Time-resolved simultaneous measurements of the gas and aerosol components of the ammonium-sulfate-nitrate system are required to investigate the processes governing inorganic aerosol formation and aerosol characteristics (e.g., phase partitioning, acidity) and the dry component of nitrogen deposition. The Monitor for Aerosols and Gases in ambient Air (MARGA, Metrohm Applikon) provides near real-time simultaneous measurement of water soluble particulate species as well as their gaseous precursors.

The objective of this study is to evaluate MARGA performance with a focus on accuracy and precision characteristics related to chromatogram processing. MARGA software calculates concentrations from chromatogram peak areas online and a MARGA tool can be used for batch post-processing. To examine MARGA chromatography software characteristics and improve efficiency and flexibility in the reprocessing of raw chromatograms, an alternative to the MARGA chromatography tool was employed. Using field measurements and laboratory standards, a multipoint series of liquid external standards were processed by the MARGA tool and Chromeleon.

Results and discussion

Laboratory study of chromatography characteristics

- MARGA chromatograms were systematically examined by running a multipoint series of liquid external standards.

Table 1. Method detection limits (MDL) for chromatograms processed by MARGA tool and Chromeleon.

<table>
<thead>
<tr>
<th>Component</th>
<th>MDL (µg/m³)</th>
<th># of samples</th>
<th>MARGA tool</th>
<th>Chromeleon</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>0.02</td>
<td>78</td>
<td>0.04</td>
<td>78</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.02</td>
<td>78</td>
<td>0.04</td>
<td>78</td>
</tr>
<tr>
<td>SO₂⁻</td>
<td>0.08</td>
<td>80</td>
<td>0.13</td>
<td>76</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.05</td>
<td>80</td>
<td>0.08</td>
<td>76</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0.08</td>
<td>80</td>
<td>0.14</td>
<td>76</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.08</td>
<td>80</td>
<td>0.14</td>
<td>76</td>
</tr>
</tbody>
</table>

- Method detection limits calculated using the MARGA software are larger than corresponding detection limits calculated with Chromeleon.

Field study

- The site was impacted by an arctic air mass late in the study period.

Figure 2. High concentration periods (cold event) observed during mid-November 2014. Period 1: highest SO₄²⁻; Period 2: highest NH₄⁺ and NO₃⁻; Period 3: highest OC. Corresponding back trajectories (arrival at 500AGL, backwards for 168 hrs) of individual period peaks (±2 hrs) are also presented.

Table 2. Summary of concentrations (µg/m³) of aerosol and precursor gases during and outside of cold air mass periods.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cold Event</th>
<th>Non-Cold Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.35</td>
<td>0.30</td>
</tr>
<tr>
<td>SO₂⁻</td>
<td>3.22</td>
<td>3.12</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.99</td>
<td>0.88</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>1.07</td>
<td>0.72</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1.93</td>
<td>1.66</td>
</tr>
<tr>
<td>Temperature</td>
<td>4.54</td>
<td>5.00</td>
</tr>
</tbody>
</table>

- During cold event periods 1 and 2, the majority (estimated inorganic portions summing SO₄²⁻, NO₂⁻ and NH₄⁺ were 61±1% and 83±24%, respectively for period 1 and 2) of the PM₂.₅ mass was inorganic compounds, while in contrast, inorganic compounds only accounted for 22 ± 11% of PM₂.₅ mass during period 3.

- NO₃⁻ and SO₄²⁻ from MARGA software were ≈ 30% and 10% larger than Chromeleon, respectively, for concentrations below ≈ 1 µg m⁻³.

- Differences increase at lower concentrations.

Impact of chromatography related biases were assessed using aerosol neutralization state as an example. Two metrics based on molar ratios include:

\[
R_1 = \frac{NH_4^+}{SO_4^{2-}} \quad \text{and} \quad R_2 = \frac{NH_4^+}{NO_3^- + 2 × SO_4^{2-}}
\]

Figure 4. a) Time series of molar ratios (R1 and R2) of particulate NO₃⁻, SO₄²⁻ and NH₄⁺ and b) box plots of relative differences in R1 and R2 between Chromeleon and MARGA tool. Negative values indicate Chromeleon > MARGA tool.

- Average differences in aerosol neutralization state were ≈ -13% and -14% for R1 and R2, respectively.

Conclusions

- Close examination of chromatograms revealed a number of issues with the MARGA chromatography software tool. Hence, an alternative software, Chromeleon (Thermo Scientific Dionex), was used to reprocess the raw chromatograms.

- Differences in anion concentrations between the two chromatography methods produced non-trivial errors in concentrations < 1 µg m⁻³ and metrics of aerosol neutralization.

- The cause of this bias is unclear but can be controlled by correcting anion concentrations with multi-point calibration curves rather than relying solely on the MARGA LibIR internal standard.

Acknowledgments

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