EU-Project: MASTER (EVK4-CT-2002-00093)

Specific Dosimeters for Museum Environment

Sara Rentmeister, Michael Hanko, Jürgen Heinze - Final Workshop, London (GB) - 10.01.2006
The development of specific opto-chemical dosimeters for the measurement of ozone, nitrogen dioxide and sulphur dioxide for indoor gas concentrations.
Structure

- Background dosimeters
- Indoor gas concentrations
- Techniques used for air pollutant analysis
- Components / Measuring method
- Performance of the method
- Limitations / Advantages
Background

What is a dosimeter?
A dosimeter is the primary part of a measuring chain which converts the input variable into a signal suitable for measurement.

Important parameters:
- Selectivity
- Stability
- Reproducibility
- Accuracy
- Resolution
Indoor gas concentrations

<table>
<thead>
<tr>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur dioxide (SO$_2$)</td>
</tr>
<tr>
<td>Ozone (O$_3$)</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO$_2$)</td>
</tr>
</tbody>
</table>
Indoor gas concentrations

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur dioxide (SO₂)</td>
<td>lower ppb-range</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>up to ~ 50 ppb</td>
</tr>
<tr>
<td>Nitrogen dioxide (NO₂)</td>
<td>up to ~ 50 ppb</td>
</tr>
</tbody>
</table>

Measurement method:
- Continuously
- Discontinuously
Main techniques

- Continuously
  - Electrochemical method (SO₂, NO₂, O₃)
  - Spectrophotometric method (SO₂, NO₂, O₃)
  - Chemiluminescent method (NO₂, O₃)
    - low gas concentration
    - direct reading
    - potential interferences to other gases
    - expensive
    - size
Main techniques

- Continuously
Main techniques

- **Continuously**
- **Discontinuously**
  - Passive samplers / Diffusion tubes
  - low gas concentration (mean value)
  - no electronic supply
  - inexpensive (compared to continuous methods)
  - uncertainty
  - analysis at a laboratory
    - time-consuming, costly
Components / measuring method

Transparent polymeric film with homogeneous immobilised indicator-reagent (Spin-Coating-Technique)

Glass carrier

-opto-chemical Dosimeters
Components / measuring method
Components / measuring method
Components / measuring method

![Graph showing absorption versus wavelength](chart.png)

Absorption / --

Wavelength / nm

0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2

240 290 340 390 440 490 540
Components / measuring method

Gas

Wavelength / nm

Absorption / --
Components / measuring method

Gas

Absorption / --

Wavelength / nm

Components / measuring method

Gas
Components / measuring method

Gas

Absorption / --

Wavelength / nm

Components / measuring method
Performance of the method

Linear response (NO₂):

- c = 100 ppb, y = 0.0035x, R² = 0.9966
- c = 75 ppb, y = 0.0028x, R² = 0.9915
- c = 50 ppb, y = 0.0016x, R² = 0.9768
- c = 20 ppb, y = 0.0006x, R² = 0.9681
Components / measuring method

Indicator-reagent requirements:

- Reaction as specific as possible
- Irreversible reaction, without follow-up reactions
- Possibility of immobilisation into the polymer
- Stability
Components / measuring method

Polymer requirements:

- Inert, rugged
- Optically transparent
- Compatibility with indicator-reagent
- Adjustable gas permeability

Exposure time
Measuring range
Components / measuring method

Permeability coefficient [cm$^3$ cm$^{-2}$ s$^{-1}$ Pa$^{-1}$]

- Silicone resin 185/R100/25
- Nature caoutchouc NK 100
- PDMS-PC (MEM-213)
- PPO
- PS
- PSU
- PC
- Eastar BIO GP
- CA
- PES
- PVAc
- PBT
- PMMA
- PVC
- PET
- PEI

- Gas Permeability of Oxygen (online database)
- Gas Permeability of Oxygen (handbook)
- Gas Permeability of Oxygen (datasheet)
- Gas Permeability of Carbon dioxide (online database)

Decreasing Permeability
Developed dosimeters for the main gases from external sources \((\text{SO}_2, \text{O}_3, \text{NO}_2)\)
Performance of the method

Characteristic (SO₂):
- Indicator-reagent: hydrophobic Chromate-derivative
- Polymer: Silicone-Polycarbonate-Copolymer
Performance of the method

Characteristic (SO$_2$):

\[ c_{SO_2} = -1217.4 \left( \frac{\Delta A}{t} + 3.06 \cdot 10^{-4} \right) \]

\[ y = -0.023x + 0.0086 \]

\[ R^2 = 0.9921 \]
Performance of the method

Characteristic \( (O_3) \):

- Indicator-reagent: hydrophobic Indigo-derivative
- Polymer: Polycarbonate
Performance of the method

Characteristic (O₃):

\[ c_{O_3} = -3636.4 \cdot \frac{\Delta A}{t} \]

\[ y = -0.0077x \]

\[ R^2 = 0.9878 \]
Performance of the method

Characteristic (NO$_2$):

- Indicator-reagent: aromatic Amine
- Polymer: Polycarbonate
Performance of the method

Characteristic (NO$_2$):

\[ c_{NO_2} = 28000 \cdot \frac{\Delta A}{t} \]

\[ y = 0.001x \quad R^2 = 0.9903 \]
Performance of the method

Specification:

- Functionality: limitation of gas flow (gas permeability)
- Time of exposure: days - weeks - months
- Flow: diffusion

SO$_2$-specific dosimeter:

- Measurement range: $0 < 3$ ppb (28 days)
- Stability: $\approx 30$ days (new composite: $> 180$ d)
- Influence of humidity: $0 - 80$ % rH
Performance of the method

Specification:
- Functionality: limitation of gas flow (gas permeability)
- Time of exposure: days - weeks
- Flow: diffusion

O₃-specific dosimeter:
- Measurement range: 0 - 30 ppb (28 days)
- Stability: ≈ 60 days
- Cross sensitivity: 100 ppb NO₂ ≈ 6.2 ppb O₃
- Influence of humidity: 0 - 60 % rH
Performance of the method

Specification:
- Functionality: limitation of gas flow (gas permeability)
- Time of exposure: days - weeks
- Flow: diffusion

NO$_2$-specific dosimeter:
- Measurement range: 0 < 100 ppb (28 days)
- Stability: > 180 days
- No influence of humidity: 0 - 60 % rH
- Cross sensitivities: ozone
First field test

October

NO₂-Konzentration [ppb]

- Passive samplers
- Opto-chemical dosimeter

Cities:
- Oslo (N)
- Trondheim (N)
- Norfolk (GB)
- London (GB)
- Stuttgart (D)
- Huelva (D)
- Krakow (PL)
- Zakopane (PL)
- Rabat (MT)
- Heraklion (GR)
Principal limitations and advantages of this method
Principal limitations of the method

- Concentration of immobilised indicator-reagent is limited
- Compatibility of polymeric material with indicator-reagent
- Not universal: Often chemical modification of polymer or indicator-reagent necessary to produce a viable system
Principal advantages of the method

- Opto-chemical dosimeter ("electronic nose")
  - Detects SO$_2$, O$_3$, NO$_2$ (main target factors)
  - Versatile system: Could be extended to other gases and environmental parameters
- Threshold values give correlation to organic objects
- Early warning (before harm happens to objects)
Principal advantages of the method

- No need of a laboratory (cost-efficient)
- Easy to use
- Easy to read out, because of a portable electronic device (direct visual output)
- Time-flexible, because of the linearity of dosimeter response (1 week to several months)
- Universal polymer matrix: Nanophase-separated polymer conetworks with hydrophilic and hydrophobic domains
Attending members of our group

Prof. Dr. Jürgen Heinze (leader of the working group)

Dipl.-Chem. Michael Hanko (development long term dosimeters)

Dipl.-Ing. Sara Rentmeister (development long term dosimeters)