Advanced Monitoring Method for Air Environment by Ogawa Passive Sampler

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Abstract 1st

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 triethenolamine 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.

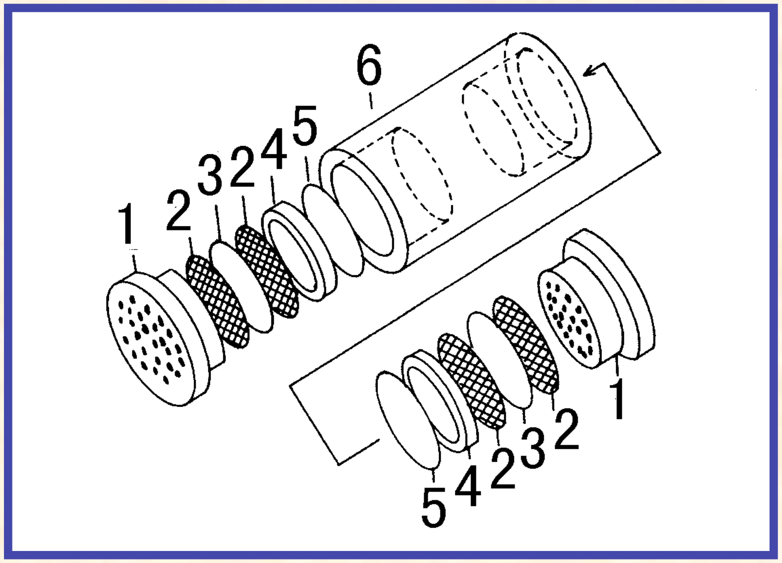
The second advantage of Ogawa Sampler is to be reusable countless times, only the pre-coated collection filter pad is expendable. The same sampler can be used for all above shown gasses. Consequently, Ogawa Sampler can be represented as one of the lowest cost effective device for accurate measurements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

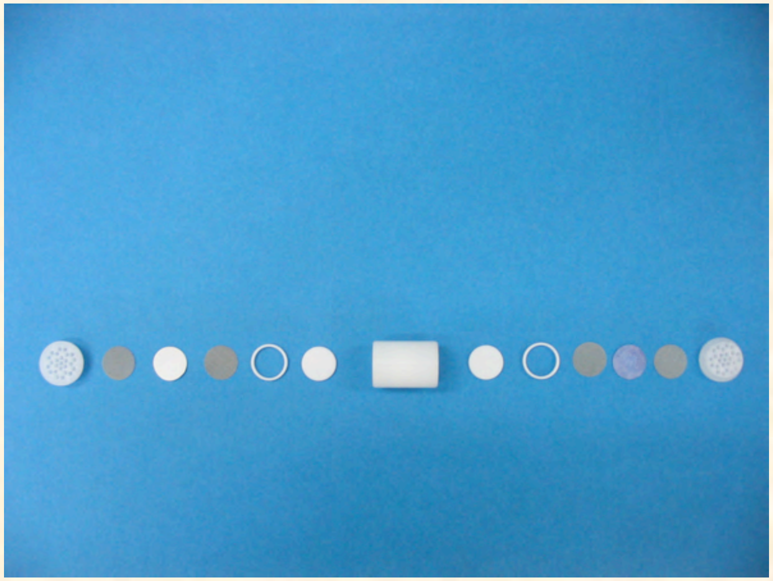
Abstract 2nd

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, NO_2, NOx, SO_2, NH_3 and O_3 . 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(15mmi.d.,19mmo.d.,6mm length)

Set up of Ogawa Sampler

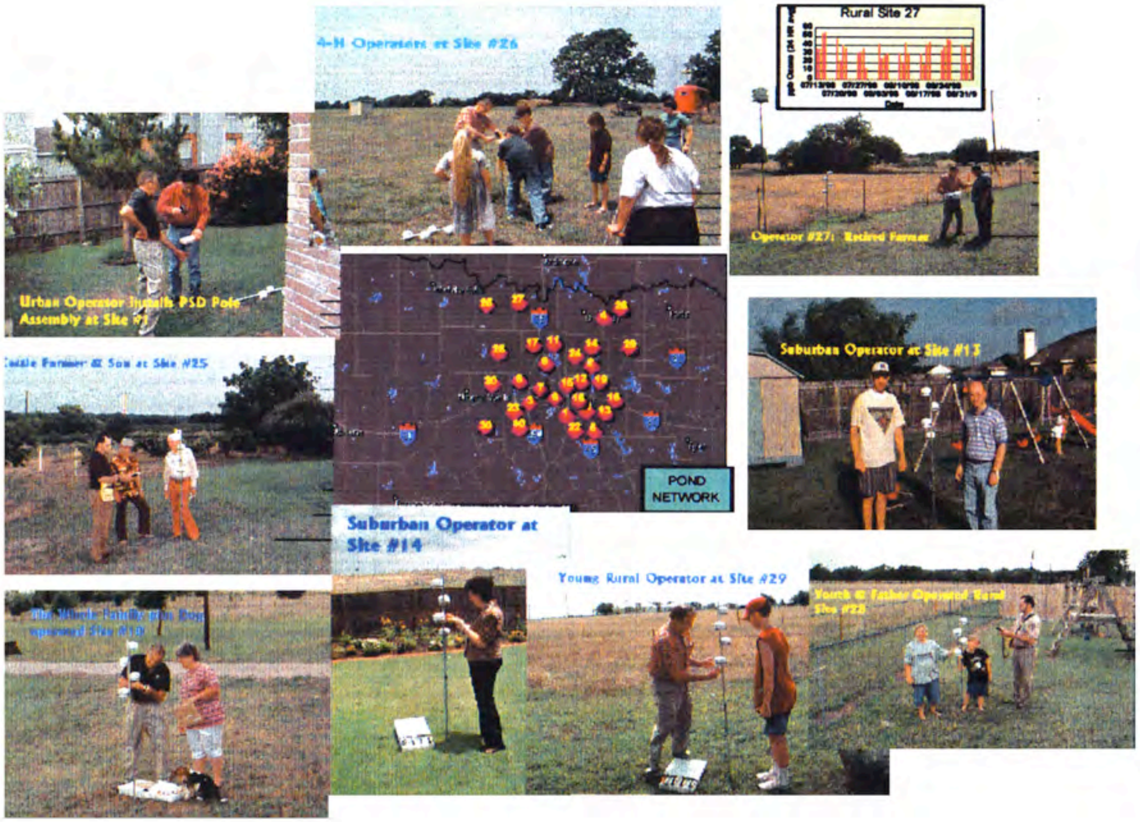
The shelter is used for protecting rain, sun shine and strong wind.

Beside the observation van

Personal exposure

View of general setting up

Beside automated monitoring site


4-H Operators at Site #26
Rural Site 27
0
10
20
30
40
50
60
07/13/98
07/20/98
07/27/98
08/03/98
08/10/98
08/17/98
08/24/98
08/31/9
Date
Operator #27: Retired Farmer
Urban Operator Installs PSD Pole Assembly at Site #1
attle Farmer & Son at Site #25
POND NETWORK
Suburban Operator at Site #13
Suburban Operator at Site #14
Young Rural Operator at Site #29
Youth & Father Operated Rural Site #28
The Whole Family plus Dog operated Site #19

Over all measurement procedure

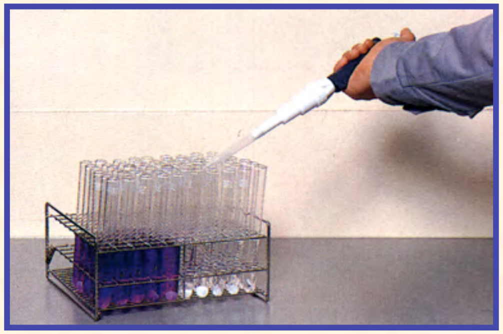
Collection

Set Ogawa Sampler up the measuring site

Exposure and collection for 1〜7 days

Extraction

Extraction into pure water



Analysis

Analysis by FIA, IC and colorimetry

Calculation

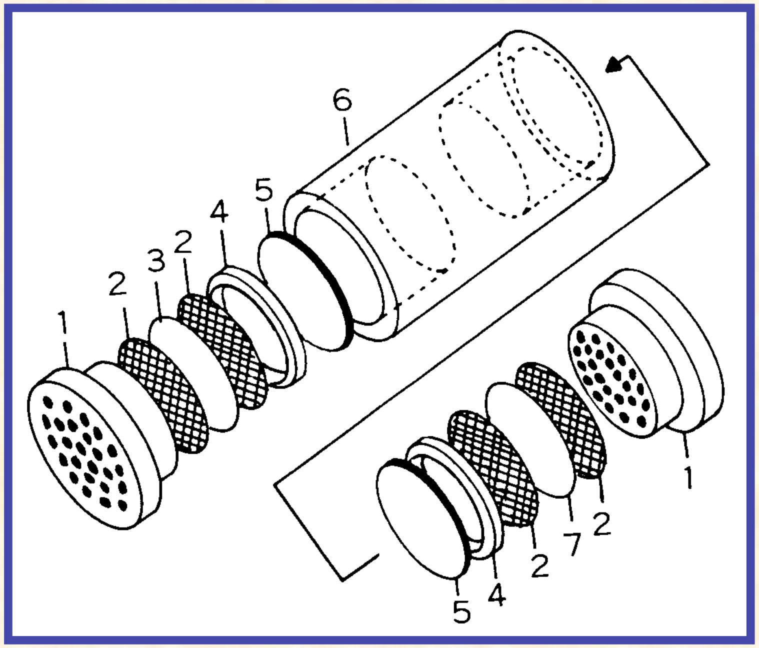
Calculation by conversion equations

Absorption reagent, Analytical method and Analyte

NO_2	Triethanolamine, Colorimetry, Diazo-coupling reaction, NO_2^-	
NO_x	Triethanolamine +PTIO, Colorimetry, Diazo-coupling reaction, NO_2^-	
SO_2	Triethanolamine,	Ion chromatography, SO_4^{2-}
NH_3	Citric Acid,	Ion chromatography, NH_4^+
O_3	Nitrite ion,	Ion chromatography, NO_3^-

Simultaneous measurement of NO and NO_2

Preparation of Sampler

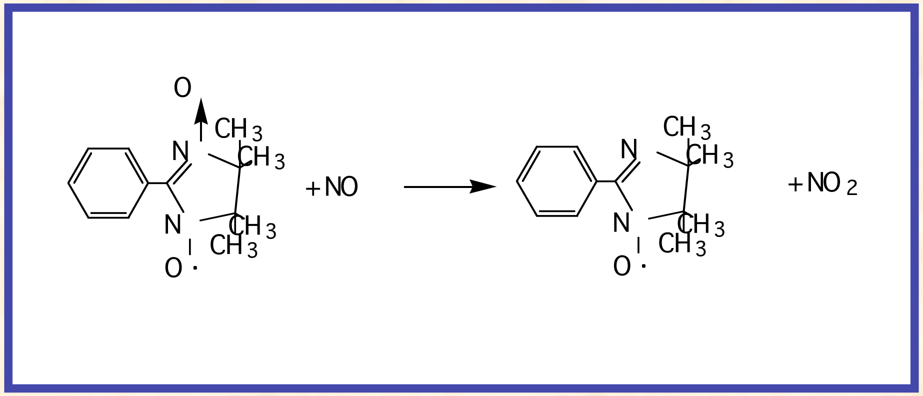


1.Diffuser end cap
2.Stainless screen
3.NO_2 collection filter (14.5mmφ)
4.Teflon ring
5.Teflon disk
6.Body
7.NOx collection filter (14.5mmφ)

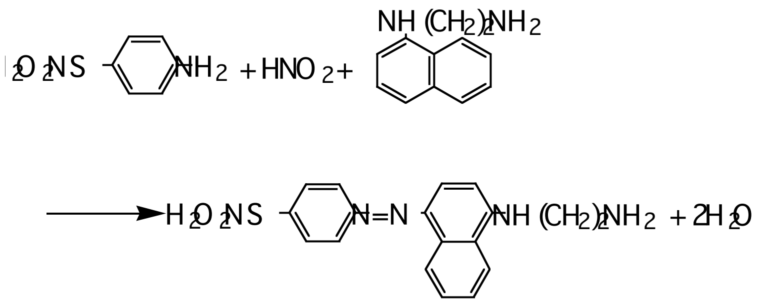
NO_2 collection filter and NOx collection filter were placed in each of the two chambers of the samplers respectively.

Chemistry for oxidation of NO and analytical procedure

Oxidation of NO



Analytical procedure



540 nm

Calculation for the concentration in ambient air

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 NOx 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

α_{NO}, α_{NO2}, α_{SO2}, α_{NH3}, α_{O3}: ppb concentration conversion coefficient (ppb·min / ng)

normally at 20℃, 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 NO_2

In order to enhance the accuracy of Ogawa sampler measurement method

α_{NO} and α_{NO2} can be calculated for a combination f 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

$\alpha_{SO2} = 39.4 \text{ X } (293 / (273 + T))^{1.83}$

[T] : Ambient temperature in degree Centigrade

$\alpha_{NH3} = 43.8 \text{ X } (293 / (273 + T))^{1.83}$

[T] : Ambient temperature in degree Centigrade

$\alpha_{O3} = 46.2 \text{ X } 10^2 \text{ X } (293 / (273 + T))^{1.83} / (9.94 \text{ X } \ln (t) – 6.53)$

[T] : Ambient temperature in degree Centigrade

t : Exposure time (min)

What is the lowest detectable range?

	NO_2	NOx	SO_2	O_3
24 hrs exposure	2.3 ppb	2.3 ppb	3.8 ppb	2.7 ppb
168 hrs exposure	0.32 ppb	0.32 ppb	0.54 ppb	0.39 ppb

What is the upper detectable range?

	NO_2	NOx	SO_2	O_3
24 hrs exposure	25 ppm	25 ppm	25 ppm	0.8 ppm
168 hrs exposure	3.6 ppm	3.6 ppm	3.6 ppm	0.11 ppm

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.

Selectivity

Precision

Automation

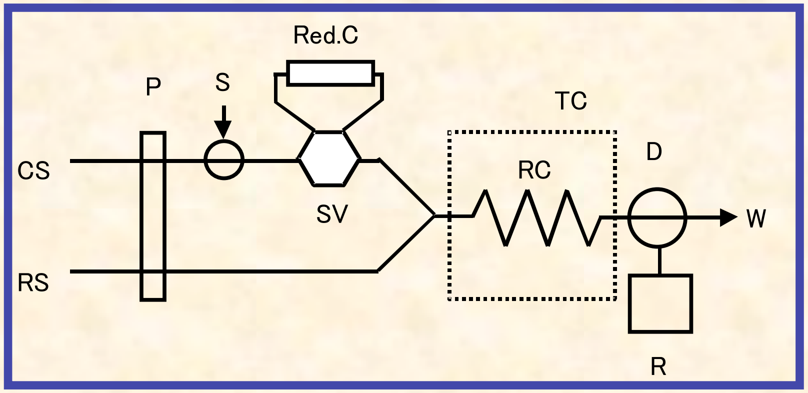
Simplicity

Sensitivity

Zero Emission

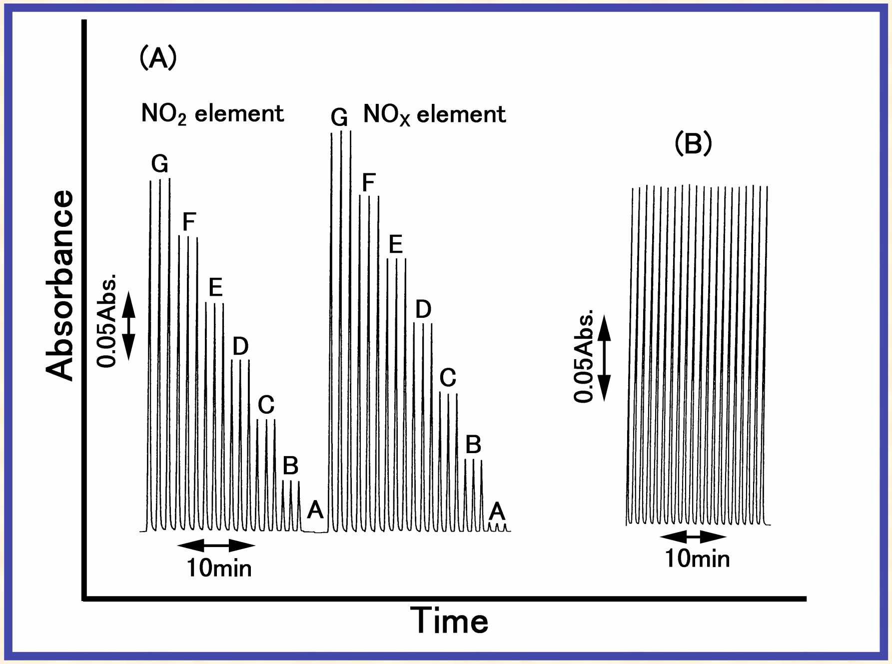
Accuracy

Rapidity



FIA diagram for nitrite ion equipped with copperized cadmium

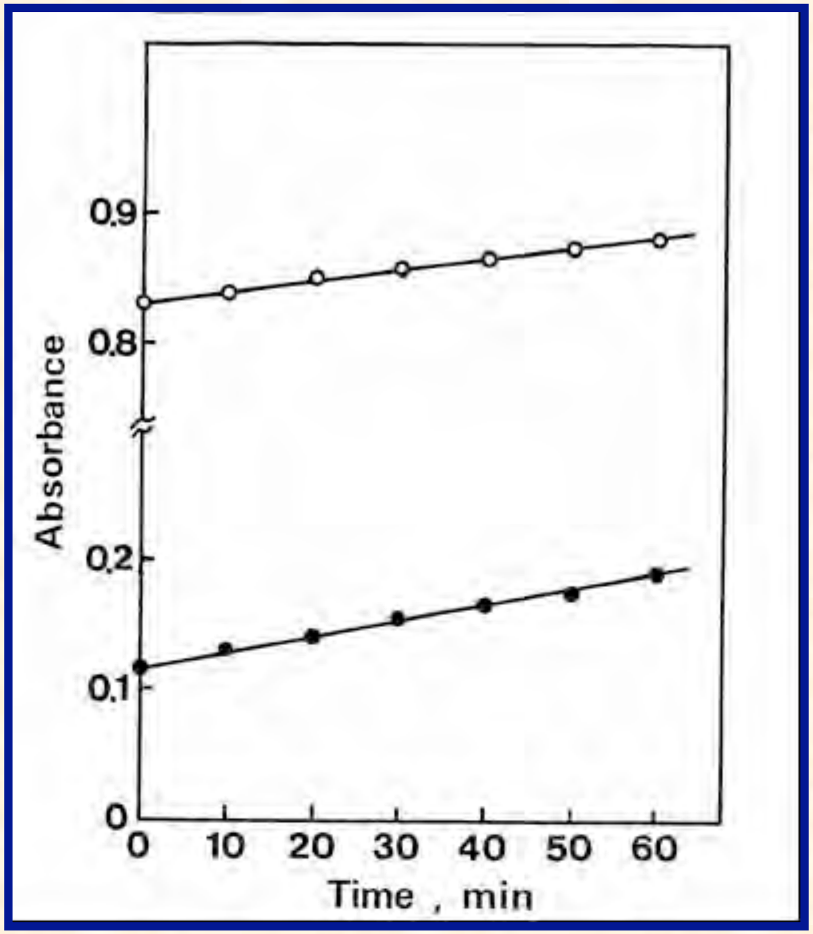
CS : carrier solution (EDTA + NH_4Cl), RS : reagent solution (Sulfanilamide + N-1-Naphthylethylenediamine), P : micro pump (1.0ml/min), S : sample injector (100µl), SV : six-way rotary valve, Red.C : Cd/Cu reduction column (2mmi.d.×10cm), TC : temperature controlled air bath(40℃), RC : reaction coil (0.5mm i.d.×2m), D : detector (540nm), R : recorder, W : waste



Flow signals for calibration graphs and the reproducibility test

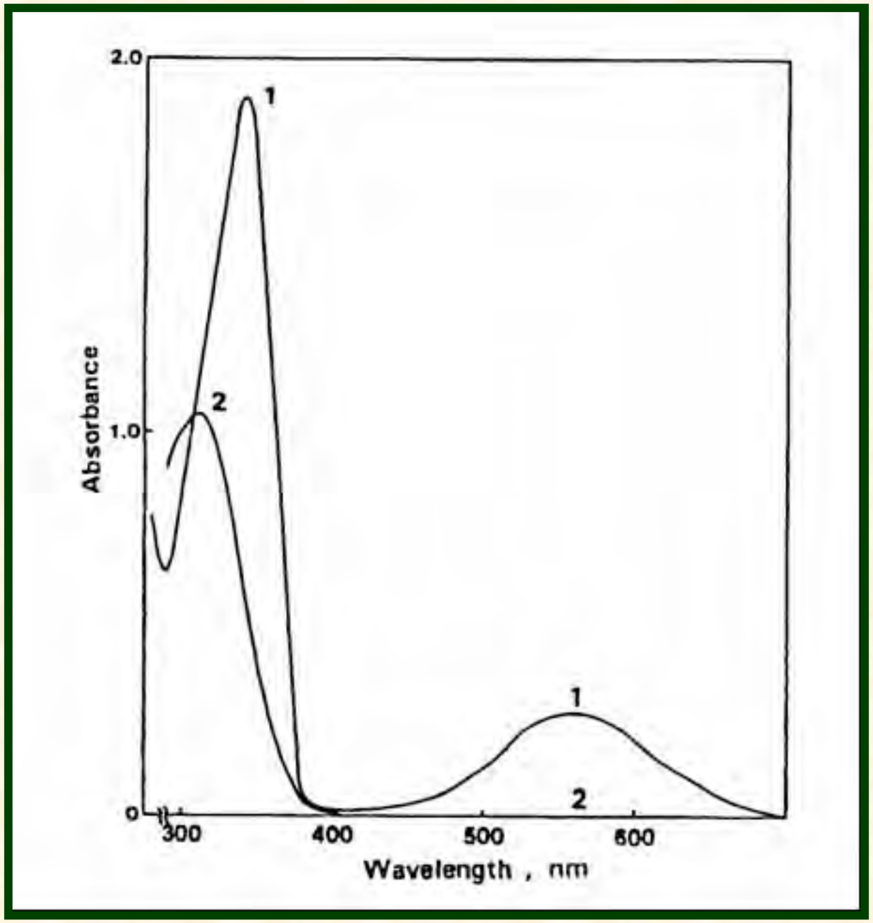
**(A) [NO_2^-]:µg/ml A; 0, B; 0.4, C; 0.8, D; 1.2,
E; 1.6, F; 2.0, G; 2.4**

**(B) NOx sampling element
[NO_2^-]:1.2µg/ml RSD=0.35%**



Effect of PTIO on the absorbance for NOx analysis after adding the color producing reagents

1 : [NO_2^-] : 0.8μg/ml; 2 : Reagent blank

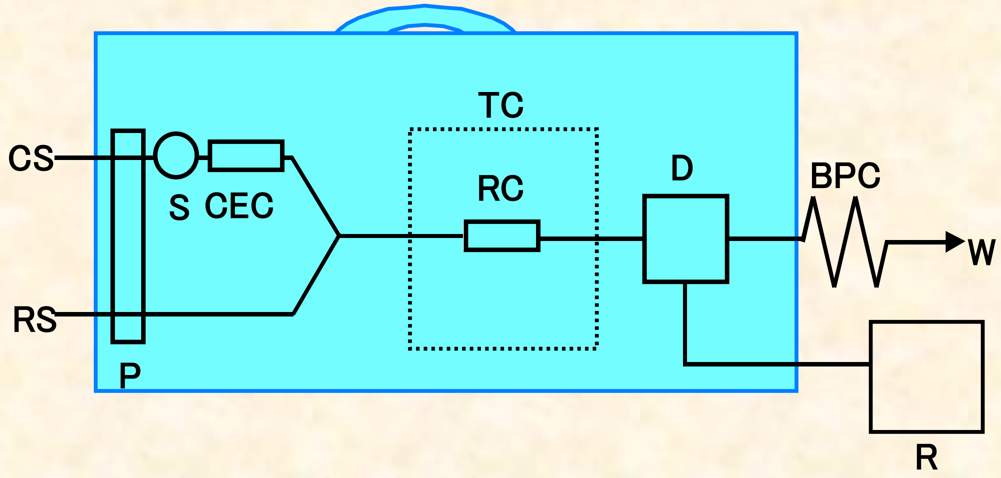


Absorption spectra of PTIO solution

1: PTIO solution,

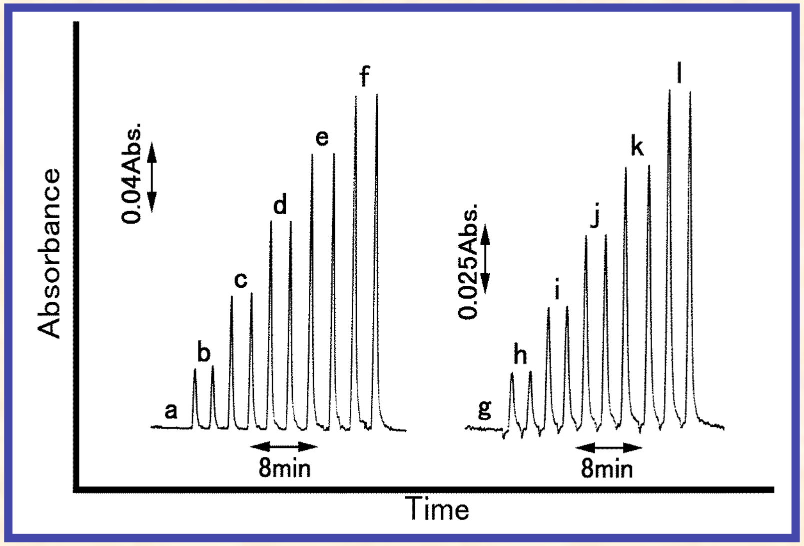
2: after reduction by Cd/Cu column

Flow diagram for the determination of SO_2

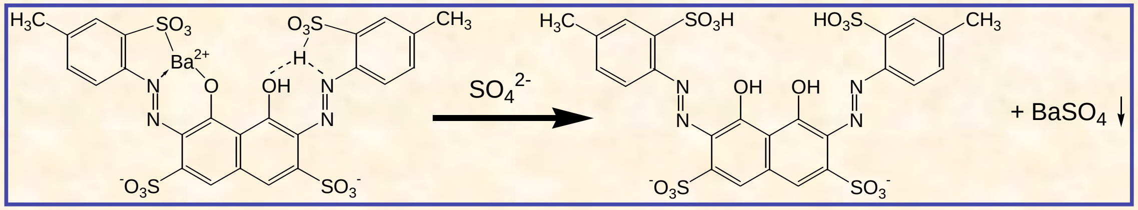


CS:carrier solution (H_2O)
RS:reagent solution(DimethylsulfonazoⅢ-Bacomplex)
P:double-plunger micro pump (1.0ml/min)
CEC:cation exchange resin column (2mmi.d.×10cm)
RC:reactor column ($BaSO_4$-immobilized glass beads or crushed $BaSO_4$, 2mmi.d.×10cm)
TC:temperature controlled air bath(35℃)
D:detector(LED:660nm,interferencefilter:660nm)
BPC:back pressure coil (0.25mmi.d.×2m)
R:recorder W:waste

Flow signals for calibration graphs of SO_4^{2-}

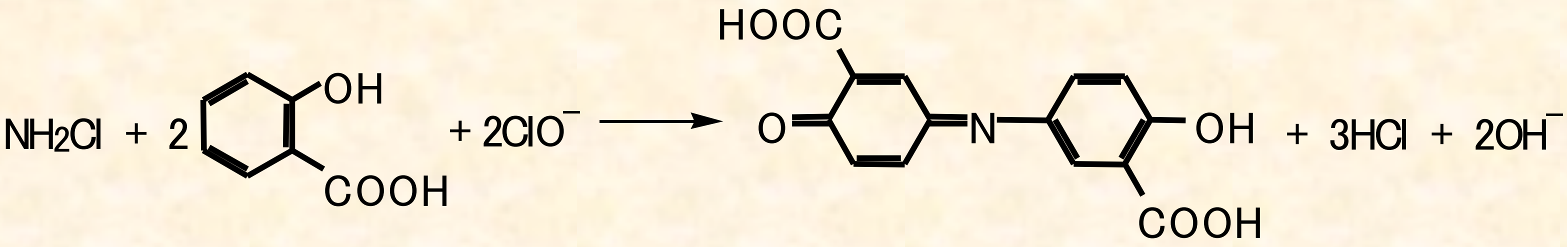


Sample volume 50μl
$[SO_4^{2-}]$ (μg/ml)
a:0, b:2, c:4, d:6, e:8, f:10
Sample volume 200μl
$[SO_4^{2-}]$ (μg/ml)
g:0, h:0.4, i:0.8, j:1.2, k:1.6, l:2.0

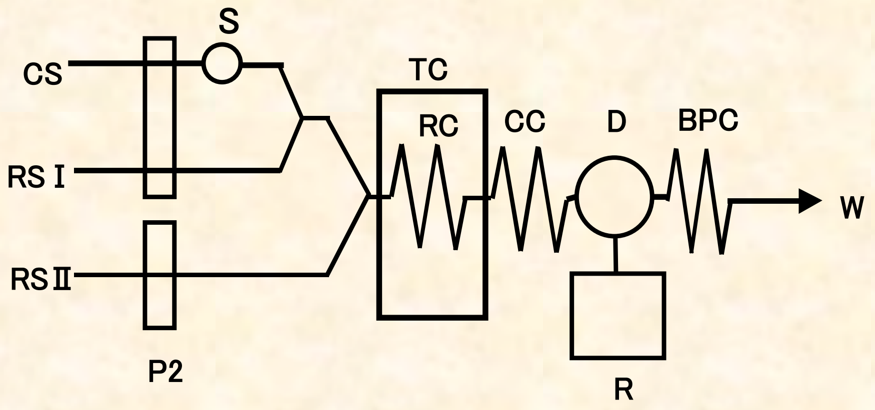


Chemistry for the detection of ammonium ion

$$NH_3 + ClO^- \longrightarrow NH_2Cl + OH^-$$

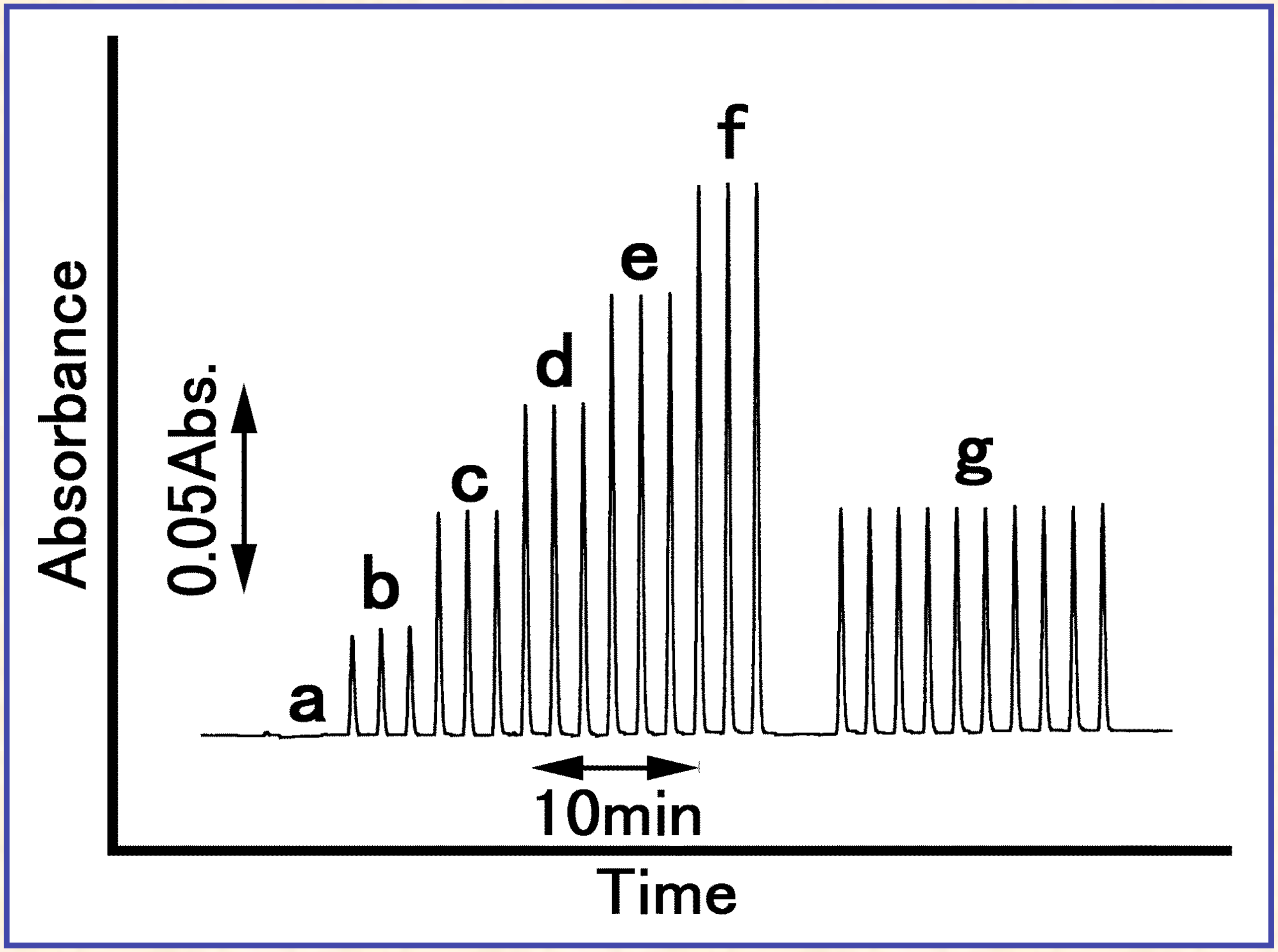


Flow diagram for ammonium ion



CS	: Carrier solution （H_2O）
RSI	: Reagent solutionI (Sodium salycilate+nitrprusside)
RSII	: Reagent solution Ⅱ(NaClO)
P_1, P_2	: Double-plunger pump
S	: Sample injector (100µl)
TC	: Reactor (50℃)
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

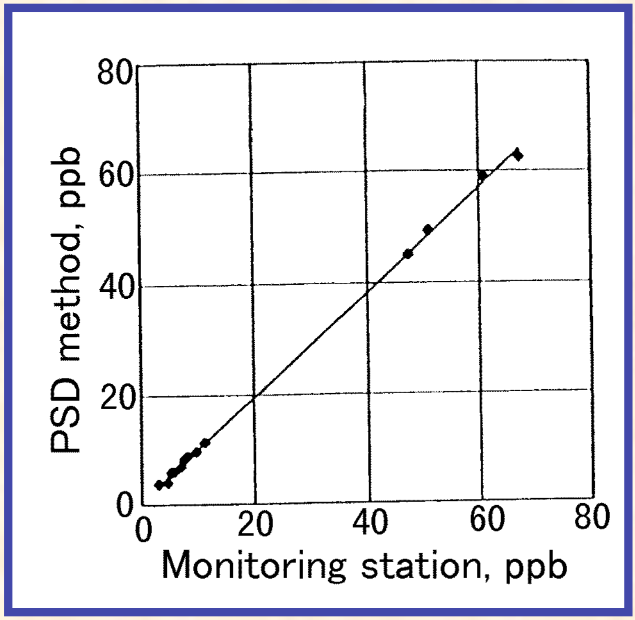
Flow signals for calibration curve and repeatability test



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)

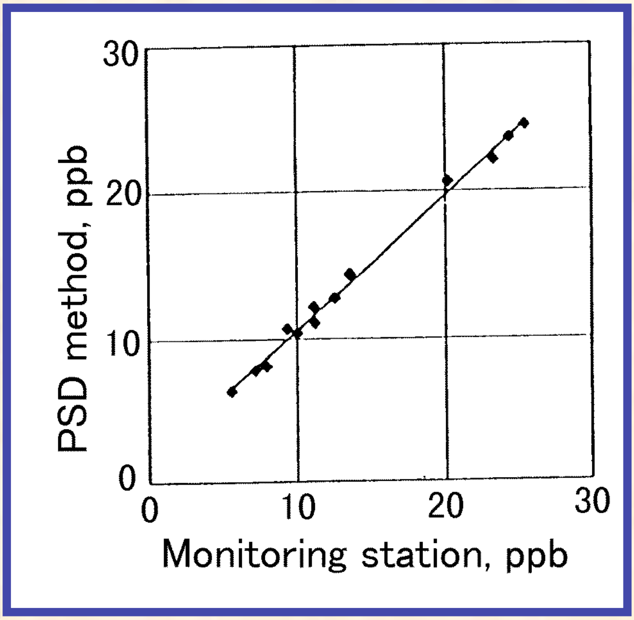
Correlation between the results obtained by Ogawa Sampler and automatic monitoring station

NO



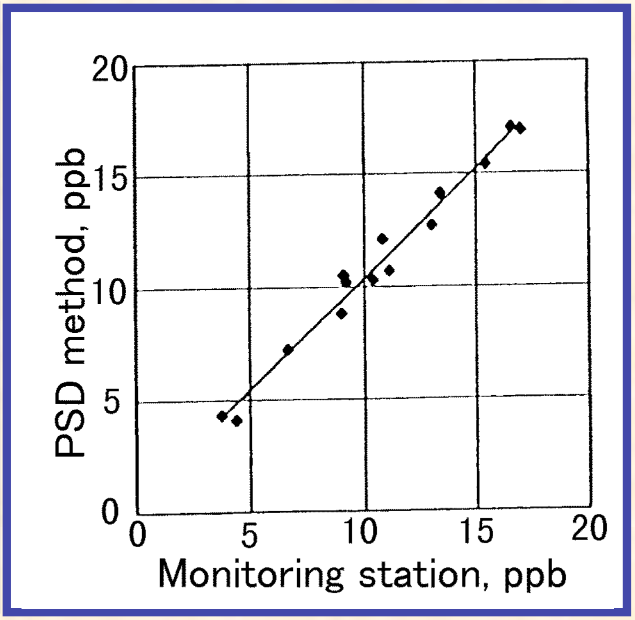
y = 0.9398x + 0.6233
R2 = 0.9991

NO_2



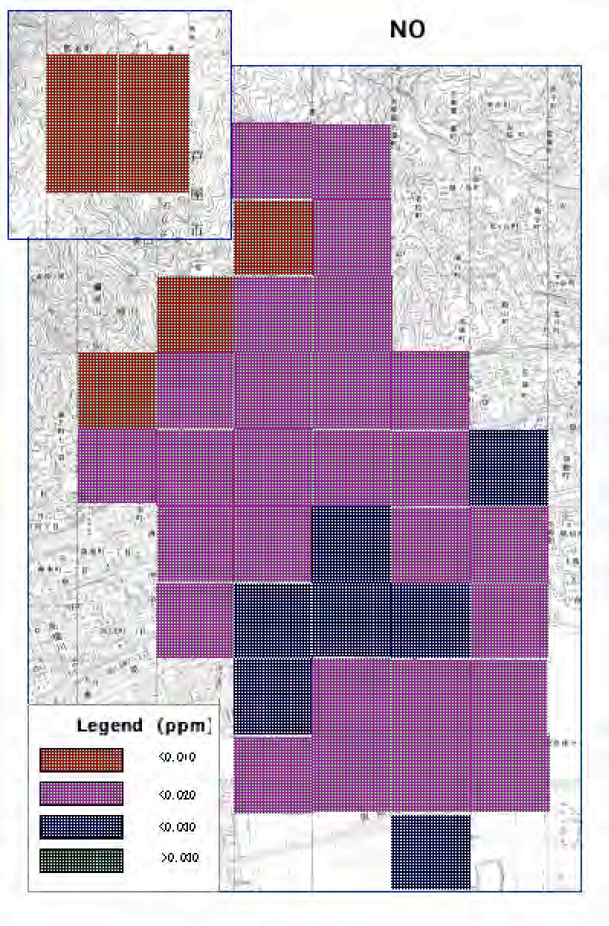
y = 0.909x + 1.5029
R2 = 0.9936

SO_2

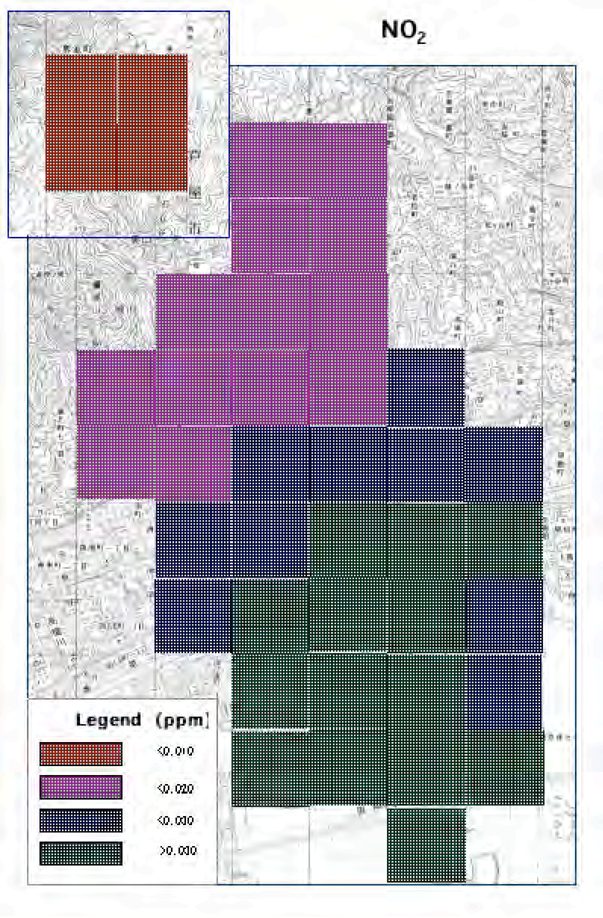


y = 0.9816x + 0.5116
R2 = 0.9782

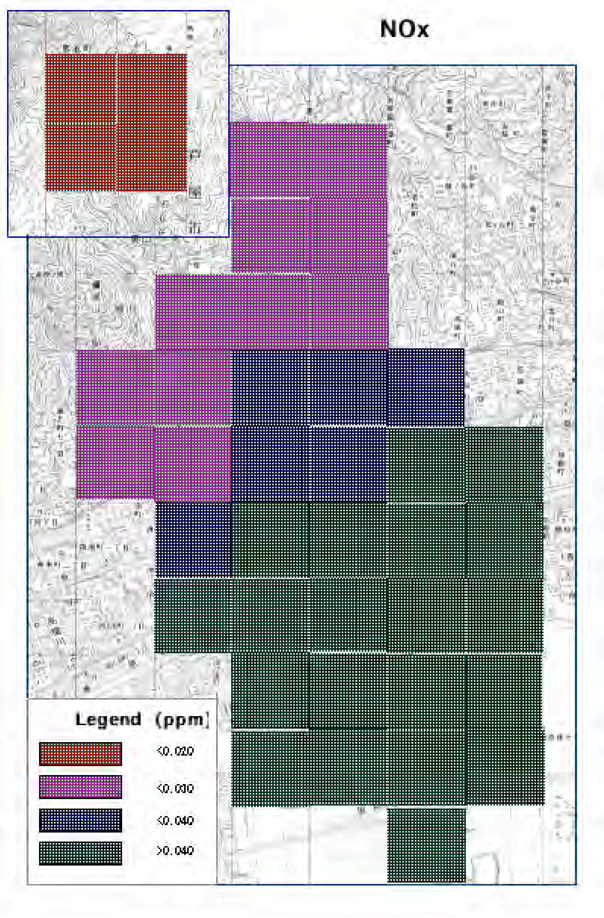
Distribution Map of Nitric Oxides in the air



NO

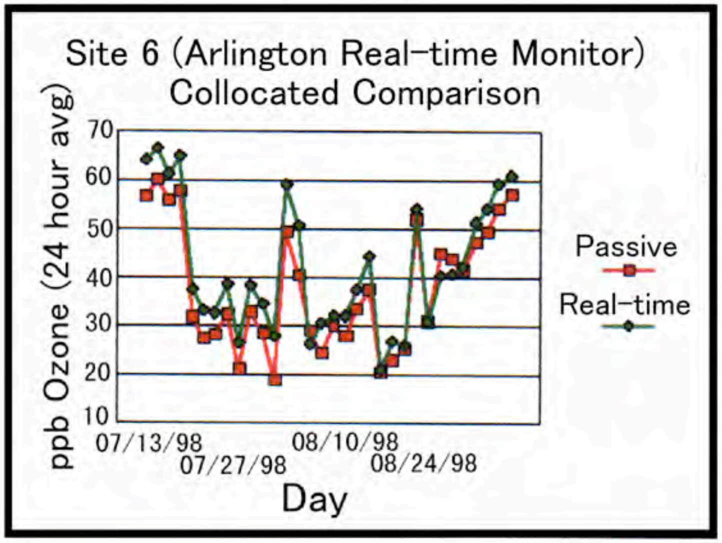


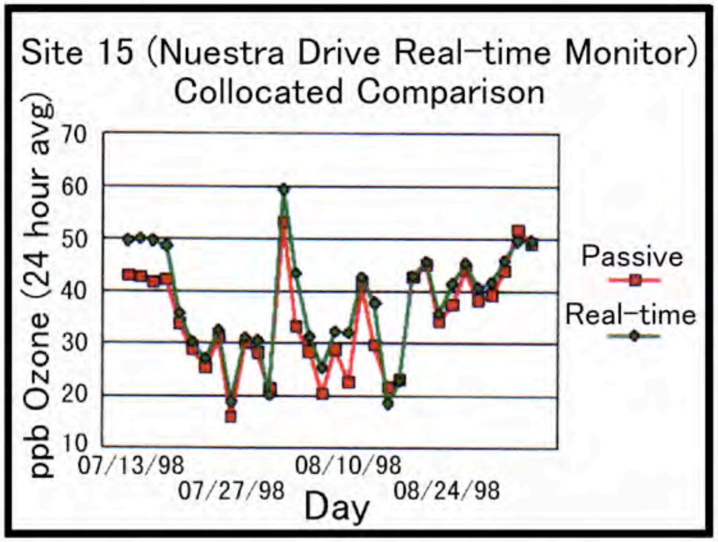
NO_2

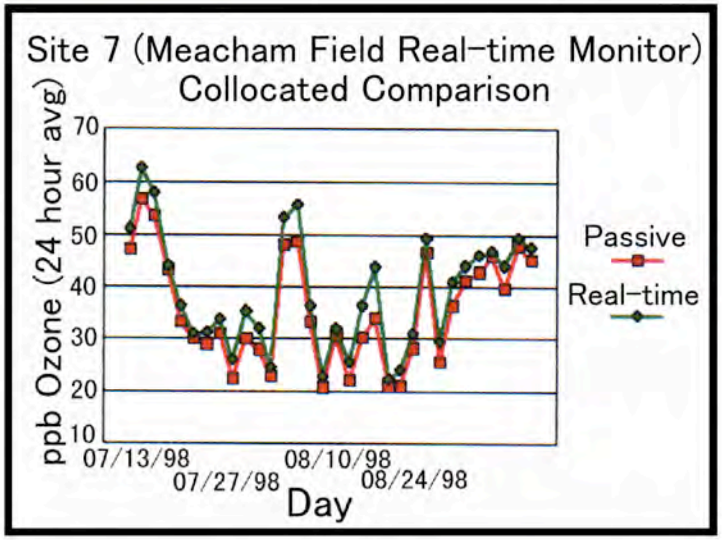


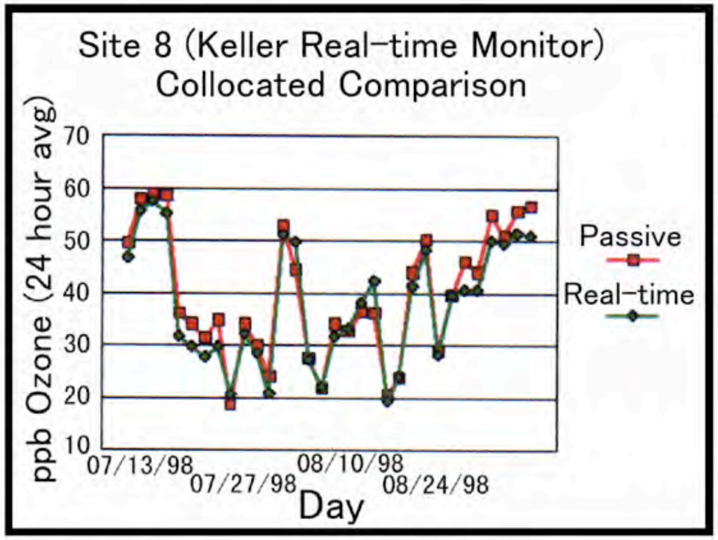
NOx

Correlation of Ozone between the results obtained by Ogawa Sampler and automatic monitoring station


Site 6 (Arlington Real-time Monitor)
Collocated Comparison


Site 15 (Nuestra Drive Real-time Monitor)
Collocated Comparison


Site 7 (Meacham Field Real-time Monitor)
Collocated Comparison


Site 8 (Keller Real-time Monitor)
Collocated Comparison