Quantitative single particle mass spectrometry with the AMS: development of a new classification algorithm and application to field data

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How to analyze AMS single particles?

- retrieve quantitative information on chemical composition of single particles:

  \[ \text{single particle MS} \]

  - \[ \text{Frag Table?} \]
    - \[ \text{... but so few ions!} \]

- sort particles according to their constituents into unambiguous clusters:

  \[ \text{thousands of single particle MSs} \]

  - \[ \text{Statistical clustering methods?} \]
    - \[ \text{... but different degrees of mixing!} \]
How to analyze AMS single particles?

- Identification AND quantification by comparison to reference mass spectra

- Sort particles into groups according to constituents found

Classified as „OOA and inorganics“

(Freutel et al., AMTD 2013)
How to analyze AMS single particles?

1. Dataset of mass spectra
   - Similarity with mass spectra of NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$ and presence of marker m/z
   - Subtract signal
   - Similarity with mass spectra of glucose, oleic acid, gasoline engine exhaust and/or OOA and presence of marker m/z
   - Subtract signal
   - Residual mass spectrum

2. Modify algorithm
   - Found new particle types?
     - Clustering / manual sorting
     - Unclassified particle MS
     - Classified particle MS

3. Yes
   - No

4. Quantification (ion number) along with determination of components
Application to lab data

- Qualitative and quantitative validation

- Estimated uncertainty: 15-25 % (depending on substance)
- Observed: ~30%

(Freutel et al., AMTD 2013)
Application to field data

In most particles: at least one constituent identified

Unidentified particles: largely due to low signal intensity

~25 000 single particle mass spectra from measurement in suburb of Paris, July 2009

(Freutel et al., AMTD 2013)
Application to field data

(Freutel et al., AMTD 2013)

Reliable separation even of very similar MS

- Direct observation of nitrate partitioning
- Potential influence of particles growing into the detection regime (low OOA, SO$_4$ at high NO$_3$)
- Larger increase at noon of OOA than of sulfate

"OOA and inorganics"

[Graphs showing particle number concentration and mass concentration over local time]
- Extend algorithm to further new particle types found
- More laboratory studies, especially on detection limits