Low cost Passive Monitoring of Nitrogen dioxide and Sulphur dioxide in ambient air

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Abstract

Standard nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) 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 nitrogen dioxide and sulphur dioxide using Triethanolamine (TEA) as absorbent. After extraction with double distilled water, modified Griese-Saltzmann method and West-Gaeke method were used for analysis of nitrite and sulphate adduct formed due to reaction of NO_2 and SO_2 respectively 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 enough for monitoring of NO_2 and SO_2 in ambient air.

Keywords: Nitrogen dioxide; Sulphur dioxide; passive sampler; diffusive sampling.

Introduction

Nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) are two of the ubiquitous pollutants found in the ambient air which exhibit documented adverse effects on health and welfare. [1] While standard NO_2 and SO_2 monitoring techniques require expensive instrumentation, diffusive samplers, also called passive samplers, are lightweight, inexpensive and do not need maintenance, on-site power and pumping. [1,2] Therefore passive samplers which offer a simple, cost-effective means of measuring air pollutants have been performed for the monitoring of ambient NO_2 and SO_2 levels worldwide. [3-6] The simplest diffusion sampler is the tube-type sampler first introduced by Palmes et al. [2] These earlier tubes use triethanolamine (TEA) as absorber. With the time several different types of passive samplers been developed using different absorbers. Noticeably, at present at least five reasonably well developed passive sampling methods for determination of NO_2 in addition to the Palmes tube; the Yanagisawa and Nishimura method,[7] the modified Amaya-Sugira method [8, 9, 10, 11]; the Cadoff and Hodgeson method[12] ; the Lewis and Mulik method [13, 14] , and the Ferm method.[15]

Likewise, two absorbers have been utilized in Palmes type diffusion tubes for the determination of SO_2. Hargreaves and Atkins (1988) used mesh discs impregnated with potassium hydroxide (an absorbent for SO_2) and glycerol (a humifactant).[16] Hangartner et al.

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(1989)[17] used SO_2 diffusion tubes of the same design as Hargreaves and Atkins (1988), but used a triethanolamine (TEA)/glycol mixture as the absorber and stabilizer for sulphite, and the pararosaniline method of analysis [18]. Ferm described yet another method using badge-type sampler with carbonate impregnated filter to trap SO_2 and analyzed as sulphate using ion chromatography.[4]

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 cost rate according to manufacturer. 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 and logistically feasible to be sampled and analyzed in our environment. In this line we describe here such an attempt to use locally available polyethylene tubes with triethanolamine coated filter paper to be used as NO_2 and SO_2 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:

$$J = D_{12} \, dc/dz \qquad (1)$$

Where, J = the flux of gas (1) through gas (2) across unit area in the z direction ($\mu g \, m^{-2} \, s^{-1}$)

C = the ambient ozone concentration ($\mu g \, m^{-3}$)

Z = the length of the diffusion path (m)

D_{12} = the molecular diffusion coefficient of gas (1) in gas (2) ($m^2 \, s^{-1}$)

For a cylinder of cross-sectional area a (m^2) and length l (m) then Q (μg), the quantity of gas transferred along the tube in t seconds (taken as the quantity of gas absorbed during t) is given by:

$$Q = D_{12} \, (C_1 - C_0) \, at \, / \, l \qquad (2)$$

Where, C_0 and C_1 and 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. C_0 is zero) and the concentration C_1 is the average concentration of the gas (1) at the open end of the tube over the period of exposure. Hence:

$$C = Ql \, / \, D_{12} \, at \qquad (3)$$

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:

$$SR = D_{12}\, a\, /l \qquad\qquad (4)$$

Then they were expressed as ml of air sampled per second. This makes it possible to compare directly sampling rates of passive samplers with those of active samplers.[19]

Methodology

Diffusion sampler preparation

Polyethelene tubes of 5cm 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. 8 tubes each were used for 10 µl of 50% TEA water, 20 µl of 50% TEA water, 15 µl 20% TEA water respectively for NO_2 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. Similar set were prepared for SO_2 as well.

Exposure

All the sets of diffusion tubes prepared (48 diffusion tubes) were exposed at Padova university premises during months of Nov-December, 2006. Samplers were exposed for two weeks for NO_2 and one and two weeks for SO_2. 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 as shown in Figure1. The diffusion tubes were fixed inside polyethylene box with adhesive tape.

Sample Extraction

To the diffusion tubes collected after exposure of prescribed time period weeks, 1 ml and 2 ml of double distilled water was added respectively for NO_2 and SO_2 sampler respectively. The tube was left for 15 minutes for extraction of all the NO_2^- and SO_4^{-2} present on the filter paper, and the tube was closed. The tubes were shaken occasionally to increase the extraction process.

Figure 1: Exposure of passive sampler tubes

Analysis

Spectrophotometric analysis

Standard nitrite solution and Extracted samples were analyzed for nitrite using Modified Griess-Saltzman method spectrophotometrically at 540 nm. [2, 14, 12, 15] Similarly SO_4^{-2} analysis was carried out following West –Gaeke method at 560 nm. [17, 20]

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 Palmes et.al (1976)[2]; Miller (1984)[21]; Gair et.al. (1991 and 1995) [22,23] Plaisance et.al. (2002) [24]. 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 are 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 of tubes. The DL for the spectrophotometer was calculated from a calibration curve with the help of equation 5.[21] 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.

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

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.

$$DL = SB * t_{(á, n-1)} \qquad (6)$$

Where, *SB* = standard deviation of blank values, $t_{(á, n-1)}$ = critical value of t-distribution with n-1 degrees of freedom and *a* significance level of á (0.01 level).

Results and Discussion

This work presents an affordable cheap method to passively measure ambient NO_2 and SO_2 using locally available polyethylene tubes. Passive measurement includes development of these tubes into diffusive tubes using triethanolamine (TEA) as absorbent. After extraction with water, modified Griese-Saltzmann method[2, 14, 12, 15] and West-Gaeke[17,20] methods were used for analysis of nitrite and sulphate adduct formed due to reaction of NO_2 and SO_2 respectively using spectrophotometer. 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. [19]

Calibration curve from nitrite (NO_2^-) and sulphate (SO_4^-) 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 NO_2 and SO_2 from the exposed tubes after subtraction from that of the blanks at the corresponding sites was used in equation 3 to determine NO_2 and SO_2 in $\mu g/m^3$ concentration in ambient air respectively. Diffusion coefficients for NO_2 and SO_2 in ambient air are $1.54 \times 10^{-5}\ m^2\ s^{-1}$ and $1.27 \times 10^{-5}\ m^2\ s^{-1}$ respectively, were used for calculation of ambient concentration for field measurement.

Apart from the chemical factors, passive analysis of the pollutants depends on the several physical factors such as; diffusion samplers 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.

Table 1 presents the exposure measurement of NO_2 and SO_2 concentration for field exposure. The result of all exposures provides a reliable ambient NO_2 and SO_2 passive sampler with good precision, quite capable of comparison to the other methods. Precision of NO_2 measurement for two week exposure period was found to be 21.4% and that of SO_2 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[25]. The ambient concentration of NO_2 and SO_2 were found to be 84.1$\mu g/m^3$ and 9.4 $\mu g/m^3$, 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 are more for lower volume of TEA such that almost all of the tubes with 10μl 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 $NaI + Na_2CO_3$, $NaI + NaOH$, $KOH + glycerol$, $Na_2CO_3 + TEA$ etc, TEA is more popular as the absorbents for both NO_2 and SO_2 measurements. Some problems had also been reported with using TEA as the absorbent. The losses of NO_2 were observed by using TEA for long-term sampling [4]. NO_2^-TEA adduct is prone to photodegradation while exposing the tubes in sun [26]. Further work is required to find out the best absorbent for passive sampling of NO_2 and SO_2 measurements.

Table1: *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 NO$_2$ µg/m^3	Mean SO$_2$ µg/m^3	
	Two week Exposure	One week Exposure	Two week Exposure
Passive monitoring- Test method (test sampler + spectrophotometer)	84.1 ± 17.94 (n = 11) CV= 21.4%	4.52±0.499 (n=5) CV=11.04%	9.42±0.31 (n=5) CV=3.29%
Passive monitoring (test sampler +IC)	Not good	5.4±0.114 (n=5) CV=2.1%	11.3±0.336 (n=5) CV=2.9%
Active method (automated monitor)	94.82± 24.24 (n=11) CV=25.56% (chemiluminescence analyzer)	6 (fluorescent analyzer)	10 (fluorescent analyzer)

Comparison with active sampling measurement

The data for active sampling, measured by a chemiluminescence monitor for NO$_2$ and fluorescent analyzer for SO$_2$, was obtained from the Pollution Control Department, Padova municipality, Italy for sampling at Padova university premises.

A scatter plot diagram, Figure 2, was drawn between the average daily measurements of NO$_2$ from the chemiluminescence monitor and the results of NO$_2$ after spectrophotometric analysis of extract from tubes exposed for one week period.
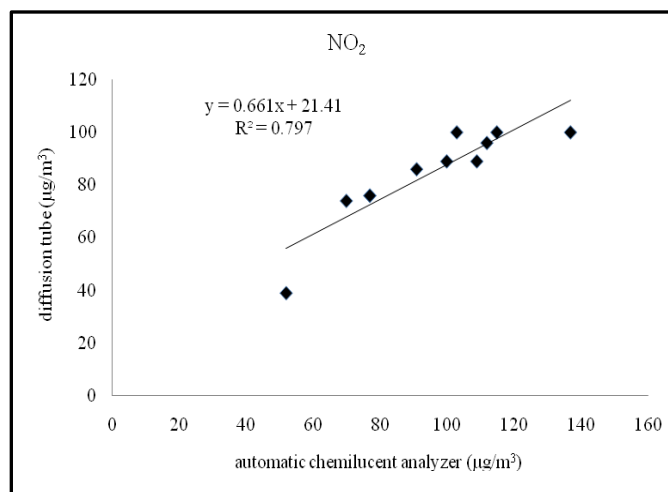

Figure 2: *Comparision of Diffusion tubes-Test Method with Active automatic chemiluminiscence monitor for ambient NO$_2$measurement, exposure at Padova University, Italy (November- December, 07)*

There was an underestimation by Test method in comparison to Active sampling – chemiluminiscence monitor data of about 10.2% for NO_2. As from many other studies [27-30] underestimation of NO_2 measurements was found from diffusion tubes compared to active sampling measurements. Kasper- Giebel and Puxbaum (1999) [31] also found 50% lower measurement of NO_2 from polyethylene tubes with TEA in comparison to chemiluminescence monitor. They describe of using two grids into the tube to correct the problems of underestimation. Santis *et al*. (2003) [26] related underestimation of NO_2 measurements by diffusion tubes with overheating and photo degradation of NO_2-TEA adduct during exposure of tubes to sun in the sampling sites. They recommended the careful extraction procedure, use of stainless steel mesh at the entrance of the tube, and use of a non-transparent plastic to reduce errors. Krochmal and Kalina (1997)[32] also recommended the use of nontransparent plastic as they found 50% lower NO_2 measurements in transparent plastic badge type compared to non-transparent plastic badge type.

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 NO_2^- and $SO4^{2-}$. There was a problem regarding the analysis of NO_2^- by ion chromatograph. A chloride peak next to the NO_2^- peak tended to overlap with the NO_2^- peak. In only few cases, these peaks were separated, those are not clear enough for analysis, Figs. 3 and 4. Different flow rates ranging from 0.5 to 2.0 ml/min and eluent concentrations in the ratio of 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$, 2.6 mM Na_2CO_3/3.3 mM $NaHCO_3$, and of 2.2 mM Na_2CO_3/2.8 mM $NaHCO_3$ were tested. These eluent concentrations were reported for the separation of NO_2^- and $SO4^{2-}$ by ion chromatography [26, 31]. The problem still persisted.

Thus, analysis of NO_2^- by IC could not be accomplished with satisfactory results because of interference with Cl^- determination by a peak adjacent to it. In most cases, NO_2^- peak was not separated. There was also a presence of NO_3^- peak in chromatograms suggesting the possible oxidation of NO_2^- to NO_3^-.

Thus, analysis of NO_2^- by IC could not be accomplished with satisfactory results because of interference with Cl^- determination by a peak adjacent to it. In most cases, NO_2^- peak was not separated. There was also a presence of NO_3^- peak in chromatograms suggesting the possible oxidation of NO_2^- to NO_3^-. Addition of H_2O_2 might have favored this oxidation process, as suggested by other researchers [33]. They mentioned of NO_2 concentrations calculated from separated NO_2^- peaks were lower than the results of NO_2 concentrations analyzed by the spectrophotometer. Lower measurements of NO_2 concentrations by IC also suggest the losses of NO_2^- because of its oxidation to NO_3^-. Chloride peak was adjacent to NO_2^- peak and because of the high chloride concentration it tended to overlap with NO_2^- peak. Separate NO_2^- peak can be obtained only for reduced chloride (Cl^-) concentration. At higher concentrations of Cl^- in the sample (>5 μg/ml), NO_2^- ion appears as a shoulder on the Cl^- peak during IC analysis [34]. The IC

conditions have to be optimized for the analysis of NO_2^-, or interferents, such as Cl^- have to be reduced or removed before injection into the IC. The chromatogram with the overlapping NO_2^- peak is shown in Figure 3 and the chromatogram with the separation of NO_2^- peak is shown in Figure 4.
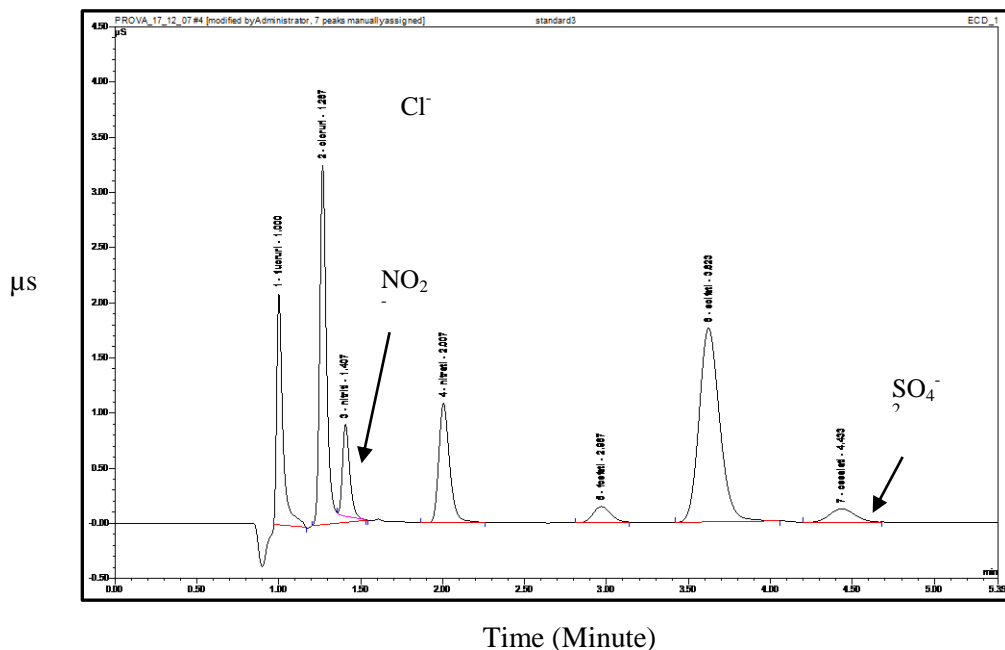

Time (Minute)

Figure 3*: Example Chromatogram presenting Standard sample run*

Time (Minute)
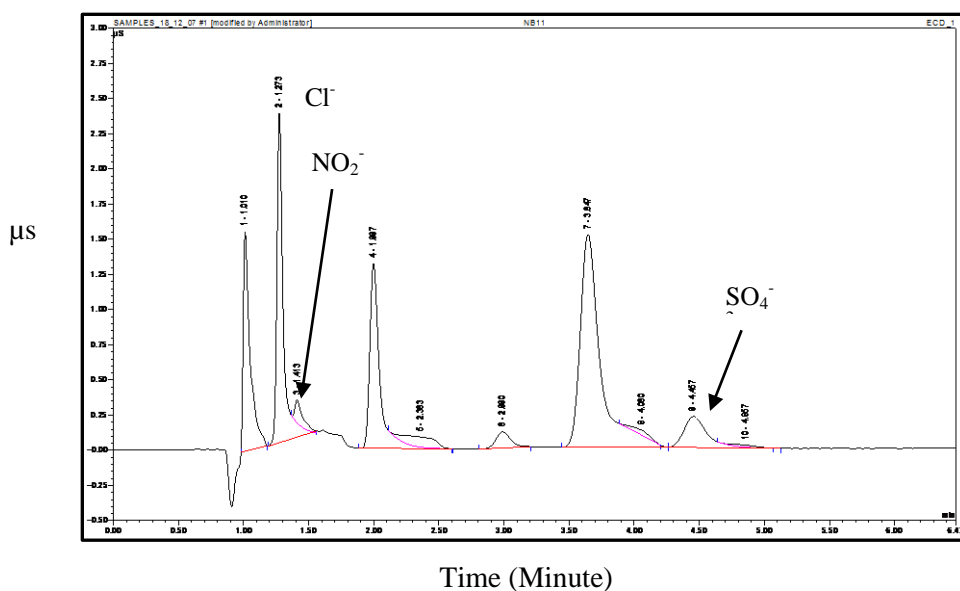
Figure 4: *Example Chromatogram presenting sample run interference of chloride peak can be distinctly observed.*

Smith and Chang (1983)[35] reported problems in NO_2^- analysis by the IC. They mentioned about due to the similar affinity of the NO_2^- and Cl^- ions for resin, making it difficult to determine NO_2^- in the presence of high Cl^- concentrations. In this case, chemical pretreatment may help to remove high Cl^- concentrations. NO_2^- ion interacts with the anion suppressor resin, and the water dip is also a problem. Increase in peak height may be observed from repetitively injected NO_2^- standards.

Sulfur dioxide (SO₂)

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 ($\mu g/m^3$) in ambient air. Good correlation was observed between the analysis of developed passive sampler exposure analysis between two methods; Spectrophotometric and Ion chromatography (Fig. 5). 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 compare to active method (automated fluorescence analyzer).

The overestimation of SO_2 measurements can be caused by interferences from wall deposition of SO_4^{2-} aerosols. [30] 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 SO_4^{2-} anions leading to overestimation of SO_2 concentrations. The porous membrane at the open end of the tube is necessary to avoid the interference from SO_4^{2-} aerosols. These membranes can also help to minimize the effects from wind driven mixing of air in the mouth of the tube. [27]
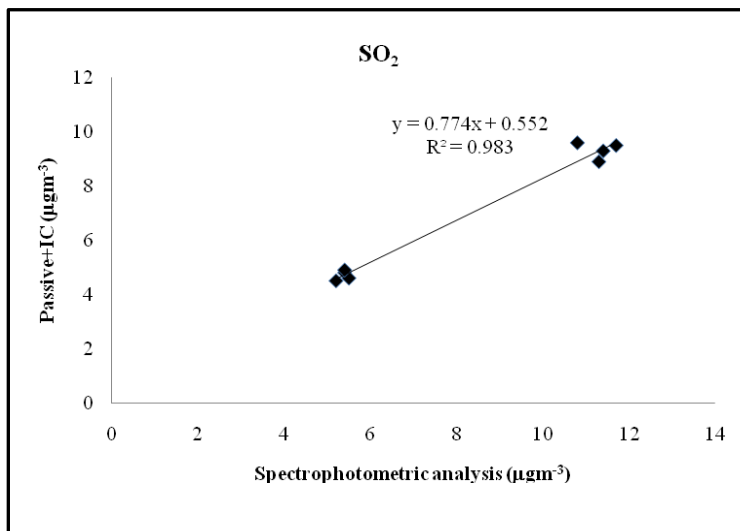

Figure 5: Comparision of Test Method with Ion chromatography analysis for field exposure at Padova University, Italy (November- December, 07)

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

SO_4^{2-} aerosol depositions on the inner surface of the tube before extraction.[24] The sampler tubes also do not have a porous membrane at the mouth of the tube. This might have contributed to the overestimation of SO_2 concentrations.

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 0.09 μg/ml of NO_2^- and that was 0.05μg/ml for SO_2. The detection limit for the ion chromatograph was obtained by injecting a mixed standard of 0.01 μg/ml each of NO_2^- and SO_4^{2-}. The equation 6 gave the detection limit of 0.04 μg/ml of NO_2^- and 0.02 μg/ml of SO_4^{2-}. The minimum detectable quantity calculated from equation 6 was 0.48 μg.sec for NO_2 - and 0.36 μg.sec of SO_4^{2-}.

The standard deviation of blank values was used to calculate the detection limit for the passive sampling method. The detection limit of NO_2 for one week was 1.74 μg/m^3(n=11) and that of SO_2 for one week and two weeks, exposure period were estimated to be 1.62 μg/m^3 (n=5) and 1.28 μg/m^3 (n=5), respectively for the study tube sampler (Table 2).

Table 2: Detection limits (DL) of NO_2 and SO_2 (μg/m^3) for field exposure

Field study parameter	Number of field blanks (n)	t-value $t_{0.01, n-1}$	Standard deviation (SB)	Detection limit (DL)
NO_2 for one week exposure	11	2.77	0.63	1.74
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 NO_2 and SO_2 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 SO_2 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. Since, the annual average concentrations of NO_2 and SO_2 was reported to be lower than the National ambient Air quality Standard (NAAQS-Nepal) in Kathmandu; which are 40 μg/m^3 and 50 μg/m^3 respectively for NO_2 and SO_2. [36] Hence the method can be used for monitoring of ambient concentration in Kathmandu as well. Some negative absorbance values for NO_2 were obtained during analysis by the spectrophotometer. Ion chromatograph under optimized conditions has to be used for the analysis of the tubes exposed in low concentrations of gases.

Conclusion

A simple locally available polyethylene tubes can be developed and used as passive sampler for monitoring of ambient NO_2 and SO_2 even in Kathmandu. The developed method can be used to determine as low as 1.74 μg/m^3 of NO_2 and 1.62 μg/m^3 and1.28 μg/m^3 of SO_2 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.

Acknowledgement

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