Using microchip electrophoresis for real-time aerosol composition measurements: Field study results from San Gorgonio Wilderness, California
Outline

- Introduction
  - Instrument comparison and advantages of ACE
  - Basics of instrument operation
  - ACE design developments
- Experimental Methods
  - Generated aerosol tests
  - Field deployment in San Gorgonio Wilderness (SAGO)
- Field Measurement Results
  - Comparison with PILS and filter measurements
  - Comparison with local meteorology
- Conclusions
Motivation

- Goal is to develop a new measurement technique to capture real-time, semi-continuous aerosol composition

- Aerosol instrument techniques include
  - *Chromatography* methods that can use steam or water vapor to collect aerosol, such as the PILS-IC
  - *Spectrometry* methods can give real-time data, such as the AMS
  - *Optical detection* methods using UV or fluorescence detection to measure vaporized particles

- ACE uses *Microchip Capillary Electrophoresis*
  - A new technique in aerosol composition measurements that offers numerous advantages to previous methods
Advantages of ACE

- **Relatively Low Cost**
  - Growth tube, microchip box, microchip, high voltage power supply, commercial conductivity detector

- **Good Sensitivity**
  - Laboratory measured LODs of 67, 86, 140, and 131 ng m\(^{-3}\) min\(^{-1}\) for chloride, sulfate, nitrate and oxalate, respectively

- **Minimal Operator Involvement** during sample collection
  - Can operate up to 4 days between manual buffer replacement with current chip design, but with potential to fully automate.

- **Portable**
  - Small footprint; ~0.5 m\(^2\) area
  - Minimal amount of separation solution needed even for extended operation and minimal waste generation

Basic ACE Operation

- Detects chloride, sulfate, nitrate and oxalate in PM$_{2.5}$
- 48 second sample analysis time
- Collects samples for 30+ minutes before ~3 minute flushing cycle
Latest ACE Design

- **Denuders** and a **cyclone** remove gases and particles larger than 2.5µm
- Water condensation **growth tube** used to collect particles was interfaced with a microchip box
- **High voltage power supply** controls microchip capillary electrophoresis separation
- **Microchip box** keeps microchip separation at controlled temperature and constant pressure
- **Conductivity detector** measures signal from separation

Block diagram showing the current ACE design. All measurements are shown in millimeters.
ACE Microchip and Improvements

The microchip shown inside the microchip box and the basic components for the electrophoresis separation

- **Improved microchip design** to extend operation time
- **Improved shielded wires** for high voltage and detection inside box
- **Detection wire material** changed to improve sensitivity and tensile strength
- **More reliable flushing pump system** added
Generated ammonium sulfate aerosol was produced for concentration comparison and particle count tests (following slide).

Generated aerosol instrument set up. A second CPC was added to measure particle count on the ACE outlet to measure collection efficiency.
ACE Collection Efficiency

Growth Tube Collection Efficiency

Previously Measured Growth Tube Collection Efficiency

Data Analysis: Uncertainty

Total uncertainty in the calculation of ambient concentration ($C_{aer}$) is calculated by finding the relative standard deviations (RSD) of the following components in the equations below:

\[ C_{i,liq} = \frac{C_{IS} P_i}{F P_{IS}} \]

\[ \frac{dC_{i,aq}}{dt} = \frac{50C_{i,aer} Q_{samp}}{3M_i V_{liq}} \]

| Internal Standard Concentration ($C_{IS}$) | 1.9% |
| Volume of sample air ($Q_{samp}$) | 1.4% |
| Aqueous sample volume ($V_{liq}$) | 5.6% |

<table>
<thead>
<tr>
<th></th>
<th>Chloride</th>
<th>Sulfate</th>
<th>Nitrate</th>
<th>Oxalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (F)</td>
<td>0.25%</td>
<td>0.30%</td>
<td>0.66%</td>
<td>0.28%</td>
</tr>
<tr>
<td>Aqueous Conc. ($C_{i,aq}$)</td>
<td>15%</td>
<td>0.22%</td>
<td>0.27%</td>
<td>6.6%</td>
</tr>
</tbody>
</table>

**Total Uncertainty**

<table>
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<th>Oxalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total RSD</td>
<td>15.9%</td>
<td>6.08%</td>
<td>6.11%</td>
<td>9.00%</td>
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Data Analysis: LOD

- The standard deviation of the ensemble averaged baseline signal was used to calculate the LOD. The signal was converted into an aqueous concentration using the slope of the calibration curve.

### Estimated LODs

<table>
<thead>
<tr>
<th>LOD (µM)</th>
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<th>Nitrate</th>
<th>Oxalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (µM)</td>
<td>0.40</td>
<td>0.22</td>
<td>0.51</td>
<td>0.30</td>
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</table>
Field Study in San Gorgonio Wilderness

- Sampling Dates: June 14-July 5, 2012, excluding July 3

Average daily weather during field study
Why sample in San Gorgonio?

- A unique sampling location that provides both high and low concentrations of sulfate and nitrate in a relatively short time scale.

Concentrations measured by a PILS-IC in San Gorgonio, CA in July 2003

ACE at SAGO

- Sample injection every 48 sec.
- Sample solution replaced every 30 min.
- Buffer solution replaced daily
- Growth tube temperature difference at or above 30°C
- Used 3 point averaging for each species (2 min. 12 sec.)
- Used 4 microchips over entire field study
ACE Time Series at SAGO
Diurnal Trend of Sulfate and Nitrate

![Graph showing diurnal trend of sulfate and nitrate concentrations over time.](image)
Nitrate Comparison

![Nitrate Comparison Graph]

**Concentration (µg m⁻³)**

- ACE Nitrate
- PILS Nitrate
- Filter Nitrate

**Local Time (PDT)**

- 6/17/2012
- 6/20/2012
- 6/23/2012
- 6/26/2012
- 6/29/2012
- 7/2/2012
ACE Nitrate Comparison

**PILS Comparison**
- Nitrate ACE PILS Comparison
- Linear Fit
  - $R^2 = 0.803$
  - $m = 0.456 \pm 0.007$
  - $y$-int = $-0.150 \pm 0.029$
- 1:1 Line

**Filter Comparison**
- Nitrate ACE Filter Comparison
  - $R^2 = 0.664$
  - $m = 0.708 \pm 0.03095$
  - $y$-int = $-0.431 \pm 0.335$
- Linear Fit
- 1:1 Line
Sulfate Comparison

![Graph showing sulfate concentration over time](image)

- ACE Sulfate
- PILS Sulfate
- Filter Sulfate

Concentration (µg m⁻³)

Local Time (PDT)

Dates: 6/17/2012 to 7/2/2012
ACE Sulfate Comparison

**PILS Comparison**

- Sulfate ACE PILS Comparison $R^2 = 0.801$
  - $m = 0.263 \pm 0.004$
  - $y$-int = $0.133 \pm 0.012$

**Filter Comparison**

- Sulfate ACE Filter Comparison $R^2 = 0.770$
  - $m = 0.298 \pm 0.031$
  - $y$-int = $-0.095 \pm 0.108$
Conclusions

- Continuous ACE sample collection for 18 consecutive days collecting 2 minute and 12 second samples
- Uncertainties for nitrate and sulfate at ~6% and LODs in the μM range for aqueous concentrations
- Both ACE sulfate and nitrate lower than both PILS and filter measurements
- R² value ~0.8 for both sulfate and nitrate for PILS comparison
Acknowledgements

- Arsineh for SAGO PILS and filter data (and for driving the mobile lab) and Ezra for helping with generated aerosol tests
- Funding from NSF and NIH