Advanced Monitoring Method for Air Environment by Ogawa Passive Sampler

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Abstract

The Ogawa Passive Sampler is one of the only known methods of passive simultaneous monitoring of more than two components in the air. The first advantage of Ogawa Sampler is to have two chambers with the same configuration where one can place two different kinds of collection filter pads. In the case of simultaneous collection of NO and NO\(_2\), The NO\(_2\) collection filter coated with triethanolamine and the NOx collection filter coated with both triethanolamine and PTIO, which is specially prepared oxidation reagent of NO to NO\(_2\), are set in each of two chambers respectively. NO\(_2\) can be collected on the NO\(_2\) filters. NO is oxidized to NO\(_2\) by PTIO and then collected on the NOx filter together with NO\(_2\). On the other hand, SO\(_2\) is also collected on the NO\(_2\) collection filter at the same time. Today, The Ogawa Sampler can collect and measure NO, NO\(_2\), NOx, SO\(_2\), NH\(_3\) and O\(_3\) in the air.

The second advantage of Ogawa Sampler is to be reusable countless times, only the pre-coated collection filter pad is expendable. The same sampler can be used for all above shown gasses. Consequently, Ogawa Sampler can be represented as one of the lowest cost effective device for accurate measurements of large scale or local pollution, as well as indoor pollution and personal exposure.
Abstract 2nd

The analytical procedures, after collecting, have been developed by spectrophotometric method and ion chromatographic method for each analysis. In order to carry out an advanced monitoring, an analytical procedure should be simple and high through-put, because the number of sampler used in a research program will be extremely large. Analytical method coupled with flow injection analysis (FIA) has been proved to be useful and versatile in many practical analyses, moreover, FIA technique is easy to apply to an automatic procedure. By coupling Ogawa passive sampling method with FIA technique, the performance of the monitoring for air environment could be extremely enhanced.

Today Ogawa Sampler is being used world-wide for the collection of NO, NO₂, NOₓ, SO₂, NH₃ and O₃. In Japan, this proposed monitoring method has been performed to carry out special programs for the research of the air environment. The results obtained have been successful and have been continued for a long time.
Structure of Ogawa Sampler

1. Diffuser end cap
2. Stainless screen
3. Collection filter (14.5mmφ)
4. Teflon ring
5. Teflon disk
6. Body (15mm i.d., 19mm o.d., 6mm length)
The shelter is used for protecting rain, sun shine and strong wind.

Beside the observation van

Personal exposure

View of general setting up

Beside automated monitoring site
**Over all measurement procedure**

1. **Collection**
   - Set Ogawa Sampler up the measuring site

2. **Exposure and collection for 1~7 days**

3. **Extraction**
   - Extraction into pure water

4. **Analysis**
   - Analysis by FIA, IC and colorimetry

5. **Calculation**
   - Calculation by conversion equations
Absorption reagent, Analytical method and Analyte

\[
\begin{align*}
\text{NO}_2 & \quad \text{Triethanolamine, Colorimetry, Diazocoupling reaction, NO}_2^- \\
\text{NO}_x & \quad \text{Triethanolamine +PTIO, Colorimetry, Diazocoupling reaction, NO}_2^- \\
\text{SO}_2 & \quad \text{Triethanolamine, Ion chromatography, SO}_4^{2-} \\
\text{NH}_3 & \quad \text{Citric Acid, Ion chromatography, NH}_4^+ \\
\text{O}_3 & \quad \text{Nitrite ion, Ion chromatography, NO}_3^-
\end{align*}
\]
Simultaneous measurement of NO and NO$_2$

Preparation of Sampler

1. Diffuser end cap
2. Stainless screen
3. NO$_2$ collection filter (14.5mmφ)
4. Teflon ring
5. Teflon disk
6. Body
7. NOx collection filter (14.5mmφ)

NO$_2$ collection filter and NOx collection filter were placed in each of the two chambers of the samplers respectively.

Chemistry for oxidation of NO and analytical procedure

Oxidation of NO

![Chemical reaction diagram]

Analytical procedure

![Chemical reaction diagram]

540 nm
**Conversion equation:**

NO concentration (ppb) = \( \alpha_{NO} \times (W_{NOx} - W_{NO2}) / t \)

NO\(_2\) concentration (ppb) = \( \alpha_{NO2} \times W_{NO2} / t \)

SO\(_2\) concentration (ppb) = \( \alpha_{SO2} \times W_{SO2} / t \)

NH\(_3\) concentration (ppb) = \( \alpha_{NH3} \times W_{NH3} / t \)

O\(_3\) concentration (ppb) = \( \alpha_{O3} \times W_{O3} / t \)

Where:

- \( W_{NOx}, W_{NO2} \): NO\(_2\) quantity (ng) collected in NO\(_x\) and NO\(_2\) collection elements
- \( W_{SO2} \): SO\(_2\) quantity (ng) collected in SO\(_2\) collection element
- \( W_{NH3} \): NH\(_3\) quantity (ng) collected in NH\(_3\) collection element
- \( W_{O3} \): O\(_3\) quantity (ng) converted from NO\(_3\) quantity collected in O\(_3\) element
- \( \alpha_{NO}, \alpha_{NO2}, \alpha_{SO2}, \alpha_{NH3}, \alpha_{O3} \): ppb concentration conversion coefficient (ppb·min/ng)

Normally at 20°C, R.H. 70% to be based.

- \( \alpha_{NO} = 60 \), \( \alpha_{NO2} = 56 \), \( \alpha_{SO2} = 39.4 \), \( \alpha_{NH3} = 43.8 \), \( \alpha_{O3} = 46.2 \)

There values were obtained by a theoretical calculation and an experimental basis using a glass chamber. There are also changeable depending on temperature, humidity and exposure time.

t : exposure time (min)
Calculation of concentration conversion coefficients for NO and NO₂

In order to enhance the accuracy of Ogawa sampler measurement method

\( \alpha_{NO} \) and \( \alpha_{NO₂} \) can be calculated for a combination of temperature and relative humidity using the following formulas

\[
\alpha_{NO} = \frac{10000}{( -0.78 \times [P] \times [RH] ) + 220}
\]

\[
\alpha_{NO₂} = \frac{10000}{(0.677 \times [P] \times [RH]) + (2.009 \times [T]) + 89.8}
\]

[T] : Ambient temperature in degree Centigrade

[RH] : Relative humidity %

\[
[P] = \left( \frac{2P_N}{P_T + P_N} \right)^{2/3}
\]

\( P_N \) : 17.535 \( \) (water vapor pressure in mm Hg at 20 degC

\( P_T \) : Vapor pressure of water at the ambient temperature [T]
Calculation of concentration conversion coefficients for SO$_2$, NH$_3$ and O$_3$

\[ \alpha_{\text{SO}_2} = 39.4 \times \left( \frac{293}{273 + T} \right)^{1.83} \]

[T] : Ambient temperature in degree Centigrade

\[ \alpha_{\text{NH}_3} = 43.8 \times \left( \frac{293}{273 + T} \right)^{1.83} \]

[T] : Ambient temperature in degree Centigrade

\[ \alpha_{\text{O}_3} = 46.2 \times 10^2 \times \left( \frac{293}{273 + T} \right)^{1.83} / \left( 9.94 \times \ln(t) - 6.53 \right) \]

[T] : Ambient temperature in degree Centigrade

\[ t \] : Exposure time (min)
What is the lowest detectable range?

<table>
<thead>
<tr>
<th></th>
<th>NO₂</th>
<th>NOₓ</th>
<th>SO₂</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hrs exposure</td>
<td>2.3 ppb</td>
<td>2.3 ppb</td>
<td>3.8 ppb</td>
<td>2.7 ppb</td>
</tr>
<tr>
<td>168 hrs exposure</td>
<td>0.32 ppb</td>
<td>0.32 ppb</td>
<td>0.54 ppb</td>
<td>0.39 ppb</td>
</tr>
</tbody>
</table>

What is the upper detectable range?

<table>
<thead>
<tr>
<th></th>
<th>NO₂</th>
<th>NOₓ</th>
<th>SO₂</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hrs exposure</td>
<td>25 ppm</td>
<td>25 ppm</td>
<td>25 ppm</td>
<td>0.8 ppm</td>
</tr>
<tr>
<td>168 hrs exposure</td>
<td>3.6 ppm</td>
<td>3.6 ppm</td>
<td>3.6 ppm</td>
<td>0.11 ppm</td>
</tr>
</tbody>
</table>

Please note that all of the above ranges depend on the sensitivity of the analyzing instruments, quality of reagents and quality of environments.
Improvement to Advanced Monitoring System

An analytical procedure should be *simple* and *high through-put*, because the number of sampler used in a research program will be extremely large.

**Flow Injection Analysis (FIA)** has been proved to be useful and versatile in many practical analyses, moreover, FIA technique is easy to apply to an automatic procedure.

- **Automation**
- **Sensitivity**
- **Accuracy**
- **Selectivity**
- **Precision**
- **Simplicity**
- **Rapidity**
- **Zero Emission**
FIA diagram for nitrite ion equipped with copperized cadmium

CS : carrier solution (EDTA + NH₄Cl), RS : reagent solution (Sulfanilamide + N-1-Naphthylethylenediamine), P : micro pump (1.0ml/min), S : sample injector (100µl), SV : six-way rotary valve, Red.C : Cd/Cu reduction column (2mmi.d.×10cm), TC : temperature controlled air bath(40°C ), RC : reaction coil (0.5mm i.d.×2m), D : detector (540nm), R : recorder, W : waste

Flow signals for calibration graphs and the reproducibility test

(A) [NO₂⁻]:µg/ml A; 0, B; 0.4, C; 0.8, D; 1.2, E; 1.6, F; 2.0, G; 2.4

(B) NOx sampling element
[NO₂⁻]:1.2µg/ml RSD=0.35%
Effect of PTIO on the absorbance for NOx analysis after adding the color producing reagents

1 : \([\text{NO}_2^-] : 0.8\mu\text{g/ml}\); 2 : Reagent blank

Absorption spectra of PTIO solution

1: PTIO solution,
2: after reduction by Cd/Cu column
Flow diagram for the determination of SO$_2$

CS: carrier solution (H$_2$O)
RS: reagent solution (Dimethylsulfonazo III–Bacomplex)
P: double-plunger micro pump (1.0ml/min)
CEC: cation exchange resin column (2mmi.d. x 10cm)
RC: reactor column (BaSO$_4$-immobilized glass beads or crushed BaSO$_4$, 2mmi.d. x 10cm)
TC: temperature controlled air bath (35°C)
D: detector (LED: 660nm, interference filter: 660nm)
BPC: back pressure coil (0.25mmi.d. x 2m)
R: recorder
W: waste

Flow signals for calibration graphs of SO$_4^{2-}$

Sample volume 50µl
[SO$_4^{2-}$] (µg/ml)
  a:0, b:2, c:4, d:6, e:8, f:10
Sample volume 200µl
[SO$_4^{2-}$] (µg/ml)
  g:0, h:0.4, i:0.8, j:1.2, k:1.6, l:2.0
Chemistry for the detection of ammonium ion

\[ \text{NH}_3 + \text{ClO}^- \rightarrow \text{NH}_2\text{Cl} + \text{OH}^- \]

\[ \text{NH}_2\text{Cl} + 2 \text{C}_6\text{H}_5\text{OH} + 2\text{ClO}^- \rightarrow \text{O} - \text{N} - \text{C}_6\text{H}_5\text{OH} + 3\text{HCl} + 2\text{OH}^- \]

Flow diagram for ammonium ion

CS : Carrier solution (H₂O)
RSI : Reagent solution I
    (Sodium salicylate+nitrprusside)
RSII : Reagent solution II(NaClO)
P₁, P₂ : Double-plunger pump
S : Sample injector (100µl)
TC : Reactor (50°C)
RC : Reaction coil (0.5 mm i.d.×2 m)
CC : Cooling coil (0.5 mm i.d.×1 m)
D : Detector (660 nm)
R : Recorder
BPC : Back-pressure coil (0.25 mm i.d.×2 m)
W : Waste
Flow signals for calibration curve and repeatability test

Calibration curve (a~f) \([N-NH_4^+]\) / ppm a, 0; b, 0.2; c, 0.4; d, 0.6; e, 0.8; f, 1.0

Repeatability test (g) \([N-NH_4^+]\) : 0.4ppm RSD=0.26% (n=10)
Correlation between the results obtained by Ogawa Sampler and automatic monitoring station

\[ y = 0.9398x + 0.6233 \]
\[ R^2 = 0.9991 \]

\[ y = 0.909x + 1.5029 \]
\[ R^2 = 0.9936 \]

\[ y = 0.9816x + 0.5116 \]
\[ R^2 = 0.9782 \]
Distribution Map of Nitric Oxides in the air
Correlation of Ozone between the results obtained by Ogawa Sampler and automatic monitoring station