 Comparison of Several Methods for Nitrogen Dioxide and Sulfur Dioxide in Metro Manila Air

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ABSTRACT

The pollutant gases nitrogen dioxide (NO2) and sulfur dioxide (SO2) are two of the commonly monitored parameters for air quality assessment in the Philippines. In this study, several active and passive sampling methods for the analysis of the two gases were tested. Of the methods for NO2 first tested indoors, the NaI sorbent passive sampling method was found most promising and was tested for ambient air NO2 (using both Ferm and Korean passive samplers) against a collocated automated chemiluminiscence sampler. For SO2, ambient levels were simultaneously measured using NaOH sorbent in a Ferm passive sampler and a collocated automated fluorescence sampler. Correlation and t testing indicate a positive bias for the NO2 Ferm method and a negative one for the SO2 Ferm method in comparison with their corresponding automated methods. The results of the study support the 1997 annual average SO2 and NO2 findings of a UP Natural Sciences Research Institute (NSRI) study (Quirit et al, 1999) which used Ferm passive samplers in various Department of Environment and Natural Resources (DENR) Metro Manila air sampling stations.

Key words: NO2, SO2, passive samplers, chemiluminiscence sampler, fluorescence sampler

INTRODUCTION

Nitrogen dioxide (NO2) and sulfur dioxide (SO2) play important roles in ecosystem acidification (Nishikawa, 2004). These gases are two of the air pollutants commonly monitored to assess air quality in the Philippines. The others are Total Suspended Particulates (TSP), Particulate Matter less than 10 um diameter (PM10), ozone, carbon monoxide and lead (Environmental Management Bureau (EMB), 1990).

Metro Manila (MM) data for ambient air pollutants are usually presented as levels versus time to show annual trends. For NO2 and SO2, data from 1975 to the present have been reported. However, the methods used for sampling and analysis of these two gases differ within this time period, introducing an uncertainty when trends are analyzed. Table 1 enumerates these different methods and the corresponding year(s) each was used, together with the institutions that did the sampling and analysis.

This study compared different sampling and analysis methods for NO2 and SO2, using both passive and active samplers and indoor and ambient sites. In 1998, a similar study was done with a fewer number of
methods and samples, for NO\textsubscript{2} in an indoor site and SO\textsubscript{2} in a vehicular loading and unloading campus site (Quirit et. al., 2002). The availability of automated monitoring samplers in 2003 made possible the collection of a greater number of samples in an ambient sampling site for both gases. Four general methods used for past and present MM NO\textsubscript{2} and SO\textsubscript{2} data collection were used in this study. These are: passive sampling, manual active sampling to a sorbent, and automated active chemiluminescence and fluorescence methods. The results could provide a significant basis for relating some of the past and present MM data for NO\textsubscript{2} and SO\textsubscript{2} in ambient air.

**MATERIALS AND METHODS**

A variety of active and passive sampling methods for NO\textsubscript{2} were first tested in the indoor laboratory air of the UP NSRI Room 238. Past studies have shown that indoor and outdoor NO\textsubscript{2} levels were generally comparable (Quirit et. al 2002, Quirit et. al. 1999). These methods were compared to the standard manual active method accepted by DENR, the Griess-Saltzman Method (Lodge, 1989a). All NO\textsubscript{2} methods tested for indoor air resulted in the same colored Griess-Saltzman analyte which was measured by visible light absorption at 540 nm. The best method was chosen for ambient air sampling and the results compared with the automated chemiluminescence sampler results for NO\textsubscript{2}. For SO\textsubscript{2}, indoor levels were generally lower than ambient levels (Quirit et. al. 2002, Quirit et. al. 1999) so only ambient samples were taken, using the Ferm method for SO\textsubscript{2} (Ferm, 1991). The results were compared with the automated fluorescence sampler results for SO\textsubscript{2}. The sampling site for ambient samples was the Manila Observatory grounds, situated at the Ateneo de Manila University Campus, Loyola Heights, Quezon City.

<table>
<thead>
<tr>
<th>Period (Institution)</th>
<th>NO\textsubscript{2} Method</th>
<th>SO\textsubscript{2} Method</th>
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<tbody>
<tr>
<td>1975 - 1983 (NPCC)</td>
<td>automated air sampler from Japan (EMB 1990, EMP 1996)</td>
<td>automated air sampler from Japan (EMB 1990, EMP 1996)</td>
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<tr>
<td>1991-1992 (ADB and EMB-DENR)</td>
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<tr>
<td>2003 (KFEM)</td>
<td>Korean passive sampler w/ TEA sorbent (Lee, 2002)</td>
<td>Korean passive sampler w/ sorbent\textsuperscript{a} (Lee 2002)</td>
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\textsuperscript{a}sorbent not given in reference

Table 1. Metro Manila NO\textsubscript{2} and SO\textsubscript{2} Methods (Quirit et. al., 2005)
**NO₂ Determination Methods**

**Standard Active Sampler Griess-Saltzman Method**

(Lodge, 1989a)

Ten mL of the Griess-Saltzman absorbing solution was pipetted into a dry fritted impinger (SKC 4225) attached to an air sampling pump (SKC 224-PCXR4). Flow rate was set to 0.4 L/minute (LPM), with the sampling duration varied from at least about 8 h to at most 24 h. At the end of the sampling period, the resultant pink-colored solution was transferred to a vial and analyzed immediately.

Calibration standards of NaNO₂ equivalent to 0, 0.08, 0.16, 0.24, 0.40 and 0.56 µL NO₂/mL absorbing solution were used to determine the NO₂ level in the samples. The absorbances were read in a UV-VIS spectrophotometer at a wavelength of 540 nm.


NaI-NaOH-methanol coating solutions were made fresh for each batch preparation of Ferm samplers. Fifty µL of this coating solution were pipetted onto paper filters (Whatman 40) loaded in the partially assembled samplers. The samplers are described in the reference for the method (Ferm, 1991) and in a previous publication (Quirit et. al, 2002).

The assembled samplers were then kept in a refrigerator inside polythene storage containers before and after exposure. Sampling durations ranged from at least 1 week to at most 1 month (4 weeks), wherein the samplers were taken out of storage and attached to frisbees secured on top of 1.83 m (6 ft) poles.

Prior to analysis, the paper filters were transferred into vials and extracted with 5 mL ultrapure water. Five-mL standards (0, 5, 10, 20, 40, 60, 80 µM NaNO₂) were prepared and equal volumes (5 mL) of Griess-Saltzman solution were added to both standards and samples. Absorbances were read in a UV-VIS spectrophotometer (? = 540 nm) after 15 minutes.


The TEA (triethanolamine) liquid absorber solution was prepared and used to coat paper filters, as described in the Intersociety Committee Methods of Air Sampling and Analysis (Lodge, 1989b). Samplers used were the same as those described in the NaI-Ferm Method (Ferm, 1991), except the paper filters were first dried using lint-free tissue to absorb the excess coating solution and further dried by N₂ stream prior to loading into the samplers.

Five-mL standards having concentrations of 0, 0.08, 0.16, 0.24, 0.40 and 0.56 µL NO₂/mL were prepared. Samples were extracted with 5 mL ultrapure water and equal volumes of the Griess-Saltzman absorbing solution were added to both standards and samples. Absorbances were measured at a wavelength of 540 nm.


Basically the same procedures as the TEA-Ferm Sampler Method were followed for the TEA-Korean method, except for the different sampler used. The Korean sampler is made up of a small clear plastic tube (internal diameter: 10.016 mm, outer diameter 12.092 mm, height: 43.176 mm) covered by a white plastic (probably Teflon) on one end, and removable rubber caps on both ends. Whatman 40 paper filters (cut to fit inside the tube) were coated with a liquid absorber solution prepared with five times as much TEA (triethanolamine) but the same amount of butanol and ultrapure water as that used in the TEA-Ferm method. Samples were extracted with 2.0 mL ultrapure water and standards were prepared as described previously.


Basically the same procedures as the NaI-Ferm Sampler Method were followed, except that the sampler used was the Korean passive sampler described above.
TEA-Glass Fiber Filter Active Sampler Method
(Lodge 1989b, Sickles et al. 1990)

Glass fiber filters (Sickles et al., 1990) were soaked in liquid TEA absorbing solution (Lodge, 1989b), pressed between sheets of lint-free tissue and dried in a N₂ stream to remove any excess coating solution. Filters were then placed inside sampling cassettes (SKC 225-45). NO₂ was absorbed by pulling air with an SKC 224-PCXR4 sampling pump at 1 LPM. After exposure, the filters were transferred into vials. Five-mL calibration standards (0, 0.2, 0.6, 1, 1.4 µg NO₂/mL) were prepared from a stock standard of 2 µg NO₂/mL and the liquid absorber solution. Samples were likewise extracted with 5 mL of the liquid absorber solution. Then, to both standards and samples, Griess-Saltzman reagents were added and the resulting pink-colored solutions were measured for their absorbances at 540 nm.

TEA-Molecular Sieve Active Sampler Method
(Lodge, 1989b)

The solid absorber was prepared by soaking molecular sieve in TEA absorber solution for 30 minutes then drying in a vacuum oven at 70⁰ C. These were then packed in a glass tube (measuring 55 cm in length and 5 mm in diameter) through which air was pumped into for 8 h using an SKC 224-PCXR4 sampling pump at a rate of 0.4 LPM. Ten-mL calibration standards were prepared similarly to those in the Glass Fiber method while the absorbed NO₂ was extracted using 50 mL of the liquid TEA absorbing solution. One mL of 0.02%(v/v) hydrogen peroxide, 10 mL sulphanilamide solution and 1.4 mL of 0.1%(w/v) (1-Naphtyl ethylenediamine dihydrochloride) NEDA solution were then added to the calibration standards and to a 10-mL aliquot of the extract, after which absorbance readings were measured at 540 nm.

Chemiluminisence Automated Sampler Method
(USEPA, 1996)

NO₃ levels were measured using a Horiba APNA-360CE. NO₃ is the sum of nitric oxide (NO) and nitrogen dioxide (NO₂) in a gaseous sample. Two fractions of ambient air are sampled - one has all of its NO₂ converted to NO, with the NO then made to react with ozone (O₃) to form NO₂ + O₂ + light. The chemiluminescence generated is therefore proportional to the NOx level. On the other hand, the other fraction is reacted with O3 immediately (without reducing NO₂ to NO) and since NO₂ is unreactive towards O₃, only the NO reacts, giving the NO level. The difference between the values from fraction 1 and 2 therefore gives the NO₂ level.

SO₂ Determination Methods


The same procedures as those for the NaI-Ferm method for NO₂ determination were followed in preparing the SO₂ samplers, except that a different coating solution, NaOH-methanol, was used. The absorbed SO₂, in the form of SO₄²⁻ ion, was analyzed by ion chromatography. Prior to analysis, the paper filters were transferred into vials and extracted with 2.5 mL of degassed ultrapure water. Sample solutions were filtered with 0.45 µm Millipore filters to remove particles that might clog or damage the column. Standard solutions containing 0.5, 2, 5, 10 and 20 ppm of SO₄²⁻ were prepared using degassed ultrapure water and, along with the samples, were analyzed using an ion chromatograph (Dionex Ion Chromatograph 2000i). 12.5 mM H₂SO₄ was used as a regenerant and 1.36 mM NaHCO₃/1.44 mM Na₂CO₃ as eluant. Eluant flow rate was set to 2 mL/minute and sensitivity to 30 µS.

Fluorescence Automated Sampler Method (USEPA, 1993)

SO₂ levels were obtained using a TEI 43C SO₂ analyzer, which gives SO₂ levels in ambient air by measuring the fluorescent electromagnetic radiation emitted by the SO₂ molecules when excited with ultraviolet light. The fluorescence emitted is proportional to the SO₂ mixing ratio in the sampled ambient air.
RESULTS AND DISCUSSION

Comparison of Methods (Indoor Air NO₂)

Figure 1 shows how the different methods compared with the standard Griess-Saltzman Method for NO₂, and with each other. The assumption for the comparison is 100 % NO₂ collection efficiency for the standard method.

The NaI-Ferm passive sampler gave the best results, with all sample levels having ratios (with simultaneous standard method sample levels) close to 1, indicating approximately 100 % collection efficiency. Correlation with standard method levels gave an R = 0.9954. The TEA- Korean passive sampler method had the next average ratio value closest to 1, but had significantly lower precision for the collection efficiencies, compared to the NaI-Ferm passive sampler method. The same poor precision for the ratios is true for the TEA-Glass Fiber filter method.

TEA was also tried as a sorbent for the Ferm passive sampler. Although ratio precision and correlation with the standard method (R = 0.9644) were good, sampling efficiency (around 40 %) was low. The TEA-molecular sieve active method had the lowest average collection efficiency.

Comparison of Methods (Ambient Air NO₂)

For ambient NO₂, the NaI-Ferm passive sampling method was chosen on the basis of its performance in the indoor sampling comparison. The Korean passive sampler was also tried, but with the sorbent changed to the NaI-Ferm coating solution. Therefore, what was tried was the same sorbent, but in different passive sampler configurations. Sampling (one week to one month duration per sample) was from February to December, 2004. Figures 2 and 3 show how these two passive sampler types compare with the automated chemiluminescence method for NO₂ in ambient air.

The regression equation for the NaI-Ferm Method, when correlated with the Chemiluminescence Method (without forcing the intercept to zero), gives a slope of 0.9763 and an intercept, 0.0015 ppm, which is about twice the average standard deviation, 0.0007 ppm, for the data points. This indicates an overall positive bias of the NaI-Ferm Method relative to the automated method. When the intercept of the correlation line is
forced to zero, the slope became 1.0689, as shown in Figure 2. Assuming 100% collection efficiency for the automated method, the collection efficiency of the NaI-Ferm method for NO$_2$, based on this slope, is around 107%. The correlation coefficients, 0.8981 and 0.8940 respectively, for the non-zero and zero intercept equations, are similar.

The Korean passive sampler (using TEA as coating solution) was used by a Korean Non-Government

![Figure 2. Comparison of NaI-Ferm Method with Automated Chemiluminiscence Method for Ambient Air NO$_2$ (N = 30 duplicate data points, Ferm sampler 4% average RSD, Chemiluminiscence Method, 2% RSD) (Quirit et. al., 2005)](image)

![Figure 3. Comparison of NaI-Korean Sampler Method with Automated Chemiluminiscence Method for Ambient Air NO$_2$ (N = 6 data points) (Quirit et. al., 2005)](image)
Organization (NGO), the Korean Federation for Environmental Movement (KFEM), in cooperation with a Philippine NGO, the Concerned Citizens Against Pollution (COCAP), plus students and teachers, grass-root NGO activists and some local government officials (Lee, 2002). They collected 24 h NO₂ air samples in various locations in Metro Manila from January 18 to January 19, 2002. The authors of this study used the sampler, but with a different coating solution (NaI/NaOH) as mentioned in the methodology above. Interest in the sampler was due to its simple configuration, plus its use for recently collected data by KFEM.

Data points were considerably less for the NaI-Korean Sampler Method, since the authors procured only one sampler from the local NGO, Concerned Citizens Against Pollution (COCAP), which participated in the above mentioned exercise. Duplicate data points could not be acquired, hence the absence of an average RSD. KFEM reports the sampler's precision as 9.6 % RSD. The regression equation for the NaI-Korean sampler, when correlated with the chemiluminiscence method (without forcing the intercept to zero), gives a slope of 1.2032 and an intercept of -0.0017 ppm, which is similar in magnitude to the NaI-Ferm intercept. Results shown in Figure 3, when the intercept is forced to zero, indicates approximately 110% NO₂ collection efficiency, relative to the chemiluminiscence method. The correlation coefficients, 0.8168 and 0.8136 respectively, for the non-zero and zero intercept equations, are similar.

**Comparison of Methods (Ambient Air SO₂)**

For ambient SO₂, the NaOH-Ferm passive sampling method was compared to the automated fluorescence method, and the results are shown in Figure 4. Sampling (one week to one month duration per sample) was from February to December, 2004. Only 21 duplicate data points are shown, since some of the samples were analyzed by BaSO₄ turbidimetry (instead of by ion chromatography). The turbidimetric method performed poorly, in terms of precision, compared to ion chromatography. The standard active manual method accepted by DENR uses a mercury compound (tetrachloromercurate or TCM) in the sorbent. This method was not used due to its being both cumbersome and toxic.

![Figure 4. Comparison of NaOH-Ferm Method with Automated Fluorescence Method for Ambient Air SO₂ (N = 21 duplicate data points, Ferm sampler 8% average RSD, Fluorescence Method 1% RSD) (Quirit et. al., 2005)](image-url)
The regression equation for the NaOH-Ferm Method, when correlated with the fluorescence method (without forcing the intercept to zero), gives a slope of 0.8479 and an intercept, -0.1008 ppm, the absolute magnitude of which is higher than the average standard deviation, 0.0019 ppm, for the data points. This indicates an overall negative bias of the NaOH-Ferm Method relative to the automated method. When the intercept of the correlation line is forced to zero, the slope became 0.8404, as shown in Figure 4. Assuming 100% collection efficiency for the automated method, the collection efficiency of the NaOH-Ferm method for SO2, based on this slope, is around 84%. The correlation coefficients, 0.8479 and 0.8477 respectively, for the non-zero and zero intercept equations, are similar.

$t$ Test

Aside from correlation with the automated methods, the $t$ test was also used to find out if there is a statistical difference between the results obtained using the passive sampler and the automated methods (Christian, 2004). For both NO$_2$ and SO$_2$, the passive sampler method was considered the test method, and the automated method was the accepted method. The two automated methods use calibration gases (USEPA 1996, USEPA 1993), while passive sampler levels were calculated from the dimensions of the sampler and Fick’s first law, a theoretical diffusion equation (Quirit et. al. 2002, Ferm 1991). The results are shown in Table 2. The number of degrees of freedom, other than 8, in the $t$ table was only up to 25, so the calculated $t$ was done overall (30 data points or 29 degrees of freedom) and per set of 6 data points (5 degrees of freedom) for NaI-Ferm NO$_2$. This was also to compare with the 6 data points of the NaI-Korean sampler.

The $t$ test results (magnitude of $t_{calculated}$ > magnitude of $t_{table}$) confirm the positive bias (107% collection efficiency) for the NaI-Ferm method for NO$_2$, and the negative bias (84% collection efficiency) for the NaOH-Ferm method for SO$_2$, compared to the automated methods. The opposite result (magnitude of $t_{calculated}$ < magnitude of $t_{table}$), indicating no statistical difference between the NaI-Korean sampler results and the chemiluminiscence method for NO$_2$ at the 95% confidence level, is true for the small number of data points collected. This is also true, however for the first 6 data points of the NaI-Ferm method for NO$_2$.

Figures 5 and 6 further illustrate the biases for the Ferm passive sampler methods, using % deviations from the automated sampler results. The results were compared to deviations of the Ferm passive samplers (one month samplings) from parallel 24 h active sampler data in Sweden (Ferm, 1991).
In this study, around 77% of the data points have NO₂ levels greater than the automated chemiluminiscence levels, 10% have levels close to the automated method levels, and 3% have levels lower than chemiluminiscence levels, as seen in Figure 5. This is similar to the Sweden results, where 67% of the approximately 48 data points had levels above the active sampler levels, and the rest of the data points were about equally distributed between those close to and those below active sampler levels (Ferm, 1991).

Figure 6 shows that around 80% of the data points have SO₂ levels below the automated fluorescence levels, 10% have levels close to the automated method levels, and 10% have levels higher than fluorescence levels. This is again similar to the Sweden results, where 65% of the approximately 46 data points had levels below the active sampler levels, 11% close to and 24% above active sampler levels (Ferm, 1991).

The active sampler NO₂ method done in Sweden used sintered glass filters impregnated with the same sorbent (KI) for NO₂ as the passive samplers, while the active impinger method (with 0.03% H₂O₂) was used for comparison with the SO₂ Ferm passive samplers (coating solution is K₂CO₃). The coating solutions used in Sweden are chemically similar to those used in this study (NaOH is quickly transformed to Na₂CO₃ when exposed to CO₂ in air) for the passive samplers. It is interesting to note that even for the same NO₂ sorbent used in the active and passive samplers in Sweden, the positive bias was observed for NO₂ in ambient air, for the passive relative to the active samplers. Precisions of the Ferm samplers in this study, 4% and 8% RSD respectively for NO₂ and SO₂, are similar to precisions (5% and 10% RSD respectively for NO₂ and SO₂) of the Ferm sampler in the Sweden study.

No explanation, as of now, could be offered for the higher levels predominantly observed for NO₂ passive samplers, relative to the active automated chemiluminiscence method levels. A passive sampler reported in NIOSH 6700 method for NO₂ (NIOSH, 1984) gave results for a field study (ambient air) where the passive sampler levels were 109 ± 9% of the reference method (Jones et. al., 1979). This is similar to the 107 ± 5% results for the Ferm NO₂ sampler in this study. For SO₂, it is postulated that part of the sorbed SO₂ was not transformed to SO₄²⁻, but remained as SO₃²⁻, hence the seemingly lower collection efficiency of the passive sampler compared to the automated fluorescence sampler. The corresponding author is currently part of a research where SO₃²⁻ ions are analyzed by a method called pervaporation.

![% Deviation of NaOH-Ferm from Fluor)](image)

Figure 6. % Deviation for SO₂ \[((\text{NaOH-Ferm data} - \text{fluorescence data}) \times 100/\text{fluorescence data})\] (Quirit et. al., 2005)
Preliminary results using this method on the NaOH-Ferm sampler extracts show the presence of $SO_3^{2-}$ ions in the samplers exposed to ambient air.

**CONCLUSION**

Ferm Passive sampler NO$_2$ and SO$_2$ levels in ambient air of the Manila Observatory were found to be positively and negatively biased, respectively, relative to automated chemiluminiscence NO$_2$ and automated fluorescence SO$_2$ levels. No explanation, as of now, could be found for the positive NO$_2$ bias. Incomplete oxidation of the sorbed SO$_2$ in the basic sorbent of the Ferm passive sampler is postulated to be the reason for the sampler’s negative SO$_2$ bias. This is due to the nature of the analytical method used for oxidized SO$_2$, which analyzes the fully oxidized form ($SO_4^{2-}$), but not the the partially oxidized $SO_3^{2-}$ form. This systematic error can be remedied by fully oxidizing the sorbed SO$_2$ prior to analysis by addition of H$_2$O$_2$. An alternative remedy is analyzing the sampler extract for both $SO_3^{2-}$ and $SO_4^{2-}$ ions.

The results of the study support the 1997 annual average SO$_2$ and NO$_2$ findings in a UP NSRI study using Ferm passive samplers in various DENR Metro Manila air sampling stations (Quirit et al, 1999). Two sites (Taft and Valenzuela) exceeded annual average SO$_2$ standards (84 and 86 ug/m$^3$ respectively compared to the annual SO$_2$ national standard of 77 ug/m$^3$). The 1997 average levels would even be higher if the negative bias of the Ferm SO$_2$ sampler is true. On the other hand, all sites were found to have 1997 annual NO$_2$ average levels below the national annual standard (150 ug/m$^3$). The average levels would be even lower if the Ferm NO$_2$ sampler positive bias is considered.

In spite of limited results, the simplicity of the Korean passive sampler makes it a good candidate for relatively cheap local fabrication. The Ferm sampler configuration is more complicated (Quirit et. al. 2002, Ferm 1991) and local plastic mold manufacturers have quoted quite a steep price for its fabrication (> P200,000.00 for the mold). The Korean NGO have not replied as to the material of their sampler, but the configuration does not have the stainless steel mesh nor the precisely molded parts of the Ferm sampler, hence the preliminary assessment of its cheaper fabrication, compared to the Ferm sampler. Once the molds are made, however, production of the samplers is projected to be relatively cheap, according to the plastics mold manufacturers (they did not quote actual prices, but projected less than P100 per sampler). Passive samplers are lightweight, convenient to use and does not need expensive pumps and electricity. Imported passive samplers, however, are also quite expensive (around four times projected local price, once the mold is made). It would be good to be able to fabricate and study various configurations of locally produced passive samplers.

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