8<sup>th</sup> Regional Refresher Training Programme

18-20 November, 2010

Delhi, India

## Ogawa Passive Sampler Device (OPSD) for gas monitoring

<sup>by</sup> Do Thanh Canh

Asian Institute of Technology Thailand

### OPSD



### Contents

- 1. Advantage of OPSD
- 2. Collectable gases
- 3. Components of OPSD
- 4. Air monitoring using OPSD
- 5. Chemical analysis
- 6. Calculation for ambient air concentration
- 7. Important hints
- 8. Photos

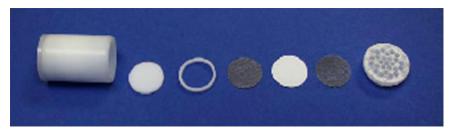
## Advantage of OPSD

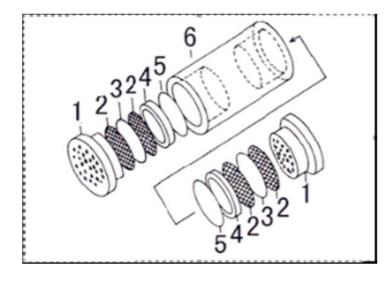
- Low cost
- Reusable
- Easy to install
- Possible for air monitoring personal, outdoors and indoors
- Simultaneous monitoring of NO and NO<sub>2</sub>

### What gases can OPSD collect?

- Ozone
- **SO**<sub>2</sub>
- NO<sub>x</sub> (NO<sub>2</sub>, NO) and
- NH<sub>3</sub>

### How is OPSD assembled? 1. Sampler body





Sampler components:

- 1 Diffusive cap
- 2 Stainless Steel Screens
- 3 Collection Filter Pad
- 4 Filter Ring
- 5 Backing Tab
- 6 Body

#### 2. OPSD: assessories



1 - Sampler with weather shelter for ozone sampling



2 - Sampler with weather shelter for  $SO_2$ ,  $NO_x$  and  $NH_3$ sampling



3– Brown container for Sampler shipment

#### 3. Coated Filter pad

#### Reagents: Coated chemicals

	Absortion Reagent	Analytical Method	Analyte
NO <sub>2</sub>	Triethanolamine	Colorimetry, Diazo-coupling reaction	NO <sub>2</sub> -
NOx	Triethanolamine + PTIO	Colorimetry, Diazo-coupling reaction	NO <sub>2</sub> -
SO <sub>2</sub>	Triethanolamine	Ion chromatography	SO42+
NH <sub>3</sub>	Citric Acid	Ion chromatography	NH4 <sup>+</sup>
<b>O</b> <sub>3</sub>	Nitrite Ion	Ion chromatography	NO <sub>3</sub> -

#### 3. Coated Filter pad (cont'd)

#### Lifetime of coated filter pad

- Original pack frozen (not open): 1 year
- Refrigerated storage:
  - Original pack: 90 days
  - After opening but resealed in vial: 90 days

- Exposed filter in airtight bag: 2-3 weeks (analysis should be done asap after exposure)

Site selection

#### 1. Ozone

- The site should be located away from local source of NO<sub>x</sub> such as trucks, buses, automobiles, internal combustion engines which will decrease the ozone concentration below the ambient concentration
- A distance of 30 cm or more from vertical surface and about 1.5 - 2 m about the ground area
- Sampler must be located inside a protective cover which prevents contact with rain and also acts as a wind barrier to stabilize the sampler collection rate

NO<sub>x</sub>, NO<sub>2</sub> and NO
 SO<sub>2</sub>
 NH<sub>3</sub>

#### Pre- sampling preparation

- Keep all components of the sampler dry during the assembly
- Place appropriate filter(s) and assemble other components
- Label on the OPSD body
- Also prepare for blank samples: lab blank, shipment blank and field blank
- Place assembled sampler into separated ziplock (resealable) bags then brown storage container

#### **Configuration Of Sampler For Various Gases**

Gas	Number Of Pads	Side A	Side B
NO	2	NO <sub>x</sub> Collection Pad	NO <sub>2</sub> Collection Pad
NO <sub>2</sub>	I	NO <sub>2</sub> Collection Pad	-
NO <sub>x</sub>	2	NO <sub>x</sub> Collection Pad	NO <sub>2</sub> Collection Pad
SO <sub>2</sub>	I	SO <sub>2</sub> Collection Pad	-
NH <sub>3</sub>	2*	NH <sub>3</sub> Collection Pad	NH <sub>3</sub> Collection Pad
<b>O</b> <sub>3</sub>	2*	O <sub>3</sub> Collection Pad	O <sub>3</sub> Collection Pad

\* Pads must be extracted as one.

- SO<sub>2</sub>, NO<sub>2</sub>: Place only one filter into one end of the sampler
- Ozone, NH<sub>3</sub>: Place one filter into each end of a sampler
- NO<sub>x</sub>, NO: Place one filter for NO<sub>x</sub> and one filter for NO<sub>2</sub>. To avoid confusing between NO<sub>x</sub> and NO<sub>2</sub> filter, labels must be properly attached at each end of the sampler body

#### Sampling ....

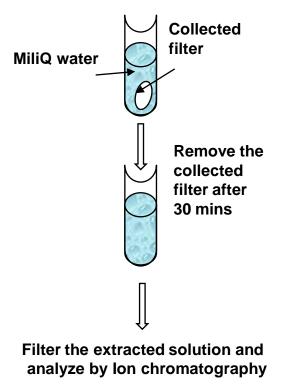
- Set up the sampler together with the shelter
- Record the sampling start/stop date, time
- Record weather condition
- After sampling, inspect appearance of the sampler (spider web, wet)

#### **Special considerations:**

- Nitrite on coated filter is slowly converted to nitrate even without exposure to ozone, and this conversion is more rapid at warmer temperature. Therefore, blank sample must be kept as long as the exposed sample at the same temperature
- Maximum exposed time should not exceed 4 weeks
- During shipping samples from the field to a lab in a distant location, use an insulated shipping box (ice box) to reduce exposure to high temperature but do not refrigerate it to avoid condensation of humidity that makes filter be wet
- Number of QC samples (field blank) at least should be 10% of total number samples

## Chemical analysis: ozone and NH<sub>3</sub>

Since filters are more stable when stored dry so filters should be extracted just before they are analyzed by IC



Analysis procedure for Ozone and NH<sub>3</sub>

## Chemical analysis : ozone and NH<sub>3</sub>

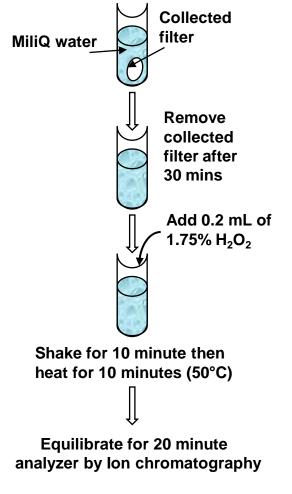
#### Analysis procedure for Ozone (NH<sub>3</sub>)

- Pipet 5-10 ml of MQ water into bottle containing filters for extraction
- Cap carefully the bottle
- Check that the filter is immersed completely in the MQ (if not shake it softly or use a forceps to depress it. Be sure to wipe the forceps clean between samples)
- Shake occasionally the extract bottle for 30 minutes at each direction vertical and horizontal
- Take out the filter
- Filter the extracted solution
- IC analysis

## Chemical analysis: SO<sub>2</sub>

- Pipet 5-10 ml of MQ water into extract containing filters for extraction
- Cap carefully the bottle
- Check that the filter is immersed completely in the MQ (if not shake it softly or use a forceps to depress it. Be sure to wipe the forceps clean between samples)
- Shake occasionally the extract bottle for 30 minutes
- Take out the filter
- Filter the extracted solution
- Add 0.2 ml of Hydrogen peroxide solution (1.75%) and shake slowly for 10 minutes
- Heat at 50°C for 10 minutes using a water bath
- Allow to equilibrate at room temperature for 20 minutes
- IC analysis

## Chemical analysis for SO<sub>2</sub>



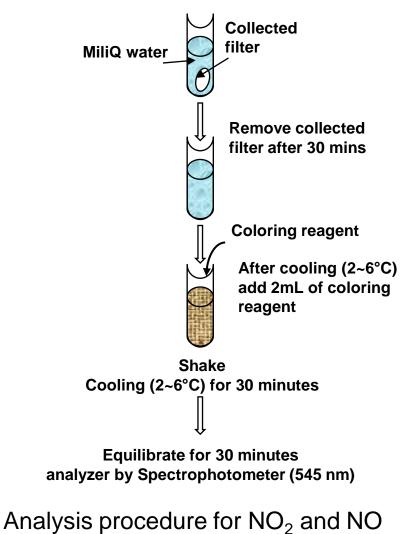
Analysis procedure for SO<sub>2</sub>

## Chemical analysis: NO<sub>2</sub> and NO

#### Reagent preparation:

- Sulfanilamide solution: 80g sulfanilamide + 200 ml concentrated phosphoric acid then dilute to 1000 ml with MQ water
- NEDA solution: dissolve 0.56 g N-(1-Naphthyl)ethylenediamine dihydrochloride into 100 ml MQ water. Store in a refrigerator (~4°C)
- Color producing reagent: prepare color-producing reagent just before use by mixing the sulfanilamide solution with the NEDA solution in a 10:1 ratio
- Nitrite standard stock solution: 1,000 ug/L
- 1,000 ug/L → 10 ug/L → standard working solutions:
  0; 0.2; 0.4; 0.6; 0.8 and 1 ug/ml (6 points)





## Chemical analysis: NO<sub>2</sub> and NO

- 1. Take out the filters (for NO<sub>2</sub> and NO: separate extraction for 2 filters)
- 2. Pipet 8 mL of MQ water into bottle containing filters for extraction
- 3. Cap carefully the bottle
- 4. Check that the filter is immersed completely in the MQ (if not shake softly or use a forceps to depress it).
- 5. Shake occasionally the extract bottle for 30 minutes
- 6. Take out the filter
- 7. Refrigerate the extract to 2-6°C (about 30 minutes)
- 8. Add 2 ml of color-producing reagent (pre-prepared), shake quickly
- 9. Continue cooling for an additional 30 minutes
- 10. Take out the bottle and equilibrate at room temperature for ~ 30 minutes

Note: Be sure to wipe the forceps clean between samples

Chemical analysis: standard curve and absorbance measurement

Prepare standard calibration curve: Preparation for working Nitrite standard series

 Take 8 ml of each prepared nitrite working standard solutions and add the reagent to develop the color (following the same steps 8-10 for sample above)

Measurement absorbance for the standard series

→ develop standard curve

Measurement absorbance for samples

(Spectrophotometer at wavelength of 545 nm)

#### Calculation for Ambient air concentration

#### **Conversion Equation:**

NO concentration (ppb) =  $\alpha_{NO} \times (W_{NOx} - W_{NO2}) / t$ NO<sub>2</sub> concentration (ppb) =  $\alpha_{NO2} \times W_{NO2} / t$ SO<sub>2</sub> concentration (ppb) =  $\alpha_{SO2} \times W_{SO2} / t$ NH<sub>3</sub> concentration (ppb) =  $\alpha_{NH3} \times W_{NH3} / t$ O<sub>3</sub> concentration (ppb) =  $\alpha_{O3} \times W_{O3} / t$ 

#### Where:

W <sub>Nox</sub>,W <sub>NO2</sub>: NO<sub>2</sub> quantity (ng) collected in NOx and NO<sub>2</sub> collection elements W <sub>SO2</sub>: SO<sub>2</sub> quantity (ng) collected in SO<sub>2</sub> collection element W <sub>NH3</sub>: NH<sub>3</sub> quantity (ng) collected in NH<sub>3</sub> collection element W<sub>O3</sub>:O<sub>3</sub> quantity (ng) converted from NO<sub>3</sub> quantity collected in O<sub>3</sub> 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.

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

t: exposure time (min)

These values are changeable depending on temperature and humidity

Calculation for Ambient air concentration for NO and NO<sub>2</sub> at actual temperature and relative humidity

 $\alpha$   $_{NO}$  and  $\alpha$   $_{NO2}$  can be calculated for a combination f temperature and relative humidity using the following formulas:

α <sub>NO</sub>= \_\_\_\_\_\_ ( - 0.78 X [P] X [RH] ) + 220

α<sub>NO2</sub>=

( 0.677 X [P] X [RH] ) + ( 2.009 X [T] ) + 89.8

10000

[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 X ( 293 / ( 273 + T ) ) <sup>1.83</sup>

[T] : Ambient temperature in degree Centigrade

 $\alpha_{NH3}$  = 43.8 X (293 / (273 + T))<sup>1.83</sup>

[T] : Ambient temperature in degree Centigrade

 $\alpha_{03} = 46.2 \times 10^2 \times (293 / (273 + T))^{1.83} (9.94 \times \ln (t) - 6.53)$ 

[T] : Ambient temperature in degree Centigrade

t : Exposure time (min)

#### Simple but important hints

- Pre-prepartion the OPSD: label for ziplock and OPSD body, then put each OPSD separately into containers
- After sample is collected, each OPSD body must be put back into the same labeled ziplock
- To prevent mislabeling of the extract bottle, at the beginning of sample extraction, extract bottle must be labeled corresponding to each sample
- The working standards (the concentration range of the standard curve) should be prepared depending on the anticipated concentration of samples
- Units used for calculation

#### Detectable concentration range 24h – sampling period

ppm	Lowest	Normal	Upper
NO2	2.3	in between	25
NOx	2.3		25
SO2	3.8		25
O3	2.7		0.8
NH3	2.3		25

Note: the ranges depend on the sensitivity of the analyzing instruments

#### Detectable concentration range 168h – sampling period

ppm	Lowest	Normal	Upper
NO2	0.32	in between	3.6
NOx	0.32		3.6
SO2	0.54		3.6
O3	0.39		0.11
NH3	0.32		3.6

Note: the ranges depend on the sensitivity of the analyzing instruments

# Example of 1 year-monitoring in Vietnam, 2009

- AIT conducted measurements in the forest in Vietnam for 1 year
- Sampling was done with cooperation with a local university
- Analysis was done at AIT

Sampling site in Danang and Song Thanh, Vietnam

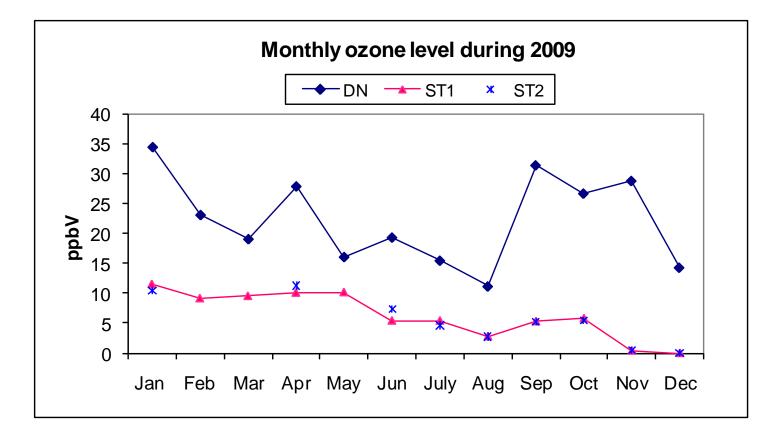
"cage" to protect from animals in ST

O<sub>3</sub> sampler



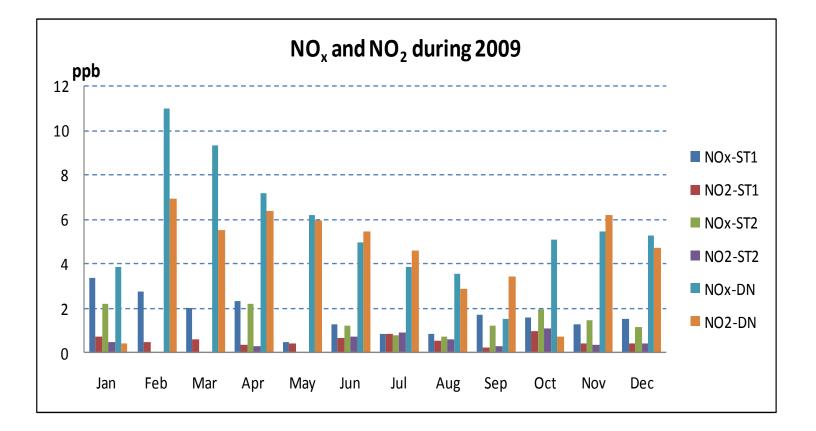


#### 1 year-monitoring in central of Vietnam, 2009



Monthly variation of ambient levels of O3 in Song Thanh (ST1 and ST2) and Da Nang (DN), Vietnam in 2009 (Kim Oanh et al, 2010)

#### 1 year-monitoring in central of Vietnam, 2009



Monthly variation of ambient levels of NOx and NO2 in Song Thanh (ST1, ST2) and Da Nang (DN), Vietnam in 2009 (Kim Oanh et al., 2010)

