Intercomparison of **standard and capture** vaporizer in aerosol mass spectrometer (AMS)

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Feature of **standard vaporizer (SV)** vs **capture vaporizer (CV)**

**SV**
- Porous Tungsten

**CV**
- Solid Molybdenum

**Species:** Organic aerosol, Sulfate

**Standard vaporizer temperature (T_v):** 600°C

**Collection efficiency (CE) depends on:**

- **Chemical composition:** e.g. NH₄NO₃ fractions, Acidity of aerosol
- **Aerosol phase:** e.g. Solid/semisolid/liquid particle, Relative humidity

Typically contribute the most uncertainty for ambient aerosol measurement

Middlebrook et al., AST, 2012
Outlook of SV and CV
Temperature measurement for CV

(a) 

(b) 

Hu et al., submitted. 2016
Experiment setup:

(a) Flow reactor

Lab

Atomizer

Nafion dryer or silica gel

SMPS

AMS with SV

AMS with CV

Bypass pump

(b) Other sampling line

PM$_{2.5}$ cyclone

Flow reactor

Nafion dryer

AMS with SV

AMS with CV

SMPS

CPC

Bypass

Only exist in SOAS study
Outline

- Does capture vaporizer make CE~1?
- Gas-phase CO$_2$(g) formation in CV
- Does the capture vaporizer preserve or diminish the chemical and physical information from AMS?
  - Fragmentation and OA source identification?
  - Size distributions?
CE of standard inorganic species

$\text{CE} = \frac{\text{AMS}}{\text{CPC}}$ mass ratio

$\text{NH}_4\text{NO}_3$, $\text{NaNO}_3$, $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{Cl}$

An improvement in CE of inorganic species in the CV

Shown results are carried out under medium vaporizer temperature 500-600°C

Hu et al., submitted. 2016
Lens transmission corrections for NaNO$_3$  
$d_m = 300 \text{nm} \rightarrow d_{va} = 670 \text{ nm}$

Hu et al., submitted. 2016
SV: CE: 0.5-0.7
CV: CE=1
Multiple results support **ambient** CE in CV =1

**CV** vs **SV**

AMS vs SMPS

- **SV vs CV**
  - **Total**
  - **OA**
  - **SO₄**
  - **NO₃**
  - **NH₄**

**AMS** vs **SMPS**

- **SV**: CDCE=0.5-0.7
- **CV**: CE=1

Hu et al., in prep. 2016
Evaluation on chemical composition CE correction

Hu et al., in prep. 2016
Outline

• Does capture vaporizer make CE~1?
• Gas-phase $\text{CO}_2(g)$ formation in CV
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  ➢ Size distributions?
  ➢ Fragmentation and OA source identification?
Production of CO$_2$(g) is negligible for the CV for NH$_4$NO$_3$ and comparable to the SV for NaNO$_3$.

Hu et al., submitted. 2016
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• Does capture vaporizer make CE~1?
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Fragmentation pattern of inorganic NH$_4$NO$_3$

Inorganic does not evaporate as intact salts. E.g., NH$_4$NO$_3$(s)$\rightarrow$NH$_4$NO$_3$(g) but go through thermal decomposition. E.g., NH$_4$NO$_3$(s)$\rightarrow$NH$_3$(g)+HNO$_3$(g); HNO$_3$(g)$\rightarrow$NO$_2$(g)+H$_2$O(g)+O$_2$(g) (Drewnick et al., 2015)

Hu et al., submitted. 2016
Thermal decomposition is LARGER in CV (esp., for oxidizes species)! 

CO enhancement

Hu et al., in prep. 2016
Fragmentation pattern of organic species

\[ C_xH_y^+ + C_xH_yO^{+} + C_xH_yO_2^{+} \]

Oleic acid \( C_{18}H_{34}O_2 \)

- Thermal decomposition is LARGER in CV (esp, for oxidizes species)!
- CO enhancement
Where CO ion came from?

Normal oleic acid

(e) Predicted isotope C13 labeled oleic acid

Measured isotope C13 labeled oleic acid
PToF show CO peak similar with aerosol phase

<table>
<thead>
<tr>
<th></th>
<th>CO in aerosol PToF</th>
<th>CO$_2$ in aerosol PToF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Squalene</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Citric acid</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>DOS</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Chamber SOA</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Isotope-labeled Oleic acid</td>
<td>√</td>
<td>√</td>
</tr>
</tbody>
</table>
Chemical information in CV is not lost

$F_{44} = \text{CO}_2/\text{OA}$

(c) SV

SOA from a-pinene ozonolysis from Ng et al., (2010)

Triangle line (Ng et al., 2010)
Ambient elemental ratio comparison

- **IA method**
  - Slope = 1.26
- **Aiken method**
  - Slope = 0.96

Hu et al., in prep. 2016
Similar PMF results for SV vs CV

IEPOX-SOA: Isoprene epoxydiols-derived SOA

Ambient

SV

CV

Hu et al., in prep. 2016
Outline

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  ➢ Size distributions?
Size-resolved detection of inorganic ions

Hu et al., submitted. 2016

SV

CV
Size distribution of ambient aerosol in CV still work

Particle size in CV recalibrated with AS.

- Total
- $\text{SO}_4$
- $\text{NO}_3$
- $\text{NH}_4$

$dM/d\log_{10}d_{va}$ (µg m$^{-3}$)

PToF size (nm)
Temperature dependent size distribution

![Graphs showing temperature dependent size distribution.](image)

Hu et al., submitted. 2016
Estimating vaporizer temperature for detecting species in size mode

Hu et al., submitted. 2016
<table>
<thead>
<tr>
<th></th>
<th>SV</th>
<th>CV</th>
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</thead>
<tbody>
<tr>
<td>CE for ambient particles</td>
<td>CDCE</td>
<td>CE=1</td>
</tr>
<tr>
<td>CE for pure inorganics in lab</td>
<td>Bounce</td>
<td>&lt;1 but better than SV</td>
</tr>
<tr>
<td>Impact of thermal decomposition</td>
<td>Longer residence time</td>
<td></td>
</tr>
<tr>
<td>CE ~1 for ambient particles</td>
<td>Substantial at high OA loading</td>
<td></td>
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<tr>
<td>Information for source apportionment (PMF)</td>
<td></td>
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<tr>
<td>Organic nitrate vs. ammonium nitrate</td>
<td>Low S/N</td>
<td></td>
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<tr>
<td>OA elemental ratios</td>
<td></td>
<td></td>
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<tr>
<td>Single particle calibration</td>
<td></td>
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<tr>
<td>CPC-based calibration</td>
<td></td>
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<tr>
<td>Heater bias dependence of signal</td>
<td>Sensitive</td>
<td>Not sensitive</td>
</tr>
<tr>
<td>Nitrate → Chloride artifact</td>
<td>Vary with instrument history</td>
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<tr>
<td>CO₂ signal decay lifetime</td>
<td>faster than SV</td>
<td></td>
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<tr>
<td>CO₂(g) formation from nitrates</td>
<td>Minor for AN, comparable for SN</td>
<td></td>
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<tr>
<td>Lab &amp; Chamber size distribution</td>
<td>For monodisperse particles</td>
<td></td>
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<tr>
<td>Ambient size distribution</td>
<td>Need AS calibration</td>
<td></td>
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<tr>
<td>SO₄ UMR quantification under high OA</td>
<td>For SO₃⁺ and HSO₃⁺ ions</td>
<td></td>
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</tbody>
</table>
Faster CO$_2$ decay in CV than SV

Citric acid

\[ \text{C}_6\text{H}_8\text{O}_7 \]

\[ \tau_{\text{CO}_2} \approx 11 \text{s} \]

\[ \tau_{\text{CO}_2} < 3 \text{s} \]
Summary

• CE ~1!

• Slower evaporation impacts size distributions
  • Still OK for ambient air.
  • Much broader for monodisperse lab exp.
  • CO$_2$ formation was neg

• Production of CO$_2$($g$) is negligible for the CV for NH$_4$NO$_3$ and comparable to the SV for NaNO$_3$.

• Mass spectra shifted to smaller fragments.
  • But information content (e.g. OA sources and elemental ratios) not lost!!

• Further analysis: CO formation influences to the quantification of OA.

Thanks for your attention.