

Research Article

Low cost passive monitoring of sulphur dioxide in ambient air: An effort from developing world

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Abstract

Standard sulphur dioxide (SO₂) monitoring techniques require expensive instrumentation which is not easily adapted for large scale monitoring by resource limited countries. This paper presents the use of locally available relatively cheaper polyethylene tubes to be developed as passive diffusive sampler and use for monitoring of ambient sulphur dioxide using Tri-ethanolamine (TEA) as absorbent. After extraction with double distilled water, modified West-Gaeke method was used for analysis of sulphate adduct formed due to reaction of SO₂ with TEA using spectrophotometer. The results are successfully compared with other standard methods. The detection limits and precision of the method as expressed as coefficient of variation are good for monitoring of SO₂ in ambient air.

Key words: Diffusive sampling, Passive sampler, Sulphur dioxide

Introduction

Sulphur dioxide (SO₂) is a ubiquitous pollutant found in the ambient air which exhibit documented adverse effects on health and welfare (Santis et al., 1997). The standard SO₂ monitoring techniques require expensive instrumentation, however, the diffusive samplers, also called passive samplers, are lightweight, inexpensive and do not need maintenance, on-site power and pumping (Palmes et al., 1973; Santis et al., 1997).

Therefore, passive samplers which offer a simple, cost-effective means of measuring air pollutants have been performed for the monitoring of ambient SO₂ levels worldwide (Ferm & Svanberg, 1998; Ferm et al., 2009; Hangartner et al., 1989; Hargreaves & Atkins, 1988). The simplest diffusion sampler is the tube-type sampler first introduced by Palmes (Palmes et al., 1976). These earlier tubes use tri-ethanolamine (TEA) as absorber. With the time several different types of passive samplers have been developed using different absorbers. Noticeably, at present, at least two absorbers have been utilized in Palmes type diffusion tubes for the determination of SO₂. Hargreaves and Atkins (1988) used mesh discs impregnated with potassium hydroxide (an absorbent for SO₂) and glycerol (a humifacant).

Hangartner et al. (1989) used SO₂ diffusion tubes of the same design as Hargreaves and Atkins (1988), but used a tri-ethanolamine (TEA) glycol mixture as the absorber and stabilizer for sulphite and the pararosaniline method of analysis (ISO, 1990). Ferm described yet another method using badge-type sampler with carbonate impregnated filter to trap SO₂ and analyzed as sulphate using ion chromatography (Ferm, 1991; Ferm et al., 2009).

Passive samplers are generally designed either in a tube-type configuration with one end open (so-called "Palmes tubes"); or in a shorter badge-type configuration, where the open end is protected by a membrane filter or other wind screen. In either case, the closed end contains an absorber for the gaseous species to be monitored. Several different types of commercial diffusion tubes are there in market in recent time. These includes; Ivl-Sweden, Gradko, UK; Rediolle, Italy; Ogawa, Japan etc. All of these samplers were developed basically from above mentioned two types of diffusion tubes and available in the different price rate according to the manufacturers. For example, Gradko tubes cost \$10 per sampler while Rediolle from Italy cost Euro 30 per sampler. Thus, these commercially available passive samplers are still costly for a developing country like Nepal. Hence it is in pertinent to have a sampler which is affordable

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and logistically feasible to be sampled and analyzed in our environment. In this line the present study describes locally available polyethylene tubes with tri-ethanolamine coated filter paper as SO₂ sampler and ambient monitoring of the same.

Operating principle of passive samplers

The basic principle on which diffusion tube samplers operate is that of molecular diffusion, with molecules of a gas diffusing from a region of high concentration (open end of the sampler) to a region of low concentration (absorber end of the sampler). The movement of molecules of gas (1) through gas (2) is governed by Fick's law, which states that the flux is proportional to the concentration gradient:

$$J = D_{12} \frac{dc}{dz} \quad (1)$$

Where,

J = the flux of gas (1) through gas (2) across unit area in the z direction (g m⁻² s⁻¹)

C = the ambient ozone concentration (g m⁻³)

Z = the length of the diffusion path (m)

D₁₂ the molecular diffusion coefficient of gas (1) in gas (2) (m² s⁻¹) For a cylinder of cross-sectional area a (m²) and length l (m) then Q (g), the quantity of gas transferred along the tube in t seconds (taken as the quantity of gas absorbed during t) is given by:

$$Q = D_{12} (C_1 - C_0) \frac{at}{l} \quad (2)$$

Where,

C₀ and C₁ are the gas concentrations at either end of the tube.

In a diffusion tube, the concentration of gas (1) is maintained at zero by an efficient absorber at one end of the tube (i.e. C₀ is zero) and the concentration C₁ is the average concentration of the gas (1) at the open end of the tube over the period of exposure.

Hence:

$$C = \frac{Ql}{D_{12} at} \quad (3)$$

The diffusion coefficient for the gas to be monitored must be determined, or obtained from the literature. The area and length of the tube are determined by measurement. The sampling rate (SR) of passive samplers can be calculated using the formula:

$$SR = D_{12} \frac{a}{l} \quad (4)$$

Then they were expressed as ml of air sampled per second. This makes it possible to directly compare sampling rates of passive samplers with those of active samplers. (UNEP/WHO/GEMS/AIR, 1994).

Materials and Methods

Diffusion sampler preparation

Polyethylene tubes of 5 cm long with 1.2 cm cross section with one end open from local supplier were used for sampling. Filter paper (GF/A) cut into the circular equal to the inner cross section of the tube dipped into double distilled water for 24 hrs followed by air drying was placed into the closed end of the tube. TEA water was fed in each diffusion tube as trapping solution on GF/A filter paper used as absorbent base.

Eight tubes each were used for 10 μl of 50 % (v/v) TEA water, 20 μl of 50 % (v/v) TEA water, 15 μl 20 % (v/v) TEA water, respectively for SO₂ sampling. Of the 8 tubes 4 (2 duplicates, one blank and one laboratory blank) were for spectrophotometric analysis and four for ion chromatographic analysis were prepared.

Exposure

All the sets (48 diffusion tubes) of diffusion tubes prepared were exposed at Padova university premise during months of Nov-December, 2006. Twenty four samplers were exposed for one week and next twenty four samplers were exposed for two weeks.

Caps of the tubes were opened at the sampling sites. The field blanks were placed at the sampling sites without opening the caps of the tubes. The laboratory blanks were placed in the laboratory at room temperature without opening the caps. Diffusion tubes were put inside an airtight plastic box during transportation to the sampling sites and also after collection from the sampling sites.

The tubes were protected from sunlight, wind, rainfall or drought by placing inside a transparent plastic box, made as sampler holder (Fig. 1). The diffusion tubes were fixed inside polyethylene box with adhesive tape.



Fig.1 Exposure of passive sampler tubes

Sample extraction and analysis

Spectrophotometric analysis

Sulphate (SO_4^{2-}) present on the filter paper of the samplers were extracted using double distilled water. Standard sulphate solution and extracted samples were analyzed for SO_4^{2-} using West-Gaeke method at 560 nm (Hangartner et al., 1989; ISO, 1990; Reiszner & West, 1973).

Ion Chromatographic analysis (IC)

The diffusion tubes were extracted with 2 ml of milli-Q water, mixed with 9.5 μl of 35 % hydrogen peroxide and analyzed for nitrite and sulfate by a Dionex ion chromatography using standard techniques: using mobile phase 1.80 mM Na_2CO_3 /1.70 mM NaHCO_3 , eluent flow rate 1.5 ml/minute, conductivity detection.

Concentrations were calculated from the calibration graph of mixed standard ion chromatogram. The average ambient air concentration then obtained according to Gair and Penkett (1995), Miller (1984), Palmes et al. (1976), Plaisance et al. (2002). All the chemicals used were of analytical grade.

Statistical analysis

Method validation

Precision was expressed as the coefficient of variation (CV), also referred to as relative precision by the US EPA (United State Environment Protection Agency), CV was calculated as the sample standard deviation divided by the sample mean times 100 %.

Accuracy of passive sampler was evaluated by comparing the measured results with the co-exposed sampler analysis by standard ion chromatographic analysis. The results were also compared with the data from the Environmental Pollution Department, Padova municipality which provides continuous ambient air quality monitoring using automatic analyzer.

Uncertainty Analysis

Detection limit and minimum detectable quantity

For this research, two kinds of detection limit (DL) were calculated. The first DL was for the analytical equipment, spectrophotometer and second DL was for the entire sampling method of NO_2 and SO_2 for different exposure. The DL for the spectrophotometer was calculated from a calibration curve with the help of equation 5 (Miller, 1984). The detection limit (Y) is the analyte concentration that gives a signal equal to the blank signal (YB) plus three standard deviations of the blank, SB.

$$Y = YB + 3SB \quad (5)$$

The detection limit for the passive sampling method was calculated by multiplying the standard deviation of blank values with one-tailed t-value (degrees of freedom at 99 % confidence level). The equation is given below.

$$DL = SB * t(a, n-1) \quad (6)$$

Where,

SB = standard deviation of blank values

t (a, n-1) = critical value of t-distribution with n-1 degrees of freedom and a significance level of (0.01 level).

Results and Discussion

This work presents an affordable cheap method for passive measurement of ambient SO_2 using locally available polyethylene tubes. This includes development of the tubes into diffusive tubes using triethanolamine (TEA) as absorbent. After extraction with water, West-Gaeke method was used for analysis of sulphate adduct formed due to reaction of SO_2 using spectrophotometer (Hangartner et al., 1989; Reiszner & West, 1973). These methods were selected in consideration to the ease of chemical analysis which was logistically feasible to be sampled and analyzed in our context to replicate in future. In addition, these methods were described in many previous studies and are proven standard test analysis (UNEP/WHO/GEMS/AIR, 1994).

Calibration curve from sulphate (SO_4^{2-}) standards were prepared and used for subsequent analysis of blanks and exposed tubes. Same standard curves were used for the calculation of detection limits as well.

Average value of SO_2 from the exposed tubes after subtraction from that of the blanks at the corresponding sites was used in equation 3 to determine SO_2 in $\mu\text{g}/\text{m}^3$ concentration in ambient air respectively. Diffusion coefficient of SO_2 in ambient air is $1.27 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, which was used for calculation of ambient concentration for field measurement (Shakey, 2004).

Apart from the chemical factors, passive analysis of the pollutants depends on the several physical factors such as: diffusion sampler's size, mounting directions and conditions, and local meteorological conditions. This study was undertaken in confined with the test of tubes which were easily available from the local market as to be used as diffusive samplers rather than manufacturing the passive samplers.

The result of all field exposures provides a reliable ambient SO_2 passive sampler with good precision, quite capable of comparison to the other methods (Table 1). Precision of SO_2 measurements were 11.04 % and 3.3 % for one week and two weeks of exposure, respectively compared adequately with the US National Institute of Safety and Health (NIOSH) acceptance criterion (25 %) for field performance of passive sampler applications in air (Seethapathy et al., 2008). The ambient concentration of SO_2 was found to be $4.5 \mu\text{g}/\text{m}^3$ and $9.4 \mu\text{g}/\text{m}^3$, for one week and two weeks exposures, respectively.

The number of samples presented in Table 1 is lower than the number of exposed tubes installed and analyzed. Some of the field blanks and the exposed tubes gave negative absorbance values. The filter papers dropped out from some of the tubes. The dropped out were more for lower volume of TEA such that almost all of the tubes with 10 μl of 50% TEA water and 15 μl of 20% TEA water were dropped out. None of the tubes with 20 μl of 50% TEA water were lost.

Thus, the selection of both volume and nature of absorbent has an important part in passive sampling. Though there are other absorbents described in the literature such as, KOH + glycerol (Hangartner et al., 1989), Na_2CO_3 + TEA (Hargreaves & Atkins, 1988), TEA is more popular as the absorbents for SO_2 measurements. Some problems had also been reported with using TEA as the absorbent as well.

Table 1 Ambient NO_2 and SO_2 concentration by test passive sampler using Test method, IC analysis and automated analyzer (Padova municipality) exposed at Padova University, Italy.

Analysis Methods	Mean SO_2 $\mu\text{g}/\text{m}^3$	
	One week Exposure	Two week Exposure
Passive monitoring-Test method (Test sampler + spectrophotometer)	4.52 \pm 0.499 (n=5) CV=11.04%	9.42 \pm 0.31 (n=5) CV=3.29%
Passive monitoring (Test sampler + IC)	5.4 \pm 0.114 (n=5) CV=2.1%	11.3 \pm 0.336 (n=5) CV=2.9%
Active method (Automated monitor)	6 (fluorescent analyzer)	10 (fluorescent analyzer)

Comparison with active sampling measurement

The data for active sampling, measured by a fluorescent analyzer for SO_2 , was obtained from the Pollution Control Department, Padova municipality, Italy for sampling at Padova university premises.

No correlation was found for the results of SO_2 between active and passive monitoring. However, it was observed that passive monitoring by test method underestimates of 15% with that of active fluorescent measurement for SO_2 in the tested exposure period.

Comparison of test method with chromatographic analysis

The exposed tubes after extraction with eluent and H_2O_2 were left for at least 15 minutes. The solution was then filtered and injected into an ion chromatograph under optimized conditions to determine SO_4^{2-} concentration (Fig. 2, 3).

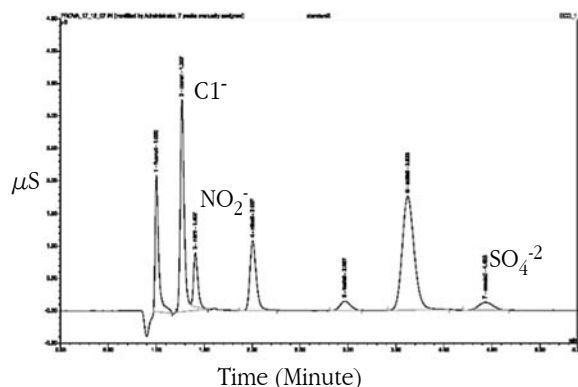


Fig. 2 Example Chromatogram presenting Standard sample run

The average value of SO_4^{2-} in the tubes from two injections and after conversion into the corresponding quantities of SO_2 in the tube and subtraction from the field blank values at the corresponding sites was to determine SO_2 concentration ($\mu\text{g}/\text{m}^3$) in ambient air.

Good correlation was observed between the analysis of developed passive sampler exposure analysis between two methods; spectrophotometric and ion chromatography (Fig. 4). According to current study spectrophotometric analysis underestimates about 16-17% over that of ion chromatography analysis measurement for ambient SO_2 . Ion chromatography analysis underestimates (10%) for one week exposure while overestimates (13%) for two week exposure periods in compared to active method (automated fluorescence analyzer).

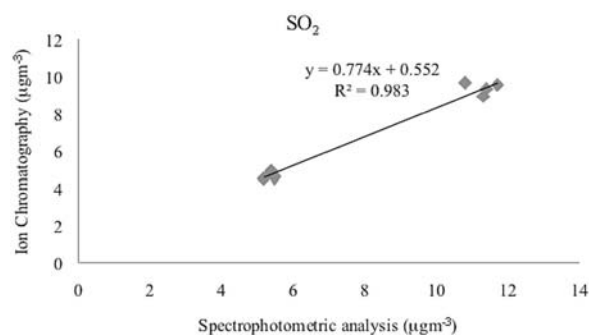


Fig. 4 Comparison of test method with ion chromatography analysis for field exposure at Padova University, Italy (November-December, 2007)

The overestimation of SO₂ measurements can be caused by interferences from wall deposition of SO₄⁻² aerosols (Campbell et al., 1992). In this study, the diffusion tubes were exposed inside the boxes to avoid interference. Dust particles were still deposited on walls of the tubes. This dust might contain SO₄⁻² anions leading to overestimation of SO₂ concentrations. The porous membrane at the open end of the tube is necessary to avoid the interference from SO₄⁻² aerosols. These membranes can also help to minimize the effects from wind driven mixing of air in the mouth of the tube (Ferm & Svanberg, 1998). Tubes with two caps might also be helpful so that the cap with the sampling medium and the tube parts could be disassembled. The body of the tube can then be cleaned to avoid the SO₄⁻² aerosol depositions on the inner surface of the tube before extraction (Plaisance et al., 2002). The sampler tubes also do not have a porous membrane at the mouth of the tube. This might have contributed to the overestimation of SO₂ concentration.

Table 2 Detection limits (DL) of NO₂ and SO₂ (μg/m³) for field exposure

Field study parameter	Number of field blanks (n)	t-value (t _{0.01, n-1})	Standard deviation (SD)	Detection limit (DL)
SO ₂ for one week exposure	5	3.747	0.43	1.62
SO ₂ for two week exposure	5	3.747	0.34	1.28

The detection limits of SO₂ for the diffusion tubes were suitable for the study areas as the concentrations measured were not found to be below the detection limit. The detection limit for SO₂ was also suitable to be analyzed by ion chromatography as it was higher than the instrument detection limit. The detection limit of the spectrophotometer may not be sufficient to measure in low concentration areas as the concentrations may be lower than the instrument detection limit. However, the annual average concentration of SO₂ was reported to be lower than the National ambient air quality standard (NAAQS-Nepal) in Kathmandu; which was 50 μg/m³ (MoEST, 2007), the method developed, hence can be used for the monitoring of ambient SO₂ concentration in Kathmandu as well.

Conclusion

A simple locally available polyethylene tubes can be developed and used as passive sampler for monitoring of ambient SO₂, which can even be used in Kathmandu. The developed method can be used to determine as low as 1.62 μg/m³ and 1.28 μg/m³ of SO₂ for a week and two weeks exposure periods, respectively, for analysis in ambient air. The precision and accuracy of the method been successfully meet the acceptance criterion required by passive air monitoring with other standard methods. The method is cheap and logistically feasible to be used in the other parts with limited resources.

Detection limit

The detection limits was calculated for the analytical equipment and the sampling method for the tubes. The detection limit of the spectrophotometer obtained from the calibration curve with the help of equation 5 was 0.05 μg/ml for SO₂.

The detection limit for the ion chromatograph was obtained by injecting a mixed standard of 0.01 μg/ml of SO₄⁻². The equation 6 gave the detection limit of 0.02 μg/ml and the minimum detectable quantity of 0.36 μg/ml for SO₄⁻².

The standard deviation of blank values was used to calculate the detection limit for the passive sampling method. The detection limit of SO₂ for one week and two weeks exposure periods were estimated (Table 2).

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