Comparison of methods for ambient air sulfur dioxide and nitrogen dioxide

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Active and passive methods for sampling and analysis of ambient air SO_2 and NO_2 were compared by simultaneous sampling. Acceptable accuracy for the passive samplers using comparison with active standard methods were obtained, based on regression correlation and significance testing. Advantages and disadvantages of the methods are discussed.

INTRODUCTION

The acid gases, SO_2 and NO_2, are among the important air pollutants which need monitoring to assess ecosystem acidification with its accompanying deleterious environmental and health effects [1, 2].

Active methods of air sampling for acid gases have been developed and standardized [3]. These methods always require the use of an electric powered pump. A passive or diffusional sampler [4–6] is small, light and does not need electricity. It is especially useful for remote places where there are no sources of electricity. The aim of this study was to investigate and compare some active and passive methods for monitoring SO_2 and NO_2 in ambient air.

The methods used are passive sampling using impregnated filters, active sampling using impregnated filters and active sampling using an impinger immersed in an absorbing solution. Passive and active sampling (for each of the two acid gases) was done simultaneously for comparison.

EXPERIMENTAL

Sampling with passive samplers. The methodology of Ferm [5] was followed. The samplers are illustrated and described in Fig. 1. Samplers were mounted on aluminum holders under a Frisbee (plastic plate) nailed horizontally to a wooden pole (~2 m) with the rounded edge facing downwards.

The samplers for SO_2 contained cellulose paper filters coated with a 50 μL solution of 1.0% NaOH in methanol, while those for NO_2 were coated with a 50 μL solution of 0.88% NaOH
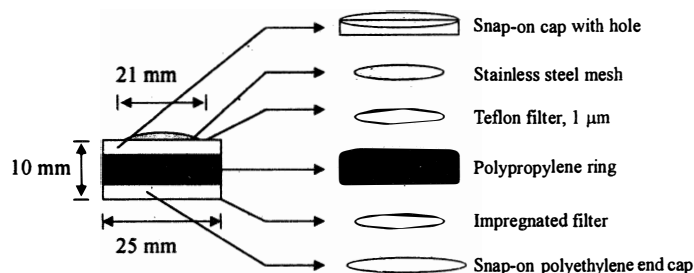

Fig. 1. Passive sampler assembly.

and 7.9% NaI in methanol. The absorbed SO_2 and NO_2 were analyzed by ion chromatography (as SO_4^-) and by spectrophotometry (as NO_2^-), respectively.

Low volume active sampling using impregnated filters. The air sampling pump was either SKC Aircheck Sampler model 224-PCXR4 or model 224-PCXR3 set at 1 L/min. The filter samplers consisted of two 37-mm diameter cassette filter holders connected in series. The front cassette used as the prefilter (for particulates) contained a 37 mm 0.8 mm cellulose ester membrane filter on a cellulose support pad while the back cassette or the backfilter contained an impregnated 37 mm Whatman 40 cellulose filter also on a cellulose support pad. Whatman 40 filter for SO_2 is impregnated with 20% KOH + 10% glycerol in ultrapure water and oven-dried at 50°C (NIOSH Method No. 6004) while that for NO_2 was impregnated with NaOH and NaI in methanol (soaking for a few minutes and then allowing to dry). The absorbed SO_2 and NO_2 were analyzed by ion chromatography (as SO_4^-) and by spectrophotometry (as NO_2^-).

Low volume active sampling using an impinger. The air sampling pump was an SKC Aircheck Sampler model 224-PCXR4 calibrated to a flow rate of 0.4 L/min. The impinger method was the reference method for NO_2 in air (ASTM Method D1607). NO_2 gas passed through a fritted impinger with 60 μL pore size and was absorbed into a 10-mL absorbing reagent made up of 0.002% N-1-Naphthylethyl- enediamine dihydrochloride (NED) and 0.5% sulfanilamide in 14% acetic acid. The absorbance of the solution was determined at 550 nm after 24-h sampling period. The sample NO_2^- concentration was calculated from a calibration curve of prepared nitrite standards.

Ion chromatographic analysis of absorbed SO_2. The instrumentation consisted of a Dionex 2000i IC System, ion conductivity detector, analytical and guard columns (AS4A-SC/AG4A-SC), and micromembrane suppressor. The chromatographic conditions were 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ (as eluant) at 2.0 mL/min flow rate, 25 mM H_2SO_4 (as regenerant) at 2.0 mL/min flow rate, 50 μL injection volume, attenuation 1024, peak threshold 10000, chart speed 0.5 cm/min, and sensitivity at 30 or 10 μS. The aqueous extracts (2.5 mL) of the SO_2 absorbed on the coated paper filters (subsequently converted to SO_4^-) were analyzed together with aqueous standard sulfate solutions.

Spectrophotometric analysis of absorbed NO_2. The instrumentation consisted of a UV Spectrophotometer, LKB Ultrospec II, or Beckman Spectrophotometer. NO_2 absorbed on the coated filters (and converted to NO_2^-) was extracted with 5 mL ultrapure water. To 2 mL of this aqueous extract (dilute if necessary) were added 2 mL reagent solution (0.8% (w/v) sulfanilamide, 0.02% (w/v) NED, and 0.8% (v/v) phosphoric acid). The absorbances of the reacted samples and standards were measured at 540 nm wavelength.

RESULTS AND DISCUSSION

Simultaneous samplings using active and passive samplers were done at UP NSRI (Natural Sciences Research Institute). The sampling locations, data and conditions are shown in Tables 1 and 2.

SO_2. Passive sampling was compared to active sampling (both modes had the same impregnating solution and sorbent filters). Table 1 and Fig. 2 summarize the results of the comparison. The data points are quite scattered, with a good slope of 0.9623, indicating approximately equal collection efficiencies for the two methods. There was a positive but not nearly so good correlation (coefficient of 0.8011) between the two methods, with a reasonably low intercept (3 μg/m³) which is close to the standard deviation values of the passive samplers.

The sorbing solution in both methods can potentially detect not only SO_2 but also HNO_3 and oxalic acid in ambient air. This study detected very low levels of oxalic acid, but not HNO_3.

NO_2. Table 2 and Figs. 3 and 4 show results of the comparison

Table 1. Sulfur dioxide sampling: Active and passive sampling

Location	Sampling Time (H)	SO_2 (μg/m³)		Weather Conditions
		Active	Passive	
NSRI Main Gas House	74.47	19 ± 1	15 ± 1	sunny
	73.15	11.0 ± 0.6	8 ± 2	cloudy
	72.87	7.6 ± 0.4	12 ± 3	sunny
IKOT Stop in front of NSRI	72.00	20 ± 1	25 ± 2	sunny
	73.02	14.0 ± 0.7	19 ± 2	sunny; cloudy
	73.22	22 ± 1	26 ± 2	sunny
	78.43	20 ± 1	30 ± 5	sunny
	73.28	29 ± 2	27.2 ± 0.9	sunny; cloudy

Sulfur Dioxide (μg/m³)
Passive vs. Active Sampling
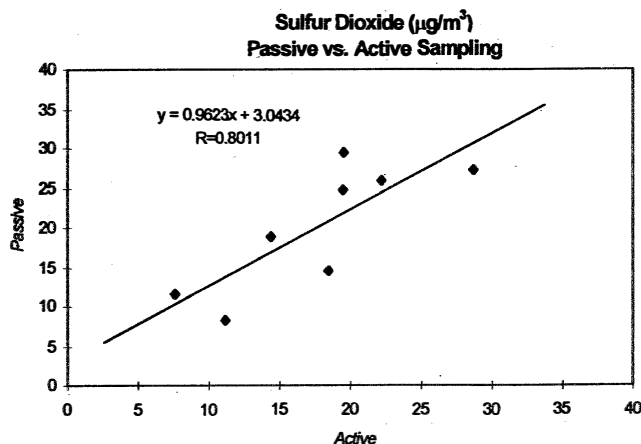
y = 0.9623x + 3.0434
R=0.8011

Fig. 2. Sulfur dioxide sampling: Correlation between Passive and Active Sampling

Table 2. Nitrogen dioxide in indoor air: A comparison of three methods of sampling (Location: Rm. 238, Natural Sciences Research Institute)
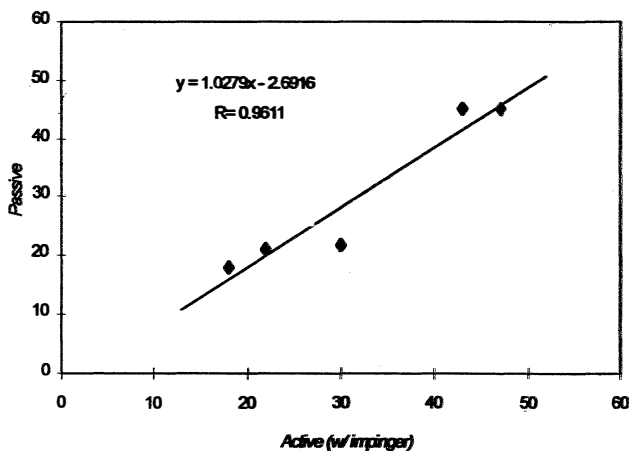
Sampling Time (H)	NO$_2$ (ug/m^3)		
	Active w/ Impinger	Active (Using Filter)	Passive
8	43.0 ± 0.6		45 ± 3
24	47.0 ± 0.7		45 ± 3
2	50.0 ± 0.8	30.0 ± 0.5	
2	109 ± 2	53 ± 1	
2	19.0 ± 0.3	2.9 ± 0.2	
7.62	22.0 ± 0.3	5.6 ± 0.3	21 ± 3
8	30.0 ± 0.4	7.3 ± 0.3	22 ± 4
7.55	18.0 ± 0.3	5.9 ± 0.3	18.3 ± 0.7

Fig. 3. Nitrogen dioxide sampling in indoor air: Passive vs. Active (w/ impinger).

Table 3. Significance testing results for passive and active sampling. All values are in μg/m^3. *S$_a$ and S$_p$ are uncertainties (Standard Deviations).
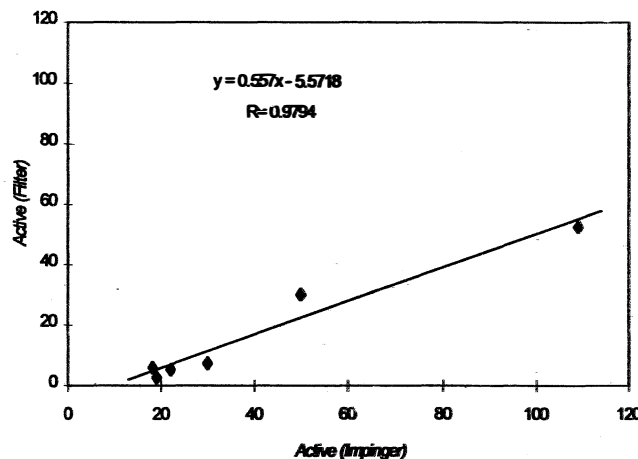
(SO$_2$)$_{active}$	S$_a$*	(SO$_2$)$_{passive}$	S$_p$*	Δ$_D$ (90%)	Δ$_D$ (95%)	D
19	1	15	1	2.9	4.3	4
11	0.6	8	2	4.3	6.3	3
7.6	0.4	12	3	6.2	9.2	4.4
20	1	25	2	4.6	6.8	5
14	0.7	19	2	4.2	6.1	5
22	1	26	2	4.6	6.8	4
20	1	30	5	10.5	15.5	10
29	1.5	27.2	0.9	3.6	5.3	1.8
(NO$_2$)$_{active}$	S$_a$*	(NO$_2$)$_{passive}$	S$_p$*	Δ$_D$ (90%)		D
43	0.6	45	3	6.3		2
47	0.7	45	3	6.4		2
22	0.3	21	3	6.2		1
30	0.4	22	4	8.3		8
18	0.3	18.3	0.7	1.6		0.3

Fig. 4. Nitrogen dioxide sampling in indoor air: Active (filter) vs. Active (impinger).

of three methods of sampling for NO$_2$ in the short term. The three methods were: the reference method (active sampling using a fritted impinger and a liquid absorbing solution for NO$_2$), active sampling using the same filter and sorbent as the passive sampler, and passive sampling.

Figure 3 shows that the accuracy for NO$_2$ was better compared with SO$_2$ for the passive samplers, based on standard active sampling methods. The slope for NO$_2$ (passive) vs. NO$_2$ (active impinger) was close to one (1.03) indicating comparable collection efficiencies for the two methods. There was good correlation (coefficient of 0.96) and the intercept (–2.7 μg/m^3) was the same level as the standard deviations of the passive sampler.

Figure 4 shows that the collection efficiency (slope of 0.56) for the active filter sampler was poorer compared to the reference method, although correlation was also good (coefficient of 0.98). The difference in collection efficiency may be attributed to two related factors: air flow rate and mode of contact of NO$_2$ with the sorbing solution. These factors are significant in view of the lower solubility of NO$_2$ in aqueous solutions, compared to SO$_2$. The slower flow rate of the reference method (0.4 L/min) compared to the filter method (1 L/min) favors greater NO$_2$ dissolution in the former. Likewise, very fine bubbles going through a liquid solution (in the reference method) is a better contact mode for NO$_2$ with the sorbing liquid, compared to NO$_2$ passing through a thin sorbing solution layer in the filter method.

Significance testing. Significance testing [7] was done in addition to correlation by linear regression. In significance testing, probability theory is used to calculate the maximum difference (Δ$_D$) that could be expected to occur for measurements by two

methods, if both methods measure random samples of the same thing. If the observed difference (D) is smaller than Δ_D, it is concluded that the observed difference is just due to random error and is not significant (at the probability or confidence level chosen). If D is larger than Δ_D, then there is a suggestion that at least one of the methods has a systematic error (at the confidence level chosen).

Results of the calculations are shown in Table 3. For SO_2, all points have D < Δ_D at the 95% confidence level. This means the results of the passive sampling method are not significantly different from those of the active sampling method at this confidence level.

For NO_2, the results of the passive sampling method are not significantly different from those of the active sampling reference method at 90% and above confidence level.

CONCLUSION

Acceptable accuracy for the passive samplers using comparison with active standard methods were obtained, based on regression correlation and significance testing.

The active impinger method for NO_2 used in this study is the accepted manual sampling and analysis method used by Department of Environment and Natural Resources (DENR) for NO_2 ambient monitoring. The good correlation and significance testing results for NO_2 (between the active standard method and the passive sampling method) indicates the validity of the cheaper and more convenient NO_2 passive sampler technique.

For ambient air monitoring of SO_2, the DENR method used is active bubbler sampling of SO_2 through an absorbing solution. The bubbler is similar to the impinger, except for the absence of the fritted glass in the bubbler. The absorbed SO_2 is determined by spectrophotometry. A comparison exercise for SO_2 between the DENR using the bubbler method and the authors of this study (using the passive sampler) was scheduled but did not push through. A similar comparison exercise with the Environmental Management Bureau (EMB) did push through but EMB did not analyze their sample due to excessive evaporation during the 24 h sampling period used.

This is one of the disadvantages mentioned in the literature [8] about bubblers and impingers. Their sampling times are limited by the evaporation of the collecting solution. Passive samplers, on the other hand can sample from 24 hrs up to two months (based on trials done in this study for both acid gases).

There was a 24 h sampling data point for NO_2 in Table 2 of this study and the authors did not encounter an evaporation problem in the standard active method. This was most probably due to the low flow rate used, plus the fact that sampling was done indoors. Results could change when sampling is done on a hot day outdoors.

The advantages of the passive, over the active, methods are lower cost (since electricity and expensive pumps, bubblers and impingers are not needed), portability (handling and shipping from a remote sampling area to the laboratory precludes the need to carry liquid solutions for the passive samplers) and the absence of the aforementioned evaporation problem. A disadvantage is the possibility of drying of the filters when relative humidity is low. The efficacy of the impregnated sorbing solutions are dependent on the hydrophilic property of the cellulose filters. A humectant, such as glycerol, can lessen this problem. Another practical disadvantage experienced by the authors is the tendency of the passive samplers to disappear during long-term sampling (i.e., one month); perhaps because the sampler set-up, with the Frisbee, looks too much like a toy.

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