Intercomparisons between AMS and ATOFMS:  

*The synergy!*

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Overview of this talk:

1. Describe ATOFMS and AMS, focusing on their limits (especially for the AMS).

2. Some examples
The perfect instrument

Cheap, quantify all single chemical species, single particles, fast, little, no complex data analysis........

.......perhaps it should make coffee too.....
• Why? Why both?

1. The aerosol time-of-flight mass spectrometer (ATOFMS) offered by TSI provides information on a polydisperse aerosol, acquiring precise aerodynamic diameter and individual particle positive and negative mass spectral data in real time.

2. The AMS (Aerodyne Research, Inc.) provides online, real time measurements of the mass of non-refractory components of aerosol particles as function of their size.

• The results aim to show that the combination of the two provides much deeper insights into the nature of the aerosol properties than each of the instruments could do alone. This is my personal approach!
Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry

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Many instruments including the ATOFMS and the AMS are providing a wealth of data from which sometimes diverging conclusions are drawn.

Sampling at different locations and under different meteorological conditions can explain some of the differences, perhaps.

But meaningful *comparisons* between measurements can only be made within the frame of carefully evaluated uncertainties.

**My comment on that…..**

1. AMS is much better characterised than the ATOFMS

2. ATOFMS gives the size and the chemical composition of single particles, this takes longer to characterise
Examples:

- S-rich particles
- PAH
- Nitrate containing particles
- Secondary Organic Aerosol during radiation fog

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m/z 32 [S⁺], 64 [S₂⁺], 96 [S₃⁺] \rightarrow [S_n]^+

Elemental Sulphur
• Sulphate and sulphuric acid: m/z 48 [SO$^+$], 64 [SO$_2^+$], 80 [SO$_3^+$], 81 [HSO$_3^+$] and 98 [H$_2$SO$_4^+$]

• Elemental Sulphur: m/z 32 [S$^+$], 64 [S$_2^+$], 96 [S$_3^+$] ([S$_n^+$])
Fragmentation Pattern of Elemental Sulfur Particles and Sulfate / Sulfuric Acid Particles (Vaporizer: 600 °C)

[SO⁺], [SO₂⁺], [SO₃⁺], AMS

Laboratory study confirm the field measurements

Dall'Osto et al (2008)
Industrial site: **ATOFMS PAH particle types**

![Graph showing PAH particle types for low and high concentrations](image)
ATOFMS and AMS are able to detect simultaneously different PAH components

Example 2:

REPARTEE
(Regent’s Park and BT Tower Environmental Experiment)
REAL TIME CHEMICAL CHARACTERIZATION OF LOCAL AND REGIONAL NITRATE AEROSOLS

AMS nitrate [µg m⁻³]

ATOFMS counts

AMS Nitrate

ATOFMS Nitrate
Local: locally produced in urban locations during nighttime (300nm)

Regional: regionally transported from continental Europe (600nm)
REAL TIME CHEMICAL CHARACTERIZATION OF LOCAL AND REGIONAL NITRATE AEROSOLS

- AMS Nitrate [µg m⁻³]
- ATOFMS counts

- Local (23:00-06:00)
- Regional

Graph showing the comparison between AMS Nitrate and ATOFMS Nitrate counts over time.
(a) local

(b) Regional

(c) local (log scale)

(d) regional (log scale)
• Unique information on the diurnal variation of this particle type can be found in the ATOFMS data.

• It shows the strong volatility of the LRT nitrate aerosol, with loss to the gas phase during day time due to the higher temperature.
Mace Head, Ireland, Spring 2008
Example 3:
REAL-TIME SECONDARY AEROSOL FORMATION DURING A FOG EVENT
Fog event during the morning of 13th November 2006

Stagnant conditions favouring radiation fog
Hydroxymethanesulphonate

\[
\begin{align*}
\text{SO}_2 (g) + H_2O & \leftrightarrow \text{SO}_2^*H_2O \\
\text{SO}_2^*H_2O & \leftrightarrow H^+ + \text{HSO}_3^- \\
\text{HSO}_3^- & \leftrightarrow H^+ + \text{SO}_3^- \\
\text{HCHO} (aq) + H_2O & \leftrightarrow \text{CH}_2(\text{OH})_2 \\
\text{HCHO} (aq) + \text{HSO}_3^- & \leftrightarrow \text{HOCH}_2\text{SO}_3^- \ (m/z \ -111) \\
\text{HCHO} (aq) + \text{SO}_3^{2-} & \leftrightarrow -\text{OCH}_2\text{SO}_3^- \\
\end{align*}
\]

OC, EC, Aromatic, N-containing, S-containing.....
Summary

1. AMS and ATOFMS are very complementary
2. AMS and ATOFMS are very complementary
3. AMS and ATOFMS are very complementary
4. AMS and ATOFMS are very complementary

Future work

• Synergy of ATOFMS ART2a and PMF HR-TOF-AMS could help to explain unclassified ATOFMS ART2a clusters and AMS PMF factors.

• ATOFMS could help to look for specific events in order to identify specific m/z in the AMS mass spectra (and vice-versa).