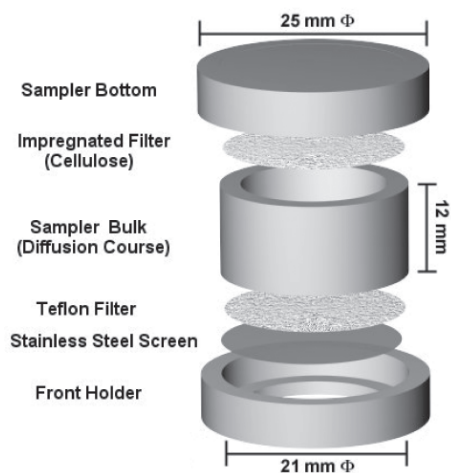

Figure 1. The passive sampler.

SO₂ absorbing medium in passive sampler

Aiming comparison of SO₂ absorption efficiency and definition of the solution to impregnate the filter used in the passive sampler, a previous study was made using different solutions as SO₂ absorbing medium: 1.0 x 10⁻² mol L⁻¹ potassium tetrachloromercurate (TCM: K_2HgCl_4),[4,34] 7 mmol L⁻¹ buffered formaldehyde,[35-37] 1.0 x

10^{-1} mol L^{-1} triethanolamine (TEA: 2,2',2"– nitrilo-triethanol),[38] and 1.0 x 10^{-2} mol L^{-1} Na$_2$CO$_3$.[33] These solutions were prepared in deionized water in the following way: 1.0 x 10^{-2} mol L^{-1} TCM (2.72 g of reagent mercuric chloride and 1.49 g of potassium chloride to 1 L); 7 mmol L^{-1} buffered formaldehyde by dilution formaldehyde solution (37%, 530 μL), 0.204 g of potassium hydrogen phthalate, and 2.0 mL of 50 mmol L^{-1} disodium (trans-1,2-cyclohexylenedinitrilo)tetraacetate (Na$_2$CDTA) to 1 L; 1.0 x 10^{-1} mol L^{-1} TEA by dilution of the concentrated reagent; 1.0 x 10^{-2} mol L^{-1} Na$_2$CO$_3$ (1.06 g of the reagent to 1 L). Absorbed SO$_2$ was determined by UV-Vis spectrophotometry in the two first cases, and by ion chromatography for TEA and Na$_2$CO$_3$ solutions. Tests consisted in bubbling a standard SO$_2$ atmosphere produced by a commercial permeation tube (Dynacal) gravimetrically calibrated (permeation rate: 141 ± 13 ng min^{-1} SO$_2$) and kept in a thermostatic bath (25.0 ± 0.1 °C). Three serial bubblers containing 10 mL of test solution each were used. As carrier gas, commercial nitrogen was used at a rate of 40 L h^{-1} for periods of one hour.

Passive sampler assembly: material preparation

Samplers were prepared in the following way: 25 mm diameter cellulose filter were cut to fit in sampler bottom, followed by washing three times with deionized water in ultrasound bath and once with ethanol for 10 min. After drying in a stove at 50 °C, filters were impregnated for 2 h in a 1.0 x 10^{-2} mol L^{-1} Na$_2$CO$_3$ solution and dried again before being put in samplers. All the other sampler parts as well as vessels used for storing and transport underwent a similar cleaning treatment. Rubber gloves and tongs were used to handle passive samplers and avoid contamination.

Exposure chamber of passive samplers

A Teflon chamber of 30 cm diameter and 120 cm length (Figure 2) based on the model proposed by Zhou and Smith,[39] was built in the laboratory for exposure in passive samplers. A small fan was put inside the chamber to minimize atmosphere stagnation effects, and to assist atmosphere homogenization, making possible to simulate different facial velocities in used samplers.

Passive sampler validation in laboratory

Check of passive sampler performance in laboratory was carried out by exposing in the Teflon chamber, sets of six passive samplers, centered and vertically arranged, hung by nylon wires, and with their front parallel to air
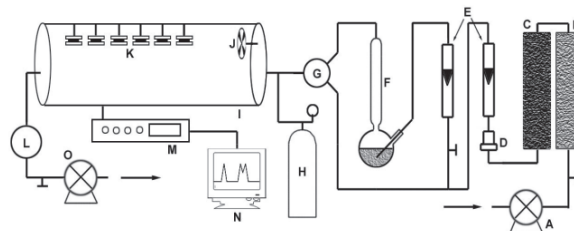

Figure 2. Exposure chamber for passive samplers with other coupled systems. A- air compressor; B- silica gel column; C- activated charcoal column; D- filter; E- flow meters; F- relative humidity generation system; G- mixing chamber; H- cylinder with a standard gaseous mixture; I- exposure chamber; J- fan; K- passive samplers; L- chamber with hygrometer; M- SO$_2$ continuous analyzer; N- data processor; O - suction pump.

flow. A SO$_2$ continuous analyzer (Thermo Environmental, Mod. 43A) was coupled to exposure chamber, in order to control the inner atmosphere. A SO$_2$ standard mixture (15 mg m^{-3} in pure N$_2$) was used to produce different gas concentration inside the chamber, by dilution in clean air from a system of silica gel and activated charcoal columns attached to a filter to prevent airborne particles. The use of a standard SO$_2$ atmosphere from cylinder provided to submit the passive sampler in the exposure chamber to more concentrated atmospheres in the period of the experiments.

Several experiments were carried out aiming to study face velocity, exposure time, pollutant concentration, relative humidity, exposure to zero concentration and interferences effects. Storage effect of exposed samplers was also studied. Atmosphere inside the chamber was kept at room temperature (24 - 26 °C) and SO$_2$ diffusion coefficient was corrected for temperature for each experiment. The period of time to homogenize SO$_2$ inside the chamber was 2 h. At the end of each experiment, samplers were separately stored in sealed polyethylene vessels and kept at 4 °C until analysis. Other experimental conditions are described in items below. All the tests were based on the protocol recommended by the *Comité Européen de Normalisation*[40] for validation of passive samplers.

Data of T and P were obtained during the periods of exposure of the passive sampler in laboratory using thermometer of precision and manometer SOCIOS, Mod. Gulpress 1001.

Analytical methodology

After exposure of passive samplers, SO$_2$ trapped as sulfite in the filter was extracted in ultrasound bath using 1.5 mL of 1.0 x 10^{-2} mol L^{-1} H$_2$O$_2$ solution, for 15 min, to ensure

complete oxidation to sulfate. The extract was centrifuged for 5 min, and analysed by suppressed ion chromatography. Analysis conditions were: suppression in micro-membrane (40-50 mmol L^{-1} H$_2$SO$_4$), separation column BT I AN 5311111 (120 x 6 mm), flow rate 1.8 mL min^{-1} and eluent 2 mmol L^{-1} Na$_2$CO$_3$/ 0.75 mmol L^{-1} NaHCO$_3$.[33]

Results and Discussion

SO$_2$ absorbing solutions

Although 1.0 x 10^{-2} mol L^{-1} TCM and 7 mmol L^{-1} buffered formaldehyde solutions had shown very high SO$_2$ absorption efficiencies (100 and 99% respectively), in bubbling tests, they were not chosen for use in passive samplers. In TCM case, the analytical method is very laborious, and in spite of many former adjustments[34] to overcome interferences from nitrogen oxides, ozone and transition metallic ions (Mn^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, V^{5+}), reproducibility is still dependent on many variables such as pH, temperature, reagent purity degree and standardization of analytical. Furthermore, toxicity of TCM (prepared with mercuric chloride) was taken into consideration. In formaldehyde case, the buffered solution (pH 4.2) used in spectrophotometric method described by Dasgupta *et al.*,[37] where SO$_2$ atmospheric is trapped as hydroxymethanesulfonic acid, has the advantage of less toxicity than TCM. Moreover, this solution is more efficient in SO$_2$ stabilization at room temperature, since only 1% degrade in 30 days,[37] whereas TCM solution has a degradation rate of 1% a day.[34] Yet this is also a very laborious analytical method and shows similar difficulties with reagent purity and temperature dependence.

TEA solution was tested at different concentrations, based on former authors,[22,25,38,41,42] but satisfactory analytical results were found only for 1.0 x 10^{-1} mol L^{-1} solution, whose maximum efficiency of SO$_2$ absorption was 88%. Moreover, TEA presents unsuitable behavior to be used in passive samplers: dependence on relative humidity, problems of sampler storage after exposure and low stability of TEA/SO$_2$ complex.[43]

1.0 x 10^{-2} mol L^{-1} Na$_2$CO$_3$ solution was chosen as SO$_2$ absorbing medium in passive sampler, as it showed other advantages besides high SO$_2$ absorption (97%) and stability after oxidation to SO$_4^{2-}$: it is a stable and non-toxic reagent, and sulfate determination by ion chromatography is simple and fast. Detection limit was 0.10 μg mL^{-1} SO$_4^{2-}$.

The capacity of the passive sampler, calculated with base in the amount of the reagent in the collecting medium (impregnated filter) and stoichiometry of the reaction was about 95 μg SO$_2$, the one that makes possible use it also in occupational environment, where it would be capable to measure, for instance, during a period of 8 h an atmosphere containing 8.6 mg m^{-3} SO$_2$.

Performance of passive sampler in exposure chamber

The statistical test[44] of comparison of mean of two samples (90% confidence level) was applied to data from each passive sampler performance test. The mean obtained by the continuous analyzer was taken as true value and compared with the mean concentration from sets of six passive samplers, and relative standard deviation were thus calculated.

Effect of face velocity

To determine the effect of face velocity on sampler performance, a series of experiments was performed, where sets of six samplers were exposed under conditions corresponding to wind velocities of 0.0, 0.7, 1.8 and 2.5 m s^{-1}, measured with an anemometer placed inside the exposure chamber. These experiments were carried out for 2 h at a relative humidity of 48 - 52%, a temperature of 24-26 °C and a SO$_2$ concentration about 52 μg m^{-3}, which corresponds to a condition of pollution.

In these experiments it was observed that under air stillness condition at the outer face of the passive sampler (face velocity = 0 m s^{-1}), SO$_2$ average concentration in the atmosphere inside exposure chamber measured with these samplers was significantly lower than measured with continuous analyzer (Table 1). This is to be expected, since under these conditions air moves very slowly, out of the sampler diffusion course, decreasing sampling velocity and producing negative errors. This effect is also called "starvation" effect.[45,46]

Relative humidity effect

Different levels of relative humidity were simulated with an hygrometer coupled to an exposure chamber by varying proportions of dried air flow (through drying columns) mixed with humid air (water steam), to varied required humidity level: 20% for low relative humidity, 50% middle, and 80% high. Sets of six passive samplers were simultaneously exposed to atmosphere containing 13 and 52 μg m^{-3} SO$_2$, at facial velocity of 1.8 m s^{-1}, for 2 h. Average SO$_2$ concentration in atmosphere inside exposure chamber measured with both passive samplers and the continuous analyzer did not show any significant difference between them due to variations in relative humidity (Table 1).

Time exposure and concentration effects

For these performance tests and those to follow, sets of six samplers were exposed under fixed conditions of facial velocity (1.8 m s^{-1}), relative humidity (48-52%) and temperature (24 - 26 °C). To study time of exposure as function of SO$_2$ atmospheric concentration, samplers were exposed to SO$_2$ concentration of 13, 52 and 210 μg m^{-3} for 0.5, 2 and 8 h. Passive sampler showed good performance in all situations except for 0.5 h exposure time, the lowest concentration, corresponding to SO$_4^{2-}$ values below the detection limit due to very short exposure time; for the other concentrations false low results were observed (Table 1).

Storage and temperature effect

In order to check storage and temperature effect, samplers were exposed in chamber for 2 h at 52 μg m^{-3} SO$_2$. After exposure, groups of samplers were stored in plastic vessels at 4 °C and at room temperature for 7, 14 and 28 days. Passive sampler showed stability for one month after exposure when stored at 4 °C or at room temperature ($\approx$ 25 °C) for one week.

Effect of interferent substances

O$_3$ and reduced sulfur compounds (RSC) interferences were checked in passive samplers performance for SO$_2$. These were exposed to different concentrations of potentially interferent substances for 2 h. As RSC a standard mixture of COS, CH$_3$SH, CS$_2$ and DMS and other mixture of H$_2$S were used both in pure N$_2$. Different concentrations of these substances were produced in the chamber by dilution with clean air. An ozonizer, based on UV light, was used as O$_3$ source and produced concentrations, which were monitored with an O$_3$ continuous analyzer. Results from this study are shown in Table 2 and Figure 3. These were exposed to different concentrations of potentially interferent substances for 2 h.

The passive sampler did not show a good performance for atmosphere containing ozone concentrations higher than 150 μg m^{-3}, which corresponds to high pollution condition (quality standard for O$_3$ in Brazil is 160 μg m^{-3} for one hour)[47] and in presence of H$_2$S concentrations higher than 7 μg m^{-3}, which also corresponds to a high pollution condition, in which H$_2$S can be sensed by its characteristic rotten egg odor (guideline from World Health

Table 1. Results of chamber performance tests of SO$_2$ passive samplers with Na$_2$CO$_3$ impregnated filter as function of face velocity, relative humidity, exposure time, storage time and temperature

Parameter	CSO$_2$ / (μg m^{-3})	
	Continuous Analyzer	Passive Samplers
Face velocity / (m s^{-1})		
0	57.8 ± 9.7	46.1 ± 2.4[a]
0.7	53.9 ± 6.0	53.4 ± 8.6
1.8	54.2 ± 5.5	55.2 ± 9.4
2.5	60.5 ± 6.0	61.0 ± 5.2
Relative humidity /%		
20	13.1 ± 4.2	14.1 ± 2.6
	49.0 ± 12	51.8 ± 7.1
50	13.6 ± 3.7	14.4 ± 2.9
	54.2 ± 5.5	55.2 ± 9.4
80	13.6 ± 4.2	14.7 ± 3.4
	56.5 ± 8.1	62.0 ± 8.9
Exposure time / h		
0.5	12.6 ± 3.7	n d
	47.9 ± 4.7	41.9 ± 1.6[a]
	191 ± 17	171 ± 9.2[a]
2.0	13.6 ± 3.7	14.4 ± 2.9
	54.2 ± 5.5	55.2 ± 9.4
	209 ± 16	203 ± 10
8.0	14.1 ± 3.9	12.8 ± 2.6
	54.4 ± 7.1	55.0 ± 2.4
	206 ± 15	207 ± 7.3
Storage time and temperature		
Analysis immediate	57.8 ± 5.2	56.8 ± 3.7[b]
7 days to 4 °C	-	58.4 ± 2.1[c]
Analysis immediate	58.4 ± 5.0	57.6 ± 8.1[b]
7 days to 25 °C	-	58.9 ± 5.5[c]
Analysis immediate	51.0 ± 7.8	50.5 ± 2.9[b]
14 days to 4 °C	-	50.8 ± 2.4[c]
Analysis immediate	53.9 ± 9.4	55.0 ± 5.8[b]
14 days to 25 °C	-	43.7 ± 1.0[a,c]
Analysis immediate	58.9 ± 5.5	57.6 ± 5.0[b]
28 days to 4 °C	-	56.3 ± 5.2[c]
Analysis immediate	52.9 ± 5.8	54.4 ± 4.2[b]
28 days to 25 °C	-	36.6 ± 8.9[a,c]

nd - no detected; [a]Average with significant difference when compared statistically with the average continuous analyzer; [b]Average from three measurements carried out in parallel and analyzed immediately; [c]Average from three measurements carried out in parallel and analyzed after storage time.

Table 2. Performance of passive samplers under exposure to SO$_2$ atmosphere containing reduced sulfur compounds

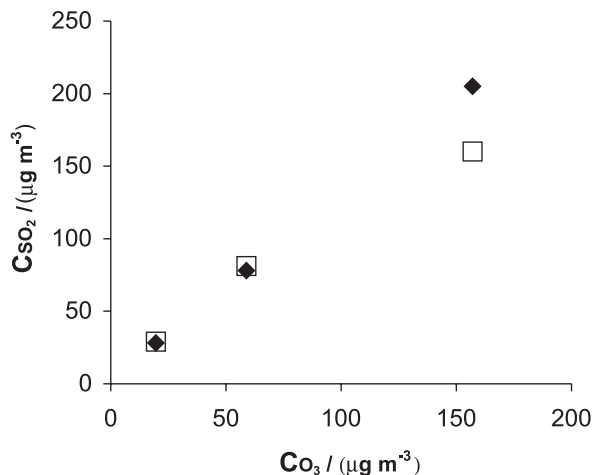| Atmosphere in the chamber / (μg m^{-3})						CSO$_2$ from the passive	RSD /%
SO$_2$	H$_2$S	COS	CH$_3$SH	CS$_2$	DMS	sampler / (μg m^{-3})	
7.47 ± 3.7	1.39	—	—	—	—	7.62 ± 2.9	2.1
6.89 ± 3.4	3.48	—	—	—	—	7.13 ± 3.0x10^{-2}	3.4
14.5 ± 3.1	6.97	—	—	—	—	15.9 ± 2.1	9.7
6.37 ± 3.7	—	6.14	4.92	7.79	6.35	6.31 ± 1.2	8.0x10^{-3}
15.7 ± 4.7	—	12.3	9.84	15.6	12.7	14.1 ± 2.5	9.9
28.0 ± 5.8	—	24.6	19.7	31.1	25.4	29.6 ± 1.6	5.6

Figure 3. Effect of ozone interference on performance of SO$_2$ diffusion passive samplers using Na$_2$CO$_3$ impregnated filter. Precision: 3-14%; Accuracy: 3-4% (except for O$_3$ concentration = 157 μg m^{-3}); (□) Mean from sets of six passive samplers; (◆) Mean from the SO$_2$ continuous analyzer in parallel with passive samplers.

Organization recommends this value as maximum exposure for 30 min). For the other RSC's at maximum tested concentration (20-30 μg m^{-3}) a good passive sampler performance was achieved (RSD about 6%).

Exposure to zero concentration effect

Experiments were carried out to study the sampler exposure to a clean atmosphere, following exposure to 52 μg m^{-3} SO$_2$ for 2 h. After this 2 h period, the six samplers were taken out from the chamber. Afterwards the clean air passed through the chamber. Next, three other samplers not previously exposed (blank) were put inside the chamber together with three samplers exposed in the first stage for 4 h, where just clean air was injected into chamber, under environmental conditions identical to previous. Analysis of the Table 3 does not confirm any significant difference in SO$_2$ amount sampled before exposure to zero concentration.

Precision and accuracy

By experiments with SO$_2$ passive sampler exposed in

chamber, estimates of precision based on relative standard deviation, ranged from 18 to 23% for 13 μg m^{-3} SO$_2$, from 4.3 to 18% for 52 μg m^{-3} SO$_2$, and from 3.5 to 5.2% for 210 μg m^{-3} SO$_2$. Simultaneous measurements under same conditions made with a continuous analyzer that recorded concentration values every 5 s, had precision between 26 and 32%, 7 and 25%, and 7 and 9% respectively. These ranges are wider than those ones of measurements with a passive sampler, which indicated that atmosphere homogenization inside the chamber might not have been complete. The International Standardization Organization (ISO) 1997[48] recommends the use of an exposure chamber with minimum size of 2 x 2 x 3 m, as the minimum as to ensure a total atmosphere homogenization. However, in this work, the chamber model suggested by Zhou and Smith[39] was the only available.

By using results from tests in chamber, 27 experiments with sets of six samplers, accuracy was determined as 96 ± 3.4%. Variability was from 91 to 100%, independent of exposure time, SO$_2$ concentration and/or interferent substances present in the chamber atmosphere, and meteorological conditions like relative humidity and wind velocity. The correlation between the average measurements from passive samplers and continuous analyzer was high and significant (R= 0.9980; p < 0.0001).

Conclusions

From all tested reagents, 1.0x10^{-2} mol L^{-1} Na$_2$CO$_3$ solution showed the most promising features as SO$_2$ absorbing medium for passive sampler (PS). Tests of PS in exposure chamber showed that: to a large extent sampler performance was not influenced by variation of relative humidity of tested air (20-80%); sampler remains stable for one month after exposure when stored at 4 °C and for one week at room temperature ($\approx$ 25 °C); in view of known atmospheric concentrations of RSC in natural and industrial areas[49-52] being much lower than levels interfering in passive sampler efficiency (> 7 μg m^{-3} H$_2$S and 20-30 μg m^{-3} for the other RSC), these samplers performance are hardly be influenced by these compounds;

Table 3. Effect of exposure to zero concentration on the performance of diffusion passive samplers with Na$_2$CO$_3$ impregnated filter for SO$_2$

Exposure Stages	CSO$_2$ / (μg m^{-3})	
	Continuous Analyzer	Passive Samplers
Stage 1: Six passive samplers, 2 h exposure, atmosphere containing SO$_2$ ($\approx$ 60 μg m^{-3})	58.6 ± 8.9	57.1 ± 3.9[a]
Stage 2: Three passive samplers previously exposed followed by 4 h exposure to clean atmosphere	——	58.1 ± 5.2[b]

[a] Average from three measurements carried out in parallel in stage 1; [b] Average from three measurements carried out in parallel in stages 1 and 2.

SO$_2$ amount trapped in PS upon exposure is not altered when sequentially exposed to zero concentration for 4 h, indicating their suitability for remote regions, whose atmosphere can stay clean for periods. In a similar way, these tests indicate that they can be used in polluted areas as well next to industrial sources, where emissions are often intermittent; PS did not show good performance only under air stillness condition (face velocity = 0 m s^{-1}), in atmosphere with O$_3$ concentration ≥ 150 μg m^{-3} and for very short time exposure, 0.5 h, for instance, where false lower results were obtained. Estimates of precision of PS in exposure chamber, based on relative standard deviation of six samplers each, ranged from 18 to 23%, from 4.3 to 18%, from 3.5 to 5.2%, respectively for exposure to 13, 52 and 210 μg m^{-3} SO$_2$. Its accuracy was de 96 ± 3.4%, independent of exposure time, SO$_2$ and/or interferent substances levels in chamber atmosphere, as well as of meteorological conditions such as relative humidity and wind velocity.

Acknowledgements

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