

Research Article

Simultaneous Sampling of NO, NO₂, HONO and HNO₃ in the Atmosphere by a Filter-Pack Method

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ABSTRACT A simultaneous sampling method for gaseous nitric oxide (NO), nitrogen dioxide (NO₂), nitrous acid (HONO) and nitric acid (HNO₃) was developed by a filter-pack sampling method to measure these concentrations at low cost in areas where monitoring stations are not available or at multiple locations. HONO and HNO₃ gases were collected with a conventional filter-pack method. NO₂ was collected with a guaiacol-impregnated filter at a flow rate of 0.3 dm³ min⁻¹. NO was collected using guaiacol by oxidizing it to NO₂ with potassium permanganate at a 0.3 dm³ min⁻¹ flow rate. The optimum concentration of KMnO₄ in the immersion solution for the impregnated filter was 0.16 mol dm⁻³ (in 0.51 mol dm⁻³ H₂SO₄). The concentrations of NO and NO₂ measured by the filter-pack method were in good agreement with those measured by the chemiluminescence method. It was calculated that 60 ppb NO could be oxidized to NO₂ with the KMnO₄-impregnated filter for 183 hours at a 0.3 dm³ min⁻¹ flow rate. This is enough time for sampling in a real environment. This method was applied to measure NO, NO₂, HONO and HNO₃ in the atmosphere at three points around Osaka, Japan.

KEY WORDS Nitric oxide, Filter-pack sampling, Nitrogen dioxide, Nitrous acid, Nitric acid

1. INTRODUCTION

Nitric oxide (NO) is formed in combustion processes in the atmosphere and is a primary product among nitrogen oxides. Therefore, NO is sometimes used as an indicator of exhaust gas from vehicles in urban areas. NO is oxidized by ozone to produce nitrogen dioxide (NO₂). NO₂ affects the respiratory system and is regulated in many countries. The photolysis of NO₂ is only one process that produces ozone (O₃) in the troposphere. O₃ relates to various oxidation processes in the atmosphere. Nitric acid (HNO₃) and nitrous acid (HONO) are mainly formed by the reactions of OH radical with NO₂ and NO, respectively. HNO₃ and HONO are causative substances in acid rain. Therefore, the concentrations of NO and NO₂ give us important information in atmospheric chemistry. Recently, these concentrations have become basic data in atmospheric chemistry research in developed countries (Akimoto *et al.*, 2015; Lurmann *et al.*, 2015; Sadanaga *et al.*, 2008).

In many developing countries with rapidly growing economies, air pollution can

often be a problem due to the priority given to economic development. However, in these countries, NO_x data may not be available because air monitoring facilities are few, or if they are available, the equipment may quickly become unusable. Therefore, it is very difficult to obtain concentrations of NO and NO_2 . Modification methods of the Griess-Ilosvay method (US Standard methods), such as the Saltzman method (Saltzman, 1954) and Jacobs and Hochheiser method (1958), are generally used to obtain these concentrations; however, there are uncertainties in this method, such as the conversion efficiency of NO_2 to NO_2^- , the absorption efficiency of NO_2 , and the oxidation efficiency of NO to NO_2 (Tamaki and Hiraki, 1988).

An annular denuder system (Allegrini *et al.*, 1987; Ferm and Sjodin, 1985) and a filter-pack sampling method (Noguchi *et al.*, 2007; Tamaki *et al.*, 2001) can be used to measure air pollutants for such purposes. The annular denuder system is expensive and easily broken because of glassware, and the operation is complicated. Therefore, in this study, filter-pack sampling was applied. There have been a few reports about filter-pack sampling for NO_2 (Toriyama *et al.*, 2019; Watanabe *et al.*, 2006; Pakkanen *et al.*, 1999; Sickles *et al.*, 1990). Sickles *et al.* studied active sampling methods for NO_2 in detail and finally chose triethanol amine (TEA) (Sickles *et al.*, 1990). They observed >90% collection efficiency with TEA-coated glass fiber filters at a flow rate of $1.5 \text{ dm}^3 \text{ min}^{-1}$. Furthermore, they mentioned that HONO and peroxyacyl nitrates could be potential interference compounds. Pakkanen *et al.* utilized a NaI- Na_2CO_3 -impregnated filter, and the results showed lower values compared to those obtained by differential optical absorption spectrometry (Pakkanen *et al.*, 1999). Watanabe *et al.* measured NO_x by a filter-pack method with one Na_2CO_3 -impregnated filter and 6 filters impregnated with PTIO (2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl) and TEA (Watanabe *et al.*, 2006). The sampling flow rate was $1.0 \text{ dm}^3 \text{ min}^{-1}$, and the collection efficiency was almost 100%. Toriyama *et al.* (2019) measured HNO_3 , HONO and NO_2 simultaneously with filter-pack sampling. TEA was used to collect NO_2 at $0.1 \text{ dm}^3 \text{ min}^{-1}$. At a flow rate faster than $0.1 \text{ dm}^3 \text{ min}^{-1}$, the absorption efficiency of NO_2 did not reach 100%. Therefore, it is not suitable to measure NO_2 in a few hours.

Buttini *et al.* (1987) applied guaiacol as an absorbent for NO_2 in a denuder system. They reported that enough NO_2 can be absorbed (99.4% at $2.0 \text{ dm}^3 \text{ min}^{-1}$ and 97.4

% at $2.9 \text{ dm}^3 \text{ min}^{-1}$). We used guaiacol to absorb NO_2 in this study. HNO_3 and HONO were absorbed with NaCl- and Na_2CO_3 -impregnated filters, respectively, according to the literature (Noguchi *et al.*, 2007), and NO_2 was collected with a guaiacol-impregnated filter. Furthermore, in this study, after HNO_3 , HONO and NO_2 were removed from the sample air with the filters mentioned above, NO was oxidized to NO_2 and collected.

NO is generally oxidized by chromium oxide (Hilliard and Wheeler, 1977), PTIO (Hauser *et al.*, 2009; Watanabe *et al.*, 2006), and KMnO_4 (Japanese Industrial Standards, 2004). In Japan, the use of chromium is socially problematic. PTIO requires an additional separation process to remove PTIO from the extraction (Hauser *et al.*, 2009; Watanabe *et al.*, 2006). In this study, KMnO_4 was used to oxidize NO. We report here on the development and performance of a simultaneous sampling method for HNO_3 , HONO, NO_2 , and NO by filter-pack sampling.

2. EXPERIMENTAL

2.1 Equipment

The filter-pack sampling system in the present study is shown in Fig. 1. The sampling system consists of two filter-pack sets (Nilu filter packs supplied by Tokyo Dylec Co.). One set is for sampling of HNO_3 and HONO, and the other is for NO_2 and NO. FP1 is for HNO_3 and HONO sampling with a sampling flow rate of $4.0 \text{ dm}^3 \text{ min}^{-1}$. This flow rate is limited by an impactor for the $\text{PM}_{2.5}$ sampling requirement of F1 (the impactor is not indicated in Fig. 1). Therefore, the flow rate can be changed when $\text{PM}_{2.5}$ is not collected. The entire air flow was drawn by a Hiblow Air Pump from Techno Takatsuki Co., Ltd. (KP-5030S, 100 V and 0.26 A). After the particles are removed with a Teflon filter, F1, all HNO_3 is collected with a NaCl-impregnated filter, F2. Next, all HONO and a few percent of NO_2 are collected with a Na_2CO_3 -impregnated filter, F3. Then, almost the same percent of NO_2 is absorbed on a Na_2CO_3 -impregnated filter, F4 (Noguchi *et al.*, 2007). After FP1, the sampling line is separated into two lines. One line is introduced to FP2 with a lower flow rate. There are two reasons for the lower flow rate of FP2. NO_2 cannot be collected completely at higher flow rates, such as FP1. Another reason is that NO_2 and NO concentrations are much higher than HNO_3 and HONO concentrations, and therefore, a high flow rate is not required for simultaneous sampling and

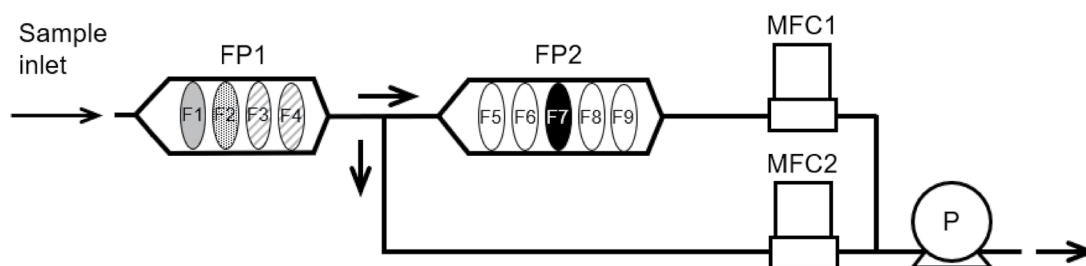


Fig. 1. Sampling setup for HNO₃, HONO, NO₂ and NO in the present method. FP1 (filter-pack set 1): for HNO₃ and HONO sampling, FP2 (filter-pack set 2): for NO₂ and NO sampling. F1: Teflon filter, F2: NaCl-impregnated filter, F3 and F4: Na₂CO₃-impregnated filters, F5, F6, F8 and F9: Guaiacol-impregnated filters, F7: KMnO₄-impregnated filter. MFC1, 2: mass flow controller, P: air pump. The flow rate of FP1 was controlled by MFC1 plus MFC2.

possibly causes adsorption breakthrough on the impregnated filter. F5 and F6 are guaiacol/NaOH-impregnated filters for NO₂ collection. One filter is enough, but we used two filters to avoid adsorption breakthrough. F7 is a KMnO₄-impregnated filter for oxidation of NO. F8 and F9 are guaiacol/NaOH-impregnated filters to collect NO₂ produced by oxidizing NO. Each nitrogen oxide concentration can be calculated from the nitrate and nitrite concentrations explained later; the volume of extraction and the flow rate of the sample are as follows.

$$[\text{HNO}_3] = [\text{NO}_3^-]_{\text{F2}} + [\text{NO}_2^-]_{\text{F2}} \quad (1)$$

$$[\text{HONO}] = [\text{NO}_3^-]_{\text{F3}} + [\text{NO}_2^-]_{\text{F3}} - ([\text{NO}_3^-]_{\text{F4}} + [\text{NO}_2^-]_{\text{F4}}) \quad (2)$$

$$[\text{NO}_2] = 2 \times ([\text{NO}_3^-]_{\text{F4}} + [\text{NO}_2^-]_{\text{F4}}) + [\text{NO}_2^-]_{\text{F5}} + [\text{NO}_2^-]_{\text{F6}} \quad (3)$$

$$[\text{NO}] = [\text{NO}_2^-]_{\text{F8}} + [\text{NO}_2^-]_{\text{F9}} \quad (4)$$

Here, subscripts indicate the filter number explained above. For the guaiacol filter, only nitrite was analyzed, since only nitrite was observed in our earlier experiment measured by ion chromatography. Additionally, it has been reported that almost all NO₂ is converted to nitrite in alkaline guaiacol solution (Nash, 1970).

To evaluate the performance of the present method, NO and NO₂ were measured by a Thermo Fisher Scientific, Model 42i chemiluminescence NO_x analyzer (CL). However, the NO₂ value obtained by the CL method includes NO₂, HNO₃, HONO and other nitrogen oxide and nitrogen-containing organics. In this study, nitrogen-containing organics were not considered, since the concentrations were generally not very high. Only HNO₃, HONO and NO₂ were evaluated.

2.2 Reagents

Guaiacol, sodium hydroxide, potassium permanganate, sodium carbonate, sodium chloride, methanol, glycerine and other chemicals were reagent grade, obtained from Fujifilm Wako Pure Chemical Corporation and used as received. Ultrapure water was obtained by using a Direct-Q 3UV from Merck Millipore, Inc. (resistivity ≥ 18.2 M Ω cm). Nitrogen dioxide (10.5 ppm, air balance) and nitric oxide (4.93 ppm, N₂ balance) were obtained from Taiyo Nippon Sanso Co. and diluted with purified air obtained by a Zero Air generator, Model 111, from Thermo Fisher Scientific, Inc. (passing through silica gel (Masuda Rika Kogyo, Ltd., 5–10 mesh), Purafil (Nippon Thermo Co., Ltd., No. 7075) and activated carbon).

2.3 Impregnated Filters and Analytical Methods

Impregnated filters F2, F3 and F4 were prepared according to the literature (Toriyama *et al.*, 2019). For the HNO₃-collecting filter (F2), 2 wt% NaCl and 1 wt% glycerine in methanol/water (1/1) were used, and for the HONO-collecting filter (F3, F4), 2 wt% Na₂CO₃ and 1 wt% glycerine in methanol/water (1/1) were used. Impregnated filters F5, F6, F8 and F9 were prepared with No. 51A cellulose filters from Toyo Roshi Kaisha, Ltd. (47 mm Φ) as follows. First, the filters were washed with ultrapure water three times and immersed for three minutes in 10–20 wt% guaiacol, 5 wt% NaOH, and 1 wt% glycerol in methanol/water (1/1) solutions three times in three separate bottles. Impregnated filter F7 was prepared with a QR-100 quartz filter from Advantec Co., Ltd. (47 mm Φ). The filter was immersed in a mixture solution of 0.16 mol dm⁻³ KMnO₄, which is the same concentration of oxidant for the Saltzman method described in Japanese Standard Method (2004), and 0.51 mol dm⁻³ H₂SO₄.

After immersion in each solution, the filters were dried

at 60°C and then kept in sealed polypropylene bags until sampling. After sampling, each filter was stored in a sealed polyethylene bag and kept cool until analysis. The absorbed components on the filters were extracted by ultrapure water, and these extracts were analyzed by ion chromatography in the laboratory. The anion chromatograph system (883 basic IC plus, Metrom, Switzerland) had a guard column (SI-90G, Shodex), separation column (SI-90 4E, Shodex), and suppressor for anions, and the eluent was 9 mmol dm⁻³ Na₂CO₃ solution at a flow rate of 1 mL min⁻¹. The detection limits of nitrite and nitrate that were defined as 3 times the standard deviation of five measurements for 20 μmol dm⁻³ were 0.42 and 0.34 μmol dm⁻³, respectively. Nitrite formed on the guaiacol-impregnated filter was extracted by ultrapure water, and the extract was analyzed by a Griess-Ilosvay method (US Standard methods) with a UV/Visible spectrophotometer (Shimadzu Co., Ltd., UV-1800) at 545 nm. Three blank filters for each were also analyzed for correction. The detection limit of nitrite that was defined as 3 times the standard deviation of six measurements was 0.11 μmol dm⁻³.

3. RESULTS AND DISCUSSION

The sampling condition of FP1 was according to that of Toriyama *et al.* (2019). In this study, the flow rate of FP1 was set to 4.0 dm³ min⁻¹, which is the measurement condition for PM_{2.5} of the filter-pack used in this study. The correction efficiencies of HNO₃ and HONO have been confirmed (Toriyama *et al.*, 2019).

3.1 Optimization of NO₂ Sampling

To determine the optimum concentration of guaiacol in the immersing solution for NO₂ sampling, NO₂ collection efficiency was investigated by comparing with NO₂ values measured with the chemiluminescence NO_x analyzer. The concentrations of glycerol and NaOH were fixed at 1 wt% and 5 wt%, respectively, and that of guaiacol was changed from 10 to 20 wt%. Here, the flow rate of the sampling was 0.1 dm³ min⁻¹ for 20–24 hours. The results are shown in Fig. 2. At 10 wt% guaiacol, NO₂ was not completely absorbed on the filter. It is speculated that higher guaiacol was required. At 20 wt%, the scattering was large. Guaiacol was deposited on the filter, probably because some NO₂ was absorbed during filter preparation. Therefore, it is considered that the results were scattered. At 15 wt%, the NO₂ concentrations measured by

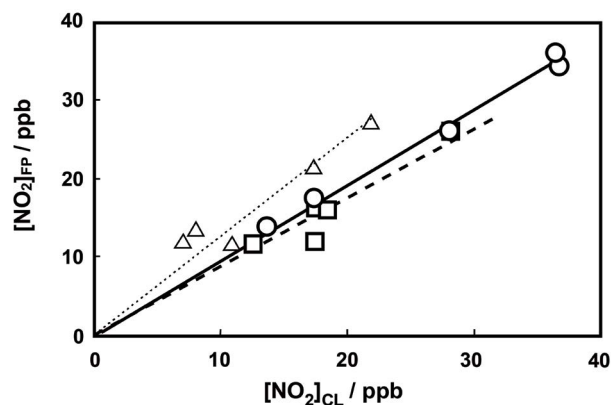


Fig. 2. Absorption efficiencies of NO₂ by guaiacol-impregnated filters prepared with 10, 15 and 20 wt% guaiacol-impregnating solution. The flow rate was 1.0 dm³ min⁻¹. R is a correlation coefficient. □: 10 wt%, [NO₂]_{FP} = 0.883[NO₂]_{CL}, R = 0.995, ○: 15 wt%, [NO₂]_{FP} = 0.963[NO₂]_{CL}, R = 0.999, △: 20 wt%, [NO₂]_{FP} = 1.27[NO₂]_{CL}, R = 0.992.

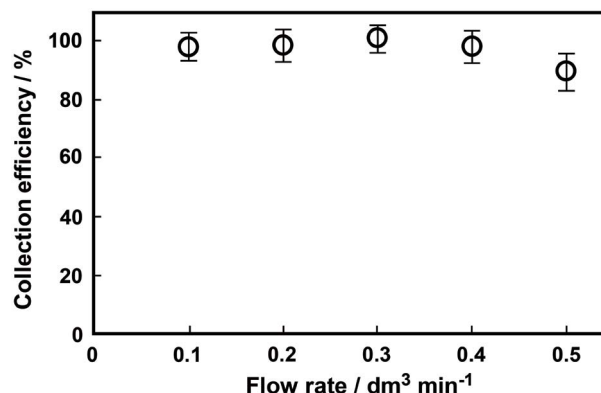


Fig. 3. Change in collection efficiencies of NO₂ with sampling flow rate. A 15 wt% guaiacol-impregnated filter was used. The circles and error bars show the average of 3–5 samples and one standard deviation, respectively. The sample air was outdoor air at the A5 building of Osaka Prefecture University.

the present method were in good agreement with those measured by the CL method.

Using 15 wt% guaiacol immersing solution, the dependence of the absorption efficiency of NO₂ on the flow rate was investigated. The sampling times were 20–24, 6–7, 3–4 and 2.4–4 hours at 0.1, 0.2, 0.3, 0.4 and 0.5 dm³ min⁻¹, respectively. The samplings were conducted with two filters in series, and the concentration was calculated from the sum of nitrite and nitrate concentrations in the two filters. The results are shown in Fig. 3. From Fig. 3, it was found that at a flow rate lower than 0.4 dm³ min⁻¹,

almost all NO₂ could be collected. Therefore, we decided that 0.3 dm³ min⁻¹ was to be used in the sampling for safety. The ratios of HONO/NO₂ were reported to be a few percent to 13.4%, and therefore, 4 dm³ min⁻¹ for HONO sampling (FP1) and 0.3 dm³ min⁻¹ for NO₂ sampling (FP2) were well balanced in the simultaneous sampling. One filter in FP2 could absorb NO₂ of approximately 80% on average, and therefore, a total of approximately 96% of NO₂ could be absorbed.

3.2 Optimization of the Oxidation of NO to NO₂

In the sample air passing through FP1 and two guaiacol-impregnated filters, NO is still present. If NO is oxidized to NO₂, the NO concentration can be obtained since NO₂ can be absorbed by the two guaiacol filters. Then, the oxidation efficiencies of NO were investigated. NO was generally oxidized by chromium oxide (Hilliard and Wheeler, 1977), PTIO (Hauser *et al.*, 2009; Watanabe *et al.*, 2006), KMnO₄ (Japanese Industrial Standards, 2004) or ozone. In Japan, the use of chromium is socially problematic. PTIO requires an additional separation process to remove PTIO from the extraction (Hauser *et al.*, 2009; Watanabe *et al.*, 2006). To produce ozone, a UV lamp is required. In field measurements, an additional electric source for the UV lamp to produce ozone is not favorable. Therefore, in this study, KMnO₄ was used to oxidize NO. First, the dependence of the concentration of KMnO₄ in the immersing solution of the oxidation filter (quartz filter) on the oxidation efficiencies of NO was investigated. The mole ratio of KMnO₄ and H₂SO₄ was constant at 0.158 mol KMnO₄ and 0.51 mol H₂SO₄, respectively. The results are shown in Fig. 4. The oxidation efficiencies were higher than 80% from 0.02–0.2 mol dm⁻³ KMnO₄ and stable at 0.16 mol dm⁻³ KMnO₄. The oxidation efficiency of NO to NO₂ at 70% is used in the Japanese Industrial Standard (2004), but almost 100% was obtained in our results. The reason is not clear. The difference is that the Japanese Industrial Standard method uses an aqueous solution, and the present method uses a wet solid on a filter. The solubility of NO in water is not very high, and therefore, it is speculated that the contact of NO with KMnO₄ is not effective in aqueous solution. Furthermore, the oxidation efficiency was 95% at 320 ppb NO with a 0.16 mol dm⁻³ KMnO₄-impregnated filter.

The oxidation efficiency of 300 ppb NO was maintained at a flow rate of at least 2.75 hours at 4.0 dm³ min⁻¹. This indicates that a total of 8.24×10^{-6} mol of NO could

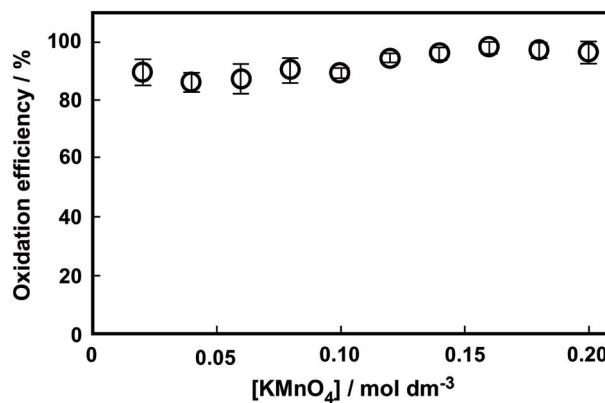


Fig. 4. Oxidation efficiencies of NO by KMnO₄-impregnated filters prepared with various concentrations of KMnO₄. The mole ratio of KMnO₄ and H₂SO₄ was 0.158 mol KMnO₄ and 0.51 mol H₂SO₄, respectively. The NO concentration was 80 ppb. The sampling was conducted at 0.3 dm³ min⁻¹ for 20–40 minutes. The error bars show one standard deviation of 3–4 samples.

be oxidized continuously. When the flow rate of the sampling was set at 0.3 dm³ min⁻¹, the KMnO₄-impregnated filter could be used for 183 hours in the case of 60 ppb NO. It is concluded that this KMnO₄-impregnated filter prepared with 0.16 mol dm⁻³ KMnO₄ can be used for field sampling sufficiently under normal ambient air conditions.

The optimum conditions for NO₂ and NO sampling (FP2) are summarized below.

- Concentration of the immersing solution (1/1; methanol/water) of guaiacol;
- Guaiacol: 15 wt%
- NaOH: 5 wt%
- Glycerol: 1 wt%
- Concentration of immersing solution (water) of KMnO₄ solution;
- KMnO₄: 0.16 mol dm⁻³
- H₂SO₄: 0.51 mol dm⁻³
- Flow rate: 0.3 dm³ min⁻¹.

Under the optimum conditions, the concentrations of NO and NO₂ in the ambient air were measured by the present method and compared with those by the CL method. Fig. 5A and 5B shows the results of NO and NO₂, respectively. Here, NO₂ concentrations measured by the CL method include NO₂, HNO₃, HONO and other nitrogen compounds. Therefore, those by the present method are expressed with the sum of NO₂, HNO₃, and HONO concentrations. Both lines showed a good linear relationship with a slope of almost 1.0; that is, for

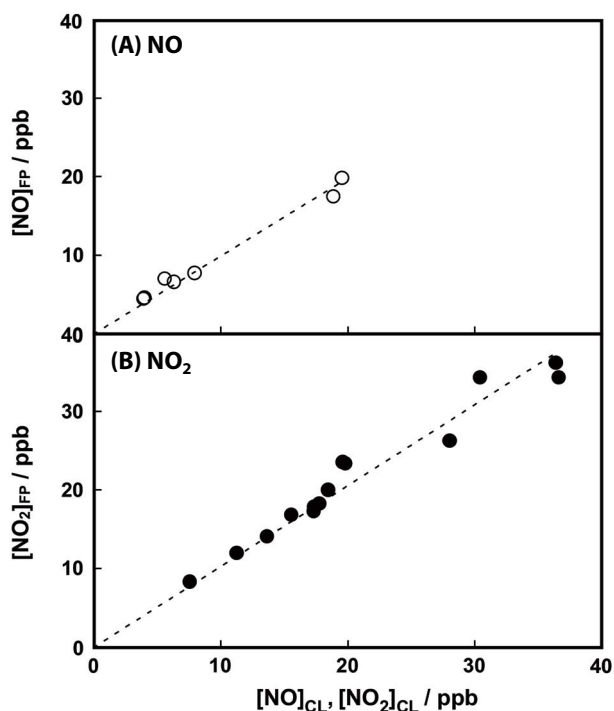


Fig. 5. Comparison of NO and NO₂ concentrations measured by the present method and the CL method. (A) NO: $[NO]_{FP} = 0.987[NO]_{CL}$, $R = 0.995$. (B): NO₂, $[NO_2]_{FP} = 1.04[NO_2]_{CL}$, $R = 0.997$ (R is a correlation coefficient).

NO, $[NO]_{FP} = 0.987[NO]_{CL}$, $R = 0.998$, and for NO₂, $[NO_2]_{FP} = 1.04[NO_2]_{CL}$, $R = 0.997$.

The detection limits of these gases depend on the sampling time. If the detection limits of HNO₃, HONO, NO₂ and NO were calculated in the case of 4 hours of sampling by considering only errors from measurements of ions and error progression including three blank filters, those were 0.17, 0.31, 4.1 and 4.1 ppb, respectively.

3.3 Applying the Present Method at 3 Different Sampling Points at the Same Time

Three sets of the present system were applied for simultaneous measurements of HNO₃, HONO, NO₂ and NO. The sampling was conducted on September 15, 2020, from 7:30–12:15 and 12:45–17:45. One set was automatically controlled with a timer and electromagnetic valve. The sampling points were 1) Osaka Prefecture University in Sakai City, Osaka (OPU); 2) Izumiotsu City, Osaka (IZM); and 3) Sango Town, Nara (SAN). OPU (34.548°N, 135.506°E) is located in an urban and residential area, and national road #310 (160 m apart) runs beside OPU. The sampling point of IZM (34.514°N,

Table 1. HNO₃, HONO, NO₂ and NO concentrations (ppb) measured at three sampling points on September 17, 2020.

| | | HNO ₃ | HONO | NO ₂ | NO |
|------|-------------|------------------|------|-----------------|-------|
| OPU | 7:30–12:15 | ND | 2.9 | 20.6 | 6.9 |
| | 12:45–17:45 | ND | 1.6 | 21.7 | 6.6 |
| IZM | 7:30–12:15 | 1.3 | 1.7 | 23.2 | 36.3* |
| | 12:45–17:45 | 1.0 | 1.5 | 83.8 | 34.6 |
| SAN | 7:30–12:15 | 0.4 | 1.3 | 15.0 | 4.8 |
| | 12:45–17:45 | 0.2 | 0.6 | 10.4 | 9.9 |
| DL** | | 0.17 | 0.31 | 4.1 | 4.1 |

ND: Lower than detection limit

*Reference value because the oxidation capacity may have exceeded the allowable value (see text).

**Detection limits calculated by assuming 4 hours of sampling. See text for details.

135.414°E) is near the cross-section (5 meters from the road) of the Osaka Prefectural Road #29 and Osaka Rinkai Line, which is a three-lane road with heavy truck traffic on each side. SAN (34.595°N, 135.682°E) is in a residential area in a suburban area, and there is not much traffic. The results are shown in Table 1.

The concentrations of nitric acid were very low at OPU and SAN. At IZM, these values were 1.3 ppb in the morning and 1.0 ppb in the afternoon. The disadvantage of filter-pack sampling is well known and artifacts come from evaporation of nitric acid from particles on the filter. However, the concentrations of HNO₃ were not very high in this sampling period, and the artifacts were not very important. It is considered that the other gases were not affected by the artifacts of particles. The concentrations of HONO were not very different at the three points. For NO₂, the highest concentration, 83.8 ppb, was observed in the afternoon at IZM. At this point, there are many traffic sources, and high NO₂ concentrations have been reported in the past (Morioka *et al.*, 2000). The NO₂ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN. The concentrations of NO were highest at IZM due to heavy traffic. In this sampling, the numbers of traffic at IZM were 2,500–4,300 vehicles/hour from 7 AM to 12 AM, including passenger cars, heavy-duty cars and motorbikes, and 2,300–3,500 vehicles/hour from 13 PM to 17 PM. Therefore, the NO and NO₂ concentrations were very high. However, in Table 1, the NO concentration in the morning at IZM must have been undercalculated. After sampling, the oxidation filter for

Table 2. HNO₃, HONO, NO₂ and NO concentrations measured by the chemiluminescence method (CL) and filter-pack method (FP). (unit: ppb)

| Date | Time | NO | | HNO ₃ | HONO | NO ₂ | NO ₂ * | |
|---------------|---------------|------|------|------------------|------|-----------------|-------------------|------|
| | | CL | FP | FP | FP | FP | CL | FP |
| Dec. 24, 2019 | 14:00–14:00** | – | – | – | 1.2 | 12.9 | 13.7 | 14.0 |
| Dec. 25, 2019 | 14:47–14:47** | – | – | – | 1.9 | 32.4 | 36.7 | 34.3 |
| Jan. 8, 2020 | 14:26–14:11** | – | – | – | 1.1 | 34.9 | 36.5 | 36.1 |
| Jan. 17, 2020 | 15:31–16:00** | – | – | – | 0.4 | 17.2 | 17.4 | 17.7 |
| Jan. 24, 2020 | 12:00–16:00 | 4.0 | 4.5 | 0.7 | 1.7 | 17.5 | 18.5 | 19.9 |
| Jan. 25, 2020 | 12:00–16:00 | 3.9 | 4.4 | ND | 1.6 | 10.1 | 11.3 | 11.8 |
| Jan. 26, 2020 | 12:00–16:00 | – | – | 0.5 | 1.5 | 6.2 | 7.6 | 8.2 |
| Jan. 27, 2020 | 12:00–16:00 | 8.0 | 7.7 | ND | 5.3 | 12.9 | 17.8 | 18.2 |
| Jan. 28, 2020 | 12:00–16:00 | – | – | ND | 0.02 | 34.2 | 30.5 | 34.2 |
| Jan. 29, 2020 | 12:00–16:00 | 19.6 | 19.8 | ND | 3.2 | 14.0 | 17.4 | 17.2 |
| Jan. 30, 2020 | 12:00–16:00 | 18.9 | 17.5 | ND | 1.9 | 14.8 | 15.6 | 16.7 |
| Sep. 15, 2020 | 7:30–12:15 | 5.6 | 6.9 | ND | 2.9 | 20.6 | 19.6 | 23.5 |
| Sep. 15, 2020 | 12:45–17:15 | 6.3 | 6.6 | ND | 1.6 | 21.7 | 19.8 | 23.3 |

–: Not analyzed, ND: lower than the detection limit.

*: CL values included NO₂, HNO₃, HONO and other nitrogen oxides, and FP values were the sum of NO₂, HNO₃ and HONO concentrations.

** : The time was the start time to the end time of the next day at a 0.1 dm³ min⁻¹ flow rate.

NO was decolorized. This indicates that most KMnO₄ was reduced. This phenomenon was never observed at OPU. Sufficient amounts of KMnO₄ compared to NO were coated on the filter as mentioned above. It is speculated that high concentrations of reductants, such as organic compounds, were emitted from vehicles that reacted with KMnO₄. Therefore, in the afternoon sampling, the KMnO₄-impregnated filter was changed every two hours before the color of KMnO₄ became lighter. The conditions in the morning sampling at IZM were very special. In the case of sampling at such highly polluted places, several KMnO₄ filters should be connected in series.

4. CONCLUSIONS

A simultaneous sampling method for NO, NO₂, HONO and HNO₃ by using a filter-pack was established. NO₂ was collected with a guaiacol-impregnated filter at a 0.3 dm³ min⁻¹ flow rate. This method can measure NO₂ at shorter sampling times than the previously reported method (Toriyama *et al.*, 2019). NO was collected using guaiacol by oxidizing it to NO₂ with 0.16 mol dm⁻³ potassium permanganate at a 0.3 dm³ min⁻¹ flow rate. The concentrations of NO and NO₂ measured by the filter-pack method were in good agreement with

those measured by the chemiluminescence method, with correlation coefficients of 0.995 and 0.997, respectively. It was calculated that 60 ppb NO could be oxidized to NO₂ with the KMnO₄-impregnated filter for 183 hours at a 0.3 dm³ min⁻¹ flow rate. This is enough time for sampling in a real environment. This filter-pack method was applied to measure NO, NO₂, HONO and HNO₃ in the atmosphere at three points around Osaka. The sampling points were 1) OPU, which is located in an urban and residential area; 2) IZM, which has heavy truck traffic on the road; and 3) SAN, which is in a residential area in a suburban area. Concentrations of nitric acid and HONO were not very different at the three points except for HNO₃ at IZM. For NO and NO₂, the highest concentrations were observed at IZM, and the lowest values were observed at SAN. These results are considered to reflect the traffic volume. It is concluded that simultaneous sampling of NO, NO₂, HONO and HNO₃ with the filter-pack can be established.

The pump we used requires only 26 W. For 3 hours sampling, electricity requires slightly more than 78 W h, including the flow controllers, and therefore, in the future, the use of a battery-powered system will make it possible to measure NO, NO₂, HONO and HNO₃ in the atmosphere in places where electric power is not available.

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REFERENCES

- Akimoto, H., Mori, Y., Sasaki, K., Nakanishi, H., Ohizumi, T., Itano, Y. (2015) Analysis of monitoring data of ground-level ozone in Japan for long-term trend during 1990–2010: Causes of temporal and spatial variation. *Atmospheric Environment*, 102, 302–310. <https://doi.org/10.1016/j.atmosenv.2014.12.001>
- Allegrini, I., Santis, F. De, Palo, V. Di, Febo, A., Perrino, C., Possanzini, M., Liberti, A. (1987) Annular denuder method for sampling reactive gases and aerosols in the atmosphere. *Science of The Total Environment*, 67(1), 1–16. [https://doi.org/10.1016/0048-9697\(87\)90062-3](https://doi.org/10.1016/0048-9697(87)90062-3)
- Buttini, P., Dipalo, V., Possanzini, M. (1987) Coupling of denuder and ion chromatographic techniques for NO₂ trace level determination in air. *Science of The Total Environment*, 61, 59–72. [https://doi.org/10.1016/0048-9697\(87\)90356-1](https://doi.org/10.1016/0048-9697(87)90356-1)
- Ferm, M., Sjodin, A. (1985) A Sodium Carbonate Coated Denuder for Determination of Nitrous Acid In the Atmosphere. *Atmospheric Environment*, 19(6), 979–983. [https://doi.org/10.1016/0004-6981\(85\)90243-4](https://doi.org/10.1016/0004-6981(85)90243-4)
- Hauser, C.D., Battle, P., Mace, N. (2009) Adjusted blank correction method for UV-vis spectroscopic analysis of PTIO-coated filters used in nitrogen oxide passive samplers. *Atmospheric Environment*, 43(10), 1823–1826. <https://doi.org/10.1016/j.atmosenv.2008.12.022>
- Hilliard, J.C., Wheeler, R.W. (1977) Catalysed Oxidation of Nitric Oxide to Nitrogen Dioxide. *Combustion and Flame*, 29, 15–19. [https://doi.org/10.1016/0010-2180\(77\)90089-X](https://doi.org/10.1016/0010-2180(77)90089-X)
- Jacobs, B.M., Hochheiser, S. (1958) Continuous sampling and ultramicrodetermination of nitrogen dioxide in air. *Analytical Chemistry*, 30, 426–428. <https://doi.org/10.1021/ac60135a032>
- Japanese Industrial Standards, JISB7953:2004 (2004) Automatic measuring instrument for nitrogen oxides in the atmosphere.
- Lurmann, F., Avol, E., Gilliland, F. (2015) Emissions reduction policies and recent trends in Southern California's ambient air quality. *Journal of Air & Waste Management Association*, 65(3), 324–335. <https://doi.org/10.1080/10962247.2014.991856>
- Morioka, J., Takenaka, N., Bandow, H., Maeda, Y., Ayaki, S., Ichino, K., Ueki, Y. (2000) Change in Two-Dimensional Distribution Patterns of NO₂ Concentration in Izumiotsu City Measured by a Diffusion Sampler - Ten Years Seasonal Study -. *Journal of Japan Society for Atmospheric Environment*, 35(4), 191–200. https://doi.org/10.11298/taiki1995.35.4_191
- Nash, T. (1970) Absorption of nitrogen dioxide by aqueous solutions. *Journal of the Chemical Society A*, 1970, 3023–3024. <https://doi.org/10.1039/J19700003023>
- Noguchi, I., Otsuka, H., Akiyama, M., Sakai, S., Kato, T. (2007) Measuring Concentrations of Nitrous Acid Gas by the Filter-Pack Sampling Method. *Journal of Japan Society for Atmospheric Environment*, 42(3), 162–174. https://doi.org/10.11298/taiki1995.42.3_162
- Pakkanen, T.A., Hillamo, R.E., Aurela, M., Andersen, H.V., Grundahl, L., Ferm, M., Persson, K., Karlsson, V., Reissell, A., Røyset, O., Fløisand, I., Oyola, P., Ganko, T. (1999) Nordic intercomparison for measurement of major atmospheric nitrogen species. *Journal of Aerosol Science*, 30, 247–263. [https://doi.org/10.1016/S0021-8502\(98\)00039-1](https://doi.org/10.1016/S0021-8502(98)00039-1)
- Sadanaga, Y., Shibata, S., Hamana, M., Takenaka, N., Bandow, H. (2008) Weekday/weekend difference of ozone and its precursors in urban areas of Japan, focusing on nitrogen oxides and hydrocarbons. *Atmospheric Environment*, 42, 4708–4723. <https://doi.org/10.1016/j.atmosenv.2008.01.036>
- Saltzman, B.E. (1954) Colorimetric Microdetermination of Nitrogen Dioxide in Atmosphere. *Analytical Chemistry*, 26(12), 1949–1955. <https://doi.org/10.1021/ac60096a025>
- Sickles, J.E., Grohse, P.M., Hodson, L.L., Salmons, C.A., Cox, K.W., Turner, A.R., Estes, E.D. (1990) Development of a method for the sampling and analysis of sulfur dioxide and nitrogen dioxide from ambient air. *Analytical Chemistry*, 62, 338–346. <https://doi.org/10.1021/ac00203a006>
- Tamaki, M., Hiraki, T. (1988) Measurement of Nitrogen Oxides in Ambient Air and in Stack Gas. *Journal of Environmental Conservation Engineering*, 17(5), 331–337. <https://doi.org/10.5956/jriet.17.331>
- Tamaki, T., Hiraki, T., Aikawa, M., Nishikawa, Y., Taguchi, K., Matsumoto, M. (2001) Evaluation of 4-Stage Filter Pack Method for Dry Deposition Monitoring. *Journal of Japan Society for Atmospheric Environment*, 36(5), 308–317. https://doi.org/10.11298/taiki1995.36.5_308
- Toriyama, K., Fukae, K., Suda, Y., Kiyose, T., Oda, T., Fujii, Y., Chi, N.D.T., Huy, D.H., Hien, T.T., Takenaka, N. (2019) NO₂ and HONO concentrations measured with filter pack sampling and high HONO/NO₂ ratio in Ho Chi Minh city, Vietnam. *Atmospheric Environment*, 214, 116865. <https://doi.org/10.1016/j.atmosenv.2019.116865>
- US Standard methods 4500-NO₂⁻ B, EN 26 777.
- Watanabe, M., Takamatsu, T., Koshikawa, M.K., Sakamoto, K., Inubushi, K. (2006) Simultaneous determination of atmospheric sulfur and nitrogen oxides using a battery-operated portable filter pack sampler. *Journal of Environmental Monitoring*, 8, 167–173. <https://doi.org/10.1039/b512217a>