Some tentative AMS improvements
(and a note on IE calibrations)

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Outline

- Integrating a Cryopump in an aircraft AMS: First notes on a successful deployment
- Vaporization of ammonium nitrate in a PCI inlet: How to tell your test aerosol is not working
- An internal fluorine standard for the HR-TOF-AMS: Worth the trouble?
- Some additional resources: AMS venting scheme, RF guide tuning
The problem: Subpar performance of (A)MS in the first hours of pump down

- Aircraft deployments involve switching the instrument off overnight and starting measurements ~2-3 h after initial pumpdown.

- This is due to a significant amount of water and organics will come off the walls when pumping ceases, even in a perfectly leak-tight system.

- There are structural ways to reduce this significantly, but the resulting vacuum manifold would not be aircraft friendly.

- It takes typically 1-2 days of pumping to reestablish an equilibrium in the ionization chamber between gas background and walls. In the meantime, the elevated gas background ruins sensitivity since:

$$ DL \sim \sqrt{I_{\text{background}}} $$

Some old-school tech to deal with it

- The pumping efficiency of HV pumps such as turbos decrease with molecular mass.

- On the other hand, a cold surface (especially if its very close to the zone of interest (ie the ionizer chamber in our case) will pump high molecular mass compounds very efficiently.
Ricor MicroStar™ Cryopump
fast pump out / background reduction in ARI Aerosol Mass Spectrometer ionizer chamber

- 1000 Ls⁻¹ pumping speed for water
- 17 kg (38 lbs)
- 400 Watts start-up at 50 VDC (~200W normal load)

- Cryoshiled surrounds ionizer
- Mounted between P5 (V301) and chamber

http://www.ricor.com

How to integrate it into an aircraft instrument

- Take advantage of new, air cooled pump model, ie no water requirements, half the weight (22 lbs) (and less power)
- Since there is no room either below P5 or in front of it, interface the AMS chamber from the back/bottom side (ie where the little window normally sits)
- This places the (still heavy) pump at the lowest point in the assembly, while orienting it in line with the airplanes g-forces
- However, a combination of a custom compression flange and rails below the pump can neutralize those g forces effectively.
Some more pictures

First Test: AMS UMR Background, cooling down
Was it worth the trouble?

ARCTAS, as above, no cryo

DC3 RF18, with cryopump @ 90 K

After 4 h of pumping, there is no change in background concentrations in the AMS with cryopump. This is very close to the (for aircraft campaigns) customary 3 h pumpdown. Hence, a cryopump enhanced AMS can guarantee consistent detection limits for almost the full flight.

But does it actually improve the ultimate detection limits of the instrument?

An attempt at apples to apples comparison...

Cryopump @ 250 K

Cryopump @ 90 K

UMR

HR
In summary...

- Integrating a cryopump is a worthwhile investment in any application where the AMS is needed <1 d after pumpdown (especially when measuring low concentrations, as in aircraft studies).
- Adds minimal complexity during operation. Cryopump needs to be switched on after turbos are up and defrosted back to 300 K before switching off the turbos (or regenerated periodically if run continuously in a lab).
- For non-time sensitive applications, it adds the benefit of higher particulate water sensitivity. Significant improvements are also seen for all other species, except organics.

Vaporization of ammonium nitrate in a PCI inlet

MS Zombies never die, they just retreat…
In the good old days, back when the User Meetings were much worse...

Middlebrook et al, first PCI inlet for the AMS

Ammonium Nitrate Evaporation?

- \(D_{\text{d,ma}}\) was 343 nm and \(D_{\text{v,ma}}\) was 10% lower with the PCI.
- More particles in the smaller mode (more crystallization/breakup?)
- Caveat – these two runs were done 8 months apart.
- Recent field experiments are inconclusive.
- This needs to be repeated (along with particle transmission).
- Additionally we found the Nitrate IE remains constant w/ upstream pressure.

After a long investigation, wrong mounting of the critical orifice (ie drill direction not in flow direction) was blamed for this.

A.D. 2012: Newish PCI with new plumbing

No matter what we did, we always got 2 modes in ptof
And since this was an aircraft study, a smaller slit chopper wheel was not an option
Strange Mass Ratio! (expected 5-6, in reality ≈2)

Plotting the IEs from analyzing each mode separately should roughly give you the mass ratio of both modes. If they were doubly charged particles, that means:

$$\frac{m_2}{m_1} \approx \frac{(2D_1)^3 C_6(2D_1)}{D_1^2 C_4(D_1)}$$

Less work to analyze, but equally telling are the PToF size of those modes and the ion signal size.

In cases such as this, trusting your own AMS size calibration is the way to go...

You did size calibrate your AMS at the beginning of your last field study, didn’t you?
Using an internal PFC standard for the HR-ToF-AMS

Some promising adventures….

Why use an internal standard?

Potential benefits of an internal standard:
- m/z calibration
- Determination of peak shape and peak width dependence (resolution)
- Monitor performance of thresholding algorithm and MCP sensitivity
- Absolute mass sensitivity standard

All of these are functions are performed in the AMS by the residual/differential air ions. This can lead to issues when:
- Accurate measurements over m/z 150 are needed
- There are external fluctuations in the AB
- No “good” ions are available for the task at hand (ie 40/28 for MCP performance)
- AB is not available (ie ACSM, hence the internal naphtalene standard)
Perfluorocarbons (PFCs) as MS standards

Typically, for general MS applications, perfluorocarbons are preferred as internal standards since:

- Few isotopes to deal with (except for $^{13}$C)
- Strong negative mass defect ensures little to no interferences in an instrument with decent resolution (dm/m > 1000) when analyzing other "regular" organic ions (but can be a problematic with some sulfates and other halogens)

External perfluorotetacosane ($C_{24}F_{50}$, MW 1238), introduced via aerosol lens.
- Not a true "internal" standard
- Hard to integrate into a field setup

A new candidate: FC-5311

- Chemical Formula $C_{14}F_{24}$, MW 624
- Liquid, 0.15 mbar vp @ RT
- Not a random mixture (like similarly inexpensive fomblin or pfk), hence reproducible signal ratios
- Unlike long chain alkylfluorides, very little intensity below m/z 131 (except for CF$_3$, m/z 69)
A few technical notes...

Similar setup as the ACSM napthalene standard, ie liquid reservoir behind a critical orifice, except as an external addition, so that

- Calibrant/orifice can easily be replaced
- Reservoir can be thermostated (not field tested yet)

Due to long inlet line, takes about 1d to equilibrate

A small orifice (1 um) is certainly advisable to get rid of evil cluster ions in your baseline….

Some noticeable improvements...

Pika Peak width: significant improvement for m/z between 50 and 200

Advanced ion threshold and transmission diagnostics!
What needs work …

Even the relatively mild temperature swings in the air conditioned BEACHON trailer had a significant impact on fluorine ion signal in the AMS. Running the calibrant reservoir at 37 C will improve this, we hope enough that inferring sensitivity becomes feasible.

At any concentration level that is workable for the AMS, there will be a significant interaction between the EI filament output and the calibrant vapor pressure. Both temperature control of the calibrant AND emission control of the filament output will help here…

HOWEVER: It remains to be seen if long term operation of the calibrant with a healthy filament is possible.

And two announcements

• A diagram and shopping list to replicate my “safe AMS venting scheme” (as discussed during the last AMS Clinic) is available under:
  [http://cires.colorado.edu/jimenez-group/ToFAMSResources/Hardware/Venting_Schematic.pdf](http://cires.colorado.edu/jimenez-group/ToFAMSResources/Hardware/Venting_Schematic.pdf)

• If you happen to use an RF ion guide instead of a lens stack for your particular flavor of HR-ToF, be aware that finding an optimal tuning is very different from a normal AMS (just “peaking your AB” WILL NOT WORK). I have some how-to’s for these, if you are interested please email me.