MARGA
Continuous monitoring of aerosols and gases in ambient air

Ed Lemon, Product Manager
Metrohm Applikon, The Netherlands
- Introduction
- Measurement principles
- Data management
- Benchmarking
- Measurement results
- Conclusions
Air quality is a concern to us all
Environmental Effects

Acid Deposition

Gases *(acid rain)* and aerosols play a large role in acid deposition in forests. Biggest contributors are SOx and NOx compounds as well as ammonia (gas) and ammonium (aerosol).

Climate Change

Pollutants released by anthropogenic activities are affecting the climate of our planet. While certain gases have a positive effect due to radiative forcing, aerosols have a reducing effect.
Air quality is a concern to us all

Human Health

Both gases and aerosols can cause:

- Respiratory symptoms
- Decreased lung function
- Aggravated asthma
- Chronic bronchitis
- Irregular heartbeat
- Heart attacks
- Premature death in people with heart or lung disease.

Aerosols: fine particles are particularly dangerous as they can entered deeper into the body
On-line Monitor for AeRosols and Gases in ambient Air

= MARGA

- Gases
  - NH$_3$
  - HNO$_2$
  - HNO$_3$
  - HCl
  - SO$_2$

- Aerosols
  - NH$_4^+$
  - Na$^+$
  - K$^+$
  - Ca$^{2+}$
  - Mg$^{2+}$
  - Cl$^-$
  - NO$_3^-$
  - SO$_4^{2-}$

Simultaneous sampling of aerosols and gases, with results every hour, 24/7
MARGA 1S

1 – Sample box
2 – Detector box
3 – Flow control box
4 – Uninterruptable power supply
5 – Absorbance liquid
6 – Suppressor regenerant
7 – Internal standard
8 – Eluents
Flow Scheme

Sample Box
- Absorbance Solution
- SIAC
- WRD
- Air Inlet

Flow Control Box
- Cold Trap
- Water Separator
- MFC
- Pulse Dampener
- Air Pump
- Air Outlet

Sample Selection
- Internal Standard
- Syringe Pump

Degasser
- Cation Eluent
- Cation IC
- Waste

Degasser
- Anion Eluent
- Anion IC
- Suppressant regenranant
- Waste

Detector Box
- Waste
Sample Box

1 – Front cover
2 – SJAC Supply Pump & Waste Pump
3 – SJAC Fill Pump
4 – WRD Fill Pump
5 – Steam Jet Aerosol Collector
6 – Wet Rotating Denuder
Gases dissolve in liquid film because of high diffusion rates.

Aerosols pass through the WRD.
**SJAC:** Steam Jet Aerosol Collector
DI water → Steam generator → Super saturated steam → Liquid level sensor → Additional DI

Air from denuder → To air pump → SJAC → Sample to syringe
Measurement principles

Analytical Box

Cation IC

Column Oven

Anion IC

Detector

Degasser

Sampling Cross manifold Degasser

Sample Valves

Space for Additional Sample Valves 2s

Syringes S-Box 1

Syringes S-Box 2

Space for Syringes S-Box 2

Human Interface (Screen + Keyboard)
- Full Screen
- All important data at a glance
- Easy access menus through Taskbar
# Filter Pack versus MARGA

## Filter Pack
- Daily/weekly integrated sample
- Flow rate 1.5 lpm
- Samples shipped from/to lab
- Sample preparation (filter extraction)
- Bias in nitrate and nitric acid
- Bias in ammonium/ammonia

## MARGA
- Hourly sample
- Flow rate 16.7 lpm (1 m³/h)
- Results within 1 hour
- No sample preparation
- Minimizes biases
- Ammonia
EPA/ETV joint verification statement

The verification process consists of multiple stages, which are as follows:

1. Project Development Phase
2. Method Development and Validation
3. Method Application
4. Data Analysis
5. Report Writing

Each stage is supervised by a team of experts from EPA and ETV. The teams are responsible for ensuring the quality and accuracy of the results.

Full report available here: http://www.epa.gov/etv/pubs/600r09083.pdf
## Theoretical detection limits

<table>
<thead>
<tr>
<th>Component</th>
<th>Detection Limit fixed loop (µg/m³)</th>
<th>Detection Limit Preconc. (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>HNO₂</td>
<td>0.02</td>
<td>0.002</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.03</td>
<td>0.003</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Aerosol</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.04</td>
<td>0.004</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.05</td>
<td>0.005</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.09</td>
<td>0.009</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.06</td>
<td>0.006</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.09</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Fixed loop: anion 250 µl + cation 500 µl
Pre-concentration: anion 2500 µl + cation 5000 µl

## Detection limits from real MARGA results

<table>
<thead>
<tr>
<th>Component</th>
<th>Limit (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.007</td>
</tr>
<tr>
<td>HNO₂</td>
<td>0.008</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.006</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.012</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.008</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.005</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.007</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.04</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.07</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.013</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fixed loop:
- anion 250 µl
- cation 500 µl
Measurement results Long Range Transport from biomass burning

Back trajectories: British Atmospheric Data Centre Back trajectory service. Images downloaded on 30/11/10.
(http://badc.nerc.ac.uk/community/trajectory/)

Cluster back trajectory analysis carried out with PloTra 2.1 (Sodemann, H. (2000), Relationships between the origin of air masses and carbon monoxide measurements at the Cape Point Trace Gas Monitoring Station, honours thesis, Dep. of Environ. and Geogr. Sci., Univ. of Cape Town, Cape Town.)

Boxes used to assign trajectories to the following categories: UK, Western Europe (WEU), Scandinavia (Sc), Eastern Europe & Russia (EEUR), Atlantic (AT) and Artic (AR).
On-line Monitor for AeRosols and Gases in ambient Air

- High time resolution (crucial for modelling – diurnal variation)
- Precursor gases (crucial for modelling)
- On-line results – remote access to data
- Internal Standard calibration with every measurement
- Aerosols & gases measured simultaneously
- Reduced lab labour costs
- Low detection limits (less contamination)
- High data quality (less artefacts like evaporation of NH₄ & NO₃)
- Results comparable with other networks (EMEP – USEPA)
- ETV verified following side by side test with CASTNET
Thank you for your attention.

Questions?