New Compact and Versatile Sampler for Uninterrupted, Time-resolved Chemical Speciation of Ambient Particulate Matter

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Aim: To combine the simplicity of filter sampling with the data completeness and automation of real time instruments.

Approach: To provide a collector with directly analyzable samples and an automated interface to lab-based analytical instruments.
New Challenges for New Applications

New approach to laminar flow, water-based condensation

WCPC output, like mixing instruments, is warm and humid...
Collection / concentrator applications want output at ambient temperature & RH
1. Development, Validation and Applications
Sequential Spot Sampler ($S^3$)

- **Conditioner (2-5°C)**
- **Initiator (32-35°C)**
- **Modulator (8-10°C)**
- **Collection chamber**
Output Droplet Size

Nearly the same as in Original Configuration

-dN/dLogDp

Droplet Diameter (µm)

Original: 06 / 40 / 40 °C

3-Stage: 06 / 40 / 25 °C

Directly coupled Growth Tube to APS
Output Droplet Size with Flow Rate

At Variable Flow
3-stage (5/40/25)

0.4 lpm
0.6 lpm
1.0 lpm
1.5 lpm
1.8 lpm
2.5 lpm

With humidified makeup air to Aerodynamic Sizer
Collection: 

1. Particles collected as dry deposits
2. Spot size: ~400 µm to ~1 mm
Bouncing?

Arizona Road Dust
1. Performance characterization: laboratory tests

- Nebulizer
- DMA
- PM2.5 ambient air
- High voltage
- Upstream
- UHASH
- S$^3$
- Downstream
a) Collection efficiency

Lab generated aerosols

Collection efficiencies >95% for particles larger than 10nm

Collection efficiencies >99% for concentrations up to $10^6$#/cc
Collection efficiencies were >95% by number for ambient PM
b) Reproducibility and Linearity

Lab generated aerosol: Ammonium sulfate and ammonium nitrate

Automated analysis by IC: extraction and injection handled by autosampler

Plate location in the autosampler

Autosampler dispenses the extraction solvent (DDW) and injects the sample
**Reproducibility: collection and analysis**

<table>
<thead>
<tr>
<th>Collection Time (min)</th>
<th>5 (n=6)</th>
<th>30 (n=6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate (%STDEV)</td>
<td>4.21</td>
<td>3.52</td>
</tr>
<tr>
<td>Nitrate (%STDEV)</td>
<td>5.36</td>
<td>4.25</td>
</tr>
</tbody>
</table>

**Linearity**

- **Sulfate**: $y = 0.007x - 0.01$, $R^2 = 0.99$
- **Nitrate**: $y = 0.005x - 0.005$, $R^2 = 0.99$
Nitrate losses were not significant for collection periods up to 20 hrs.
Temporal variability of sulfate and nitrate in ambient PM (Berkeley)
2. Field Performance
1. San Bernardino Mountains

Deployment at
San Gorgonio, IMPROVE site (7,000 ft)
June 12 – July 5, 2012
Anion measurements: sulfate and nitrate

Instruments
Spot Samplers: mostly 1-hr resolution
PILS: ~17 min resolution
URG Denuder-Filter Packs: 12-hr samples

Analysis: Dionex IC with modified autosampler
a) $S^3$ vs PILS: sulfate

A graph showing the comparison between Spot Sampler and PILS for sulfate concentration (µg/m³) from 6/16/2012 to 7/1/2012.

- Graph on the left: Sulfate concentration over time for Spot Sampler and PILS.
- Graph on the right: Scatter plot of Sulfate vs PILS with a one-to-one line for reference.
b) $S^3$ vs PILS: nitrate

![Graph showing nitrate concentrations over time]

- Nitrate (µg/m$^3$) measured by Spot Sampler and PILS.
- Graph comparing Spot Sampler and PILS data.
c) $S^3$ vs URG: sulfate
d) $S^3$ vs URG: nitrate

![Graph showing nitrate levels over time and comparison with filter samples.](image)
2. Stockton, CA

Deployment at
Stockton, CA - ARB monitoring station
Nov 2011 – Feb 2012

Instruments
Spot samplers in triplicate
12hr samples @ 1.5 lpm for PAHs
6 hr samples @ 1.0 lpm for trace elements
Parallel 48-hr filter collection (25mm, 9 lpm)
Run unattended for weeks

Analysis
CTC-PAL autosampler:
automated extraction/injection
Agilent HPLC-FL: 15 EPA-PAHs
22 min analysis
a) Automated extraction and analysis

CTC- PAL autosampler

Sonication bath
b) Optimization of the extraction method

soaking vs. mechanical agitation vs. sonication

Soaking the sample for 30 min was not enough to extract PAHs at high concentrations.

Sonication for 20 sec was more efficient than mechanical agitation for 1 min.
Individual PAH concentrations measured on filters and averaged of 12-hr spot samples.

**c) Comparison with filter collection**

Good correlation between filters and $S^3$.
**d) Spot Sampler intercomparison:**

All correspond to the same sample

Excellent reproducibility between samplers for all PAHs
e) Temporal variability: PM$_{2.5}$ in Stockton, CA

- ΣPAHs reached concentrations up to 9.53 ng/m$^3$
- BBF (401 pg/m$^3$) and BGP (380 pg/m$^3$) showed the highest concentrations
- PHE highest among the semivolatile
f) Trace Elements by LIBS

- Obtain elemental spectra in minutes
- Toxic elements such as iron and copper can be identified
Summary

- Collection efficiency $>95\%$ for a broad range of particle types, sizes and concentrations
- Reproducibility & precision between 3% - 5%
- Systems can run unattended for several weeks
- Collection plate can be extracted and analyzed directly (automated extraction and analysis)
- Good correlation with standard anion measurements (PILS and URG-filters)
- Sequential spot sampler is capable of measuring peak concentration missed by filter collection systems
- PAH - Filter Comparison: $\rightarrow 15\%$ for individual PAHs
- Spots allow fast trace elements analysis using LIBS
The Sequential Spot Sampler is a simple and reliable collection system that can be streamlined with lab equipment for uninterrupted, time-resolved chemical characterization of ambient PM.

THANK YOU!
Theodore Roosevelt National Park (ND)
Organic speciation: *TD-GCxGC-HRTOFMS*
Chemical Mass Balance (CMB8.2)

Vehicular emission profile from Eiguren-Fernandez and Miguel (2005)
Wood burning emission profile from Li and Kamens (1993)