ABSTRACT A simultaneous sampling method for gaseous nitric oxide (NO), nitrogen dioxide (NO$_2$), nitrous acid (HONO) and nitric acid (HNO$_3$) 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 HNO$_3$ gases were collected with a conventional filter-pack method. NO$_2$ was collected with a guaiacol-impregnated filter at a flow rate of 0.3 dm$^3$ min$^{-1}$. NO was collected using guaiacol by oxidizing it to NO$_2$ with potassium permanganate at a 0.3 dm$^3$ min$^{-1}$ flow rate. The optimum concentration of KMnO$_4$ in the immersion solution for the impregnated filter was 0.16 mol dm$^{-3}$ (in 0.51 mol dm$^{-3}$ H$_2$SO$_4$). The concentrations of NO and NO$_2$ 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 NO$_2$ with the KMnO$_4$-impregnated filter for 183 hours at a 0.3 dm$^3$ min$^{-1}$ flow rate. This is enough time for sampling in a real environment. This method was applied to measure NO, NO$_2$, HONO and HNO$_3$ 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 (NO$_2$). NO$_2$ affects the respiratory system and is regulated in many countries. The photolysis of NO$_2$ is only one process that produces ozone (O$_3$) in the troposphere. O$_3$ relates to various oxidation processes in the atmosphere. Nitric acid (HNO$_3$) and nitrous acid (HONO) are mainly formed by the reactions of OH radical with NO$_2$ and NO, respectively. HNO$_3$ and HONO are causative substances in acid rain. Therefore, the concentrations of NO and NO$_2$ 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, NOx 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 NO2. 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 NO2 to NO2, the absorption efficiency of NO2, and the oxidation efficiency of NO to NO2 (Toriyama 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 NOx (Toriyama et al., 2019; Watanabe et al., 2006; Pakkanen et al., 1999; Sickles et al., 1990). Sickles et al. studied active sampling methods for NO2 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 dm3 min−1. Furthermore, they mentioned that HONO and peroxyacyl nitrates could be potential interference compounds. Pakkanen et al. utilized a NaI-Na2CO3-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 NOx by a filter-pack method with one Na2CO3-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 dm3 min−1, and the collection efficiency was almost 100%. Toriyama et al. (2019) measured HNO3, HONO, and NO2 simultaneously with a filter-pack sampling. TEA was used to collect NO2 at 0.1 dm3 min−1. At a flow rate faster than 0.1 dm3 min−1, the absorption efficiency of NO2 did not reach 100%. Therefore, it is not suitable to measure NO2 in a few hours.

Buttini et al. (1987) applied guaiacol as an absorbent for NO2 in a denuder system. They reported that enough NO2 can be absorbed (99.4% at 2.0 dm3 min−1 and 97.4% at 2.9 dm3 min−1). We used guaiacol to absorb NO2 in this study. HNO3 and HONO were absorbed with NaCl- and Na2CO3-impregnated filters, respectively, according to the literature (Noguchi et al., 2007), and NO2 was collected with a guaiacol-impregnated filter. Furthermore, in this study, after HNO3, HONO and NO2 were removed from the sample air with the filters mentioned above, NO was oxidized to NOx and collected.

NO is generally oxidized by chromium oxide (Hilliard and Wheeler, 1977), PTIO (Hauser et al., 2009; Watanabe et al., 2006), and KMnO4 (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, KMnO4 was used to oxidize NO. We report here on the development and performance of a simultaneous sampling method for HNO3, HONO, NO2, 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 HNO3 and HONO, and the other is for NOx and NO. FP1 is for HNO3 and HONO sampling with a sampling flow rate of 4.0 dm3 min−1. This flow rate is limited by an impactor for the PM2.5 sampling requirement of F1 (the impactor is not indicated in Fig. 1). Therefore, the flow rate can be changed when PM2.5 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 HNO3 is collected with a NaCl-impregnated filter, F2. Next, all HONO and a few percent of NOx are collected with a Na2CO3-impregnated filter, F3. Then, almost the same percent of NOx is absorbed on a Na2CO3-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. NOx cannot be collected completely at higher flow rates, such as FP1. Another reason is that NOx and NO concentrations are much higher than HNO3 and HONO concentrations, and therefore, a high flow rate is not required for simultaneous sampling and
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.

\[
[HNO_3] = [NO_3^-]_{F2} + [NO_2^-]_{F2} \quad (1)
\]

\[
[HONO] = [NO_3^-]_{F3} + [NO_2^-]_{F3} - ([NO_3^-]_{F4} + [NO_2^-]_{F4}) \quad (2)
\]

\[
[NO_2] = 2 \times ([NO_3^-]_{F4} + [NO_2^-]_{F4}) + [NO_2^-]_{F5} + [NO_2^-]_{F6} \quad (3)
\]

\[
[NO] = [NO_2^-]_{F8} + [NO_2^-]_{F9} \quad (4)
\]

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 NOx 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 MΩ 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 mmΦ) 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 mmΦ). 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$^{-3}$ Na$_2$CO$_3$ 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 six 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 (Shimazu 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 dm$^3$ min$^{-1}$, which is the measurement condition for PM$_{2.5}$ of the filter-pack used in this study. The correction efficiencies of HNO$_3$ and HONO have been confirmed (Toriyama et al., 2019).

3.1 Optimization of NO$_2$ Sampling

To determine the optimum concentration of guaiacol in the immersing solution for NO$_2$ sampling, NO$_2$ collection efficiency was investigated by comparing with NO$_2$ 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 dm$^3$ m$^{-3}$ for 20–24 hours. The results are shown in Fig. 2. At 10 wt% guaiacol, NO$_2$ 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 NO$_3$ was absorbed during filter preparation. Therefore, it is considered that the results were scattered. At 15 wt%, the NO$_2$ concentrations measured by 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 NO$_2$ 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 dm$^3$ 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 dm$^3$ min$^{-1}$,
Filter-pack Method for NO, NO\textsubscript{2}, HONO, HNO\textsubscript{3}

almost all NO\textsubscript{2} could be collected. Therefore, we decided that 0.3 dm\textsuperscript{3} min\textsuperscript{-1} was to be used in the sampling for safety. The ratios of HONO/NO\textsubscript{2} were reported to be a few percent to 13.4\%, and therefore, 4 dm\textsuperscript{3} min\textsuperscript{-1} for HONO sampling (FP1) and 0.3 dm\textsuperscript{3} min\textsuperscript{-1} for NO\textsubscript{2} sampling (FP2) were well balanced in the simultaneous sampling. One filter in FP2 could absorb NO\textsubscript{2} of approximately 80% on average, and therefore, a total of approximately 96% of NO\textsubscript{2} could be absorbed.

3.2 Optimization of the Oxidation of NO to NO\textsubscript{2}

In the sample air passing through FP1 and two guaiacol-impregnated filters, NO is still present. If NO is oxidized to NO\textsubscript{2}, the NO concentration can be obtained since NO\textsubscript{2} 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 \textit{et al.}, 2009; Watanabe \textit{et al.}, 2006), KMnO\textsubscript{4} (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 \textit{et al.}, 2009; Watanabe \textit{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, KMnO\textsubscript{4} was used to oxidize NO. First, the dependence of the concentration of KMnO\textsubscript{4} in the immersing solution of the oxidation filter (quartz filter) on the oxidation efficiencies of NO was investigated. The mole ratio of KMnO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} was constant at 0.158 mol KMnO\textsubscript{4} and 0.51 mol H\textsubscript{2}SO\textsubscript{4}, respectively. The results are shown in Fig. 4. The oxidation efficiencies were higher than 80% from 0.02-0.2 mol dm\textsuperscript{-3} KMnO\textsubscript{4} and stable at 0.16 mol dm\textsuperscript{-3} KMnO\textsubscript{4}. The oxidation efficiency of NO to NO\textsubscript{2} 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 KMnO\textsubscript{4} is not effective in aqueous solution. Furthermore, the oxidation efficiency was 95\% at 320 ppb NO with a 0.16 mol dm\textsuperscript{-3} KMnO\textsubscript{4} impregnated filter.

The oxidation efficiency of 300 ppb NO was maintained at a flow rate of at least 2.75 hours at 4.0 dm\textsuperscript{3} min\textsuperscript{-1}. This indicates that a total of 8.24 × 10\textsuperscript{-6} mol of NO could be oxidized continuously. When the flow rate of the sampling was set at 0.3 dm\textsuperscript{3} min\textsuperscript{-1}, the KMnO\textsubscript{4}-impregnated filter could be used for 183 hours in the case of 60 ppb NO. It is concluded that this KMnO\textsubscript{4}-impregnated filter prepared with 0.16 mol dm\textsuperscript{-3} KMnO\textsubscript{4} can be used for field sampling sufficiently under normal ambient air conditions.

The optimum conditions for NO\textsubscript{2} 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 KMnO\textsubscript{4} solution:
  - KMnO\textsubscript{4}: 0.16 mol dm\textsuperscript{-3}
  - H\textsubscript{2}SO\textsubscript{4}: 0.51 mol dm\textsuperscript{-3}

- Flow rate: 0.3 dm\textsuperscript{3} min\textsuperscript{-1}.

Under the optimum conditions, the concentrations of NO and NO\textsubscript{2} 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 NO\textsubscript{2}, respectively. Here, NO\textsubscript{2} concentrations measured by the CL method include NO\textsubscript{2}, HNO\textsubscript{3}, HONO and other nitrogen compounds. Therefore, those by the present method are expressed with the sum of NO\textsubscript{2}, HNO\textsubscript{3}, and HONO concentrations. Both lines showed a good linear relationship with a slope of almost 1.0; that is, for...
$\text{NO, } [\text{NO}]_{FP} = 0.987[\text{NO}]_{CL}, R = 0.995$. 

The NO$_2$, $[\text{NO}_2]_{FP} = 1.04[\text{NO}_2]_{CL}, R = 0.997$.

The detection limits of these gases depend on the sampling time. If the detection limits of HNO$_3$, HONO, NO$_2$ 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 HNO$_3$, HONO, NO$_2$ 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, 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 HNO$_3$ 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 NO$_2$, the highest concentration, 83.8 ppb, was observed in the afternoon at IZM. At this point, there are many traffic sources, and high NO$_2$ concentrations have been reported in the past (Morioka et al., 2000). The NO$_3$ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN. At this point, there are many traffic sources, and high NO$_2$ concentrations have been reported in the past (Morioka et al., 2000). The NO$_3$ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN. At this point, there are many traffic sources, and high NO$_2$ concentrations have been reported in the past (Morioka et al., 2000). The NO$_3$ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN. At this point, there are many traffic sources, and high NO$_2$ concentrations have been reported in the past (Morioka et al., 2000). The NO$_3$ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN. At this point, there are many traffic sources, and high NO$_2$ concentrations have been reported in the past (Morioka et al., 2000). The NO$_3$ concentration at SAN was lower than that at the other two points. This was due to the lower traffic at SAN.

|          | 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.

Fig. 5. Comparison of NO and NO$_2$ concentrations measured by the present method and the CL method. (A) NO: $[\text{NO}]_{FP} = 0.987[\text{NO}]_{CL}, R = 0.995$. (B) NO$_2$, $[\text{NO}_2]_{FP} = 1.04[\text{NO}_2]_{CL}, R = 0.997$ (R is a correlation coefficient).
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 Wh, 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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