Mass spectrometric analyses of the airborne fine particles in a megacity of Yangtze River delta (YRD), China

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Background – PM chemistry

- Filter sampling and off-line analyses:
  - Coarse time resolution (daily sample, etc.), thus very limited to capture the details of fast atmospheric processes,
  - May introduce artifacts during sample storage and analyses
  - Possible loss of semi-volatile species.

- Online analyses:
  - Don’t require sample preparation
  - Real-time display
  - Fine time resolution
  - Capture detailed mechanisms
Soot Particle-Aerosol Mass Spectrometer (SP-AMS)

- Real-time and online measurements of inorganic (sulfate, nitrate, chloride, ammonium) and organic species of PM$_1$
- High chemical resolution (~6000 under W mode)
- Fine time resolution (a few mins or secs. each sample)
- Upgraded with a laser vaporizer ➔ able to detect Black carbon (BC) and associated refractory species

1. Quantitative composition

<table>
<thead>
<tr>
<th>Nitrate Equivalent Mass Concentration (µg m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8 µg/m$^3$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/z (Daltons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
</tr>
</tbody>
</table>

2. Size-resolved composition

<table>
<thead>
<tr>
<th>Size Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
</tr>
<tr>
<td>dM/dLogD (µg m$^{-3}$)</td>
</tr>
</tbody>
</table>

3. Elemental comp. (C$_n$H$_m$N$_p$O$_z$S$_w$)
For field on-line measurement
For chamber study
For off-line analyses of liquid samples
How does an AMS work?

Likely every 5 min, an averaged mass spectrum (an ensemble of all fragments from all particle-phase species) is obtained. The Mass spectrometry analysis is to sort out each species from the fragments (The Game of Puzzles!) \(\rightarrow\) chemical composition of the aerosols.

![Mass spectrum diagram]

Certain species has its unique, reproducible fragmentation pattern, which can be used to apportion the total signals.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium</td>
<td>4.8</td>
</tr>
<tr>
<td>Nitrate</td>
<td>5.8</td>
</tr>
<tr>
<td>Sulphate</td>
<td>9.4</td>
</tr>
<tr>
<td>Organics</td>
<td>13.4</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Mexico City 2/2002

MS analysis

Courtesy: Q. Zhang
How does an AMS work?

Inorganic species (sulfate, nitrate, chloride and ammonium) are easy to quantify.

BUT organics can contain numerous species.

It is almost impossible to quantify each individual organics molecules (perhaps unnecessary); BUT we Still want to know the characteristics, sources of the organics (OA). They can contain very toxic compounds!

Factor analysis (segregate the total ORG into a finite number of factors)
AMS field studies in China

Sulfate
Nitrate
Ammonium
Chloride
Black Carbon
Organics
HOA
COA
BBOA
SV-OOA
LV-OOA
CCOA
Urban
Urban downwind

No SP-AMS study

Beijing 2011
(Winter)
66.8 µg m⁻³
O/C
0.17
0.11
0.47
0.48

Beijing 2011
(Summer)
50.0 µg m⁻³

Beijing 2008
(Summer)
63.1 µg m⁻³

Beijing 2006
(Summer)
80.0 µg m⁻³

Beijing 2011
(Summer)
63.1 µg m⁻³

Beijing 2011
(Winter)
66.8 µg m⁻³

Beijing 2011
(Summer)
63.1 µg m⁻³

Beijing 2011
(Winter)
66.8 µg m⁻³

Shanghai 2010
(Summer)
29.2 µg m⁻³

Jiaxing 2010
(Summer)
32.9 µg m⁻³

Changdao 2011
(Spring)
47.0 µg m⁻³

Jiaxing 2010
(Summer)
32.9 µg m⁻³

Changdao 2011
(Spring)
47.0 µg m⁻³

Jiaxing 2010
(Winter)
41.9 µg m⁻³

Kaiping 2008
(Winter)
14.5 µg m⁻³

Hongkong 2011
(Summer)
30.0 µg m⁻³

BackGarden 2006
33.1 µg m⁻³

Shenzhen 2009
44.5 µg m⁻³

Jiaxing 2010
(Winter)
41.9 µg m⁻³

Lanzhou 2012
(Summer)
24.5 µg m⁻³

Field campaigns in Nanjing

2014 Summer

2014.08.11-2014.09.18
(Nanjing Youth Olympic: 2014.08.16-2014.08.28)

Nanjing Meteorological Bureau

2015 Winter

2015.02.16-2015.03.23
(Spring Festival: 2015.02.18-2015.02.24)

NUIST Campus
2014 Summer instruments (MOUDI, high-volume sampleer not shown)
Results and discussion

1. Overall characteristics

2014 Summer
Prevailing eastern wind both in summer and winter

2015 Winter

Graph showing various data points and trends over time, including temperature, humidity, wind direction, and pollutant concentrations.

Legend:
- Black line: Total PM
- Red line: PM2.5 from PKMC
- Blue line: PM2.5 from PKMC
- Purple line: PM2.5 from PKMC
- Green line: PM2.5 from PKMC
- Yellow line: PM2.5 from PKMC
- Pink line: PM2.5 from PKMC
- Cyan line: PM2.5 from PKMC
- Light blue line: PM2.5 from PKMC
- White line: PM2.5 from PKMC

Additional data points include:
- T (°C)
- RH (%)
- WD
- SO₂ (µg/m³)
- NO₂ (µg/m³)
- PM₂.₅ from PKMC: 62.3 µg/m³
- SP-AMS PM₁: 46.5 µg/m³

Pie chart showing percentage distribution:
- 25.5% organics
- 24.1% NO₃
- 23.2% SO₄²⁻
- 16.9% NH₄⁺
- 6.3% Cl⁻
2. Diurnal patterns

Summer

Nitrate variations were mainly governed by Temperature in Nanjing!!!
3. OA Mass spectra

2014 Summer

Organics (Laser off) + rBC (Laser on) (W mode)

Higher ON species than other places → Presence of amino compounds

2015 Winter

Higher ON and BC in suburban site → Likely Industrial emissions?
4. Volatility – PM spectra

2014 Summer

Significant amount of non-volatile organics remains in the particles under 280 °C, not only rBC. A portion of Nitrate and sulfate remains in the 280oC-denuded particles, indicating presence of other nitrate/sulfate salts.
4. Volatility – OA behavior

On average, 12% of organics remains even under 280°C, and these non-volatile organics tend to be more oxidized.

How does this relate to the Optical properties??
4. Volatility – Inorganics behavior
5. Size distribution

2014 Summer

Date and Time (Beijing)

Hour of day

m/z 36

Total PM

Nitrate

Sulfate

Organics

\(D_{V_0}\) (nm)

\(D_{V_0}\) (nm)

Mass Conc. (µg/m\(^3\))

BC (m/z 36)
2014 Summer

2015 Winter

![Graph showing mass percent (%) and Dva (nm) for 2014 Summer and 2015 Winter. The graphs compare Ammonium, Sulfate, Nitrate, Organics, and m/z 36 (scaled to BC).]
6. Source apportionment
Positive Matrix Factorization (PMF, 正矩阵因子分解)

\[ \text{ORG}_{t \times i} = \]

\[ m_{s_{\text{Organics}}} = c_{a} \cdot m_{s_{a}} + c_{b} \cdot m_{s_{b}} + c_{c} \cdot m_{s_{c}} + \ldots \]

\[ m/z (i) \]

\[ \text{Time} (t) \]

\[ t \sim 1,000 \text{s} \]

\[ i \sim 300 \]

Factor 1
Factor 2
Factor 3

PMF Analysis

Source apportionment

Courtesy: Q. Zhang
2014 Summer

Nitrogen-enriched OA

Vehicle OA

Local Cooking-related OA

OOA

COA

HOA

NOA

O/C = 0.42, H/C = 1.35, N/C = 0.018, OM/OC = 1.69

O/C = 0.12, H/C = 1.72, N/C = 0.006, OM/OC = 1.31

O/C = 0.08, H/C = 1.79, N/C = 0.009, OM/OC = 1.27

O/C = 0.44, H/C = 1.15, N/C = 0.098, OM/OC = 1.80

% of total

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% of total
2015 Winter

SVOOA  16.4%

LVOOA  21.5%

LSOA  10.0%

COA  15.5%

IOA  16.5%

HOA  20.1%

O/C = 0.15, H/C = 1.73, N/C = 0.048, OM/OC = 1.41

O/C = 0.33, H/C = 1.37, N/C = 0.036, OM/OC = 1.59

O/C = 0.24, H/C = 1.61, N/C = 0.034, OM/OC = 1.59

O/C = 0.33, H/C = 1.64, N/C = 0.040, OM/OC = 1.64

O/C = 0.59, H/C = 1.27, N/C = 0.084, OM/OC = 2.00

O/C = 0.47, H/C = 1.38, N/C = 0.032, OM/OC = 1.79

O/C = 0.33, H/C = 1.37, N/C = 0.036, OM/OC = 1.59

Mass Conc. (µg m⁻³)

Hour of Day

Date and time (Beijing time)
Conclusions

- *For the first time*, we conducted the SP-AMS study in China......and got lots of interesting results...
- *For the first time*, we discovered the occurrence of fullerenes in the ambient particles, in China atmosphere.
- Only an overview, lots of in-depth analyses are needed......
Thanks!

TO BE CONTINUED...