

## WP21- JRA2: D21.6 Final report on ACSM suitability for long-term measurements

### Summary:

This report summarises the submission of aerosol chemistry data from ACSM measurements from different stations to EBAS under the label of ACTRIS.

### 1. Introduction

Aerosol chemistry has so far been performed in networks only off-line based on filter analysis. Concerning the organic aerosol, only a sum parameter (total organic carbon, OC) has been determined on a regular basis. There has therefore been a long-standing need for data with higher time resolution and with more information on the organic aerosol than just OC.

This has become possible with recent advancements in mass spectrometry. The Aerosol Chemical Speciation Monitor (ACSM) is a new instrument which allows on-line measurement of the total mass and size distribution of non-refractory chemical composition of the submicron ambient aerosol (NR-PM<sub>1</sub>). It has the same quantification and speciation capabilities as the aerosol mass spectrometer (AMS), by also providing composition information for particulate ammonium, nitrate, sulfate, chloride, and organic mass concentration. However, it is designed to be simpler, smaller, lower cost and capable of autonomous operation, while still capable of delivering data with a time resolution of 1 hour. Through the statistical analysis of the mass spectra, also source apportionment of the organic aerosol has become possible.

### 2. Results

Within ACTRIS the performance and suitability of this instrument was assessed at the following sites: Mace Head, Cabauw, Melpitz, Hyytiälä, Finokalia, and Jungfraujoch. At each site, particulate ammonium, nitrate, sulfate, chloride, and organic mass concentration were measured, for a full year. This activity had a huge additional benefit on the European aerosol chemistry research community. A large number of additional institutions decided to contribute with their own funds to this ACTRIS activity. To facilitate the process, a website has been established by PSI, where the progress of these ACSM activities can be monitored: <http://www.psi.ch/acsm-stations/>.

Quality assurance was tested in many different ways. On the one hand, a document was started describing the best practices, which has continuously been updated (the version of 24 March 2015 is given in Appendix 1, while the latest version is found at <http://www.psi.ch/acsm-stations/acsm-best-practice>). This best practice document for ACSMs contains recommendations for operation of ACSM instruments within the ACTRIS network. The purpose of this document is to provide guidelines and standard operating procedures for data recording and treatment in order to ensure data quality and comparability.

On the other hand, an intercomparison was performed in Paris, which included 13 Q-ACSMs, 1 HR-AMS and 1xToF-ACSM. Results of the 13 Q-ACSMs from this intercomparison are given in Fig. 1. It is seen that rather good agreement is found between the individual instruments (Crenn et al., in preparation).

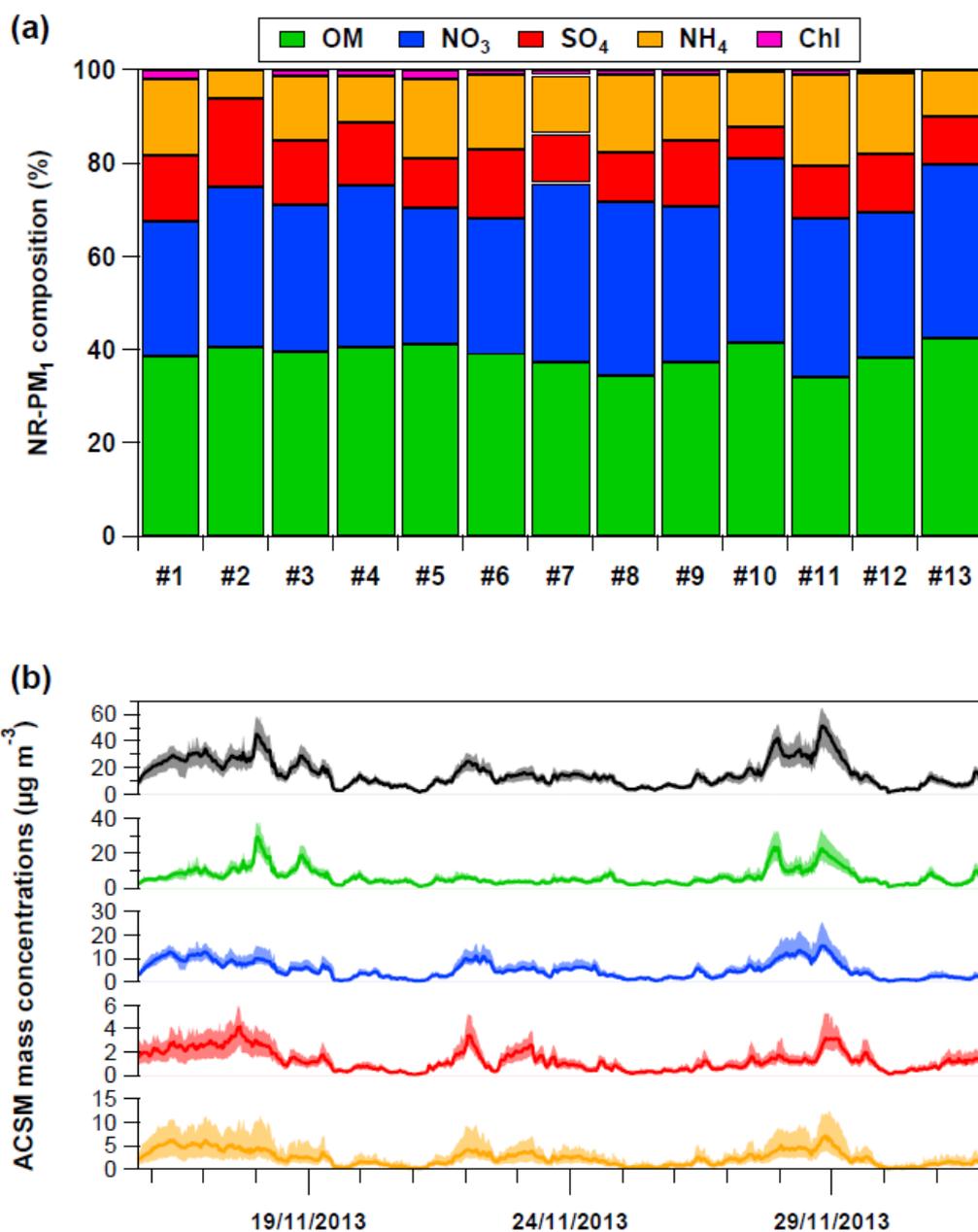


Figure 1: (a) Mean NR-PM1 relative chemical composition of 13 Q-ACSM measuring in parallel during the ACTRIS ACSM intercomparison campaign at SIRTA near Paris (FR). (b) Full time series of mass concentrations for all instruments. The thick line represents the median and the shaded area the range between min and max.

Moreover, the data of this intercomparison were also used to perform a source apportionment of the organic aerosol. As seen in Fig. 2, four sources were found from the data of all instruments, i.e., hydrocarbon-like organic aerosol (HOA), cooking-related organic aerosol (COA), biomass burning-related organic aerosol (BBOA) and secondary oxygenated organic aerosol (OOA); more details are found in Fröhlich et al. (2015). Again rather good agreement was found between all Q-ACSMs, as seen for the 13 Q-ACSMs (Fig. 2) or including all 15 participating instruments (Table 1).

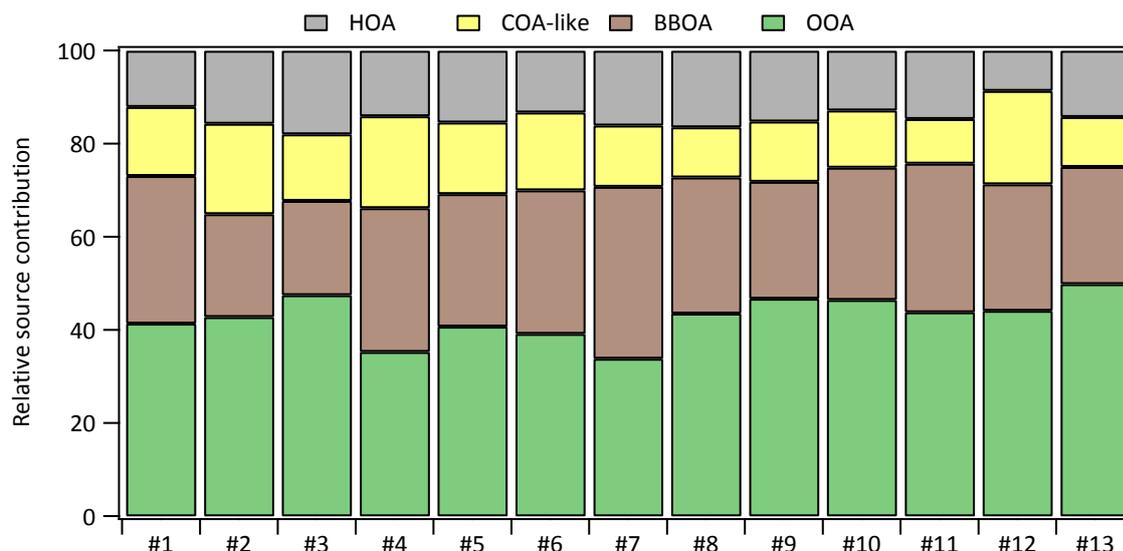


Figure 2: Relative source contributions to total OA retrieved by ME-2 source apportionment for 13 different Q-ACSM measuring in parallel at SIRTA near Paris (FR).

Table 1: Mean and median factor contributions including the first standard deviation of the OA sources (including 13xQ-ACSM, 1xHR-AMS and 1xToF-ACSM).

factor	median (%)	average (%)	SD (%)
HOA	14.7	14.3	2.2
COA-like	14.9	15.0	3.4
OOA	42.8	41.5	5.7
BBOA	29.2	29.3	5.0

To date (2015-03-26) data from 12 ACSM stations (11 x Q-ACSM, 1 x ToF-ACSM), including all six ACSM financed by the ACTRIS project (Mace Head, Cabauw, Melpitz, Hyytiälä, Finokalia, and Jungfraujoch) is available on EBAS (see Fig. 3). Several more data sets of associated partners have been promised and will be added in the coming months.



Figure 3: ACSM datasets available on EBAS server: Birkenes (NO), Hyytiälä (FI), Mace Head (IRL), Cabauw (NL), Melpitz (DE), Hohenpeissenberg (DE), Jungfraujoch (CH), Magadino (CH), Zürich (CH), Montseny (ESP), Montsec (ESP).

Overall, ACSM and AMS instruments were collecting data under the lead of ACTRIS at more than 35 different European sites over the course of three years. Site locations and corresponding measurement periods are listed in Fig. 4, showing an impressive data coverage. Most ACSM were operating for periods of one year and more.

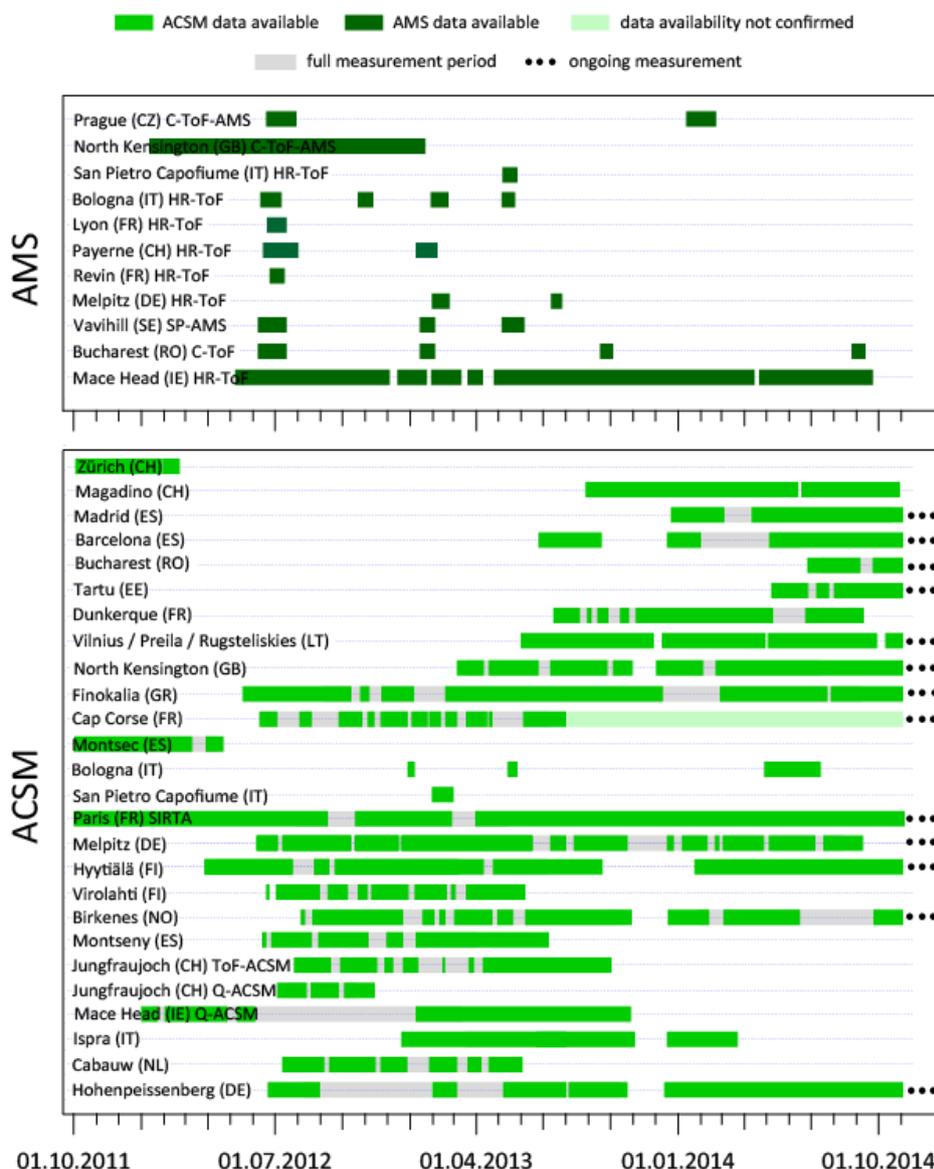


Figure 4: Full data coverage during ACTRIS project (from Oct 2011 to Oct 2014) demonstrating the suitability of the ACSM for routine long-term operation.

Currently, several publications dealing with the specific findings of the various sites are being prepared. In addition, a publication containing a comprehensive overview of the ACSM measurements during ACTRIS is in preparation by M. Bressi (JRC).

Journal publications containing ACTRIS ACSM data:

- Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Prévôt, A. S. H., Baltensperger, U., Schneider, J., Kimmel, J. R., Gonin, M., Rohner, U., Worsnop, D. R., and Jayne, J. T.: The ToF-ACSM: a portable aerosol chemical speciation monitor with TOFMS detection, *Atmos. Meas. Tech.*, 6, 3225-3241, doi:10.5194/amt-6-3225-2013, 2013.
- Petit, J.-E., Favez, O., Sciare, J., Canonaco, F., Croteau, P., Močnik, G., Jayne, J., Worsnop, D., and Leoz-Garziandia, E.: Submicron aerosol source apportionment of wintertime pollution in Paris, France by double positive matrix factorization (PMF2) using an aerosol chemical speciation monitor (ACSM) and a multi-wavelength Aethalometer, *Atmos. Chem. Phys.*, 14, 13773-13787, doi:10.5194/acp-14-13773-2014, 2014.
- Bougiatioti, A., Stavroulas, I., Kostenidou, E., Zampas, P., Theodosi, C., Kouvarakis, G., Canonaco, F., Prévôt, A. S. H., Nenes, A., Pandis, S. N., and Mihalopoulos, N.: Processing of biomass-burning aerosol in the eastern Mediterranean during summertime, *Atmos. Chem. Phys.*, 14, 4793-4807, doi:10.5194/acp-14-4793-2014, 2014.
- Pandolfi, M., Querol, X., Alastuey, A., Jimenez, J. L., Jorba, O., Day, D., Ortega, A., Cubison, M. J., Comerón, A., Sicard, M., Mohr, C., Prévôt, A. S. H., Minguillón, M. C., Pey, J., Baldasano, J. M., Burkhardt, J. F., Seco, R., Peñuelas, J., van Drooge, B. L., Artiñano, B., Di Marco, C., Nemitz, E., Schallhart, S., Metzger, A., Hansel, A., Lorente, J., Ng, S., Jayne, J. T., and Szidat, S.: Effects of sources and meteorology on particulate matter in the Western Mediterranean Basin: An overview of the DAURE campaign, *J. Geophys. Res. Atmos.*, 119, 4978–5010, doi:10.1002/2013JD021079, 2014.
- Ripoll, A., Minguillón, M. C., Pey, J., Jimenez, J. L., Day, D. A., Sosedova, Y., Canonaco, F., Prévôt, A. S. H., Querol, X., and Alastuey, A.: Long-term real-time chemical characterization of submicron aerosols at Montsec (southern Pyrenees, 1570 m a.s.l.), *Atmos. Chem. Phys.*, 15, 2935-2951, doi:10.5194/acp-15-2935-2015, 2015.
- Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haefelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, *Atmos. Chem. Phys.*, 15, 2985-3005, doi:10.5194/acp-15-2985-2015, 2015.
- Minguillón, M. C., Ripoll, A., Pérez, N., Prévôt, A. S. H., Canonaco, F., Querol, X., and Alastuey, A.: Chemical characterization of submicron regional background aerosols in the Western Mediterranean using an Aerosol Chemical Speciation Monitor, *Atmos. Chem. Phys. Discuss.*, 15, 965-1000, doi:10.5194/acpd-15-965-2015, 2015.
- Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévôt, A. S. H.: ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15

- individual, co-located aerosol mass spectrometers, *Atmos. Meas. Tech. Discuss.*, 8, 1559-1613, doi:10.5194/amtd-8-1559-2015, 2015.
- Zieger, P., Aalto, P. P., Aaltonen, V., Äijälä, M., Backman, J., Hong, J., Komppula, M., Krejci, R., Laborde, M., Lampilahti, J., de Leeuw, G., Pfüller, A., Rosati, B., Tesche, M., Tunved, P., Väänänen, R., and Petäjä, T.: Low hygroscopic scattering enhancement of boreal aerosol and the implications for a columnar optical closure study, *Atmos. Chem. Phys. Discuss.*, 15, 3327-3379, doi:10.5194/acpd-15-3327-2015, 2015.
- Stolaki, S., Haefelin, M., Lac, C., Dupont, J.-C., Elias, T., and Masson, V.: Influence of aerosols on the life cycle of a radiation fog event. A numerical and observational study, *Atmos. Res.*, 151, 146-161, 2015.

## **Appendix 1. ACSM Best Practices**

This document contains recommendations for setup, operation, maintenance and data analysis procedures for the Aerodyne aerosol chemical speciation monitor (ACSM). **It is intended as a supplement to the published ACSM DAQ and Igor manuals.** Information in this reference is drawn from the ACSM DAQ and Igor manuals, the Aerodyne ACSM website (<https://sites.google.com/site/ariacsm/home>), the ToF-AMS wiki page ([http://cires.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS\\_Main](http://cires.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS_Main)), ACSM user experiences, and discussion during the May 2012 ACSM meeting at PSI.

Last update: 24.03.2015

### **1. ACSM Resources**

*ACSM DAQ and Igor manual*

*Aerodyne's ACSM website*

<https://sites.google.com/site/ariacsm/home>

*ToF-AMS wiki page*

[http://cires.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS\\_Main](http://cires.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS_Main)

Site intended for ToF-AMS, but many issues are similar, e.g. collection efficiency, sampling line considerations, and instrument inter-comparison issues, and some operating/data analysis principles.

*ACTRIS campaign website*

<http://www.psi.ch/acsm-stations/>

### **2. Inlet and Sampling Lines**

*Construction of sampling system*

The complete sampling system should be diagrammed, including sampling line lengths, diameters, materials, and flow rates.

*Sample flow controller accessory (Aerodyne)*

Several of the issues below (cyclone, pump/flow rate measurement) are facilitated by the sample flow controller accessory available from Aerodyne.

*PM<sub>2.5</sub> Cyclone on sampling inlet*

Reduces clogging of the ACSM critical orifice and prevents transmission of large, high-mass particles. **PM<sub>1</sub> cyclones should be avoided** because the PM<sub>1</sub> size cut is then applied twice (at cyclone and at ACSM inlet). Further, a PM<sub>1</sub> cyclone may introduce an RH-dependent transmission function.

### *Construct sampling lines from stainless and/or copper tubing*

Conductive tubing materials reduce particle losses. Critically, **black conductive tubing (e.g from TSI) should not be used**, because this can cause siloxane contamination of the mass spectrum, including at m/z 73 (an important marker for biomass burning). Stainless steel is ideal for long-term sampling. If copper is used, lines should be periodically checked for corrosion.

### *Line losses and leaks*

Residence time in the sampling lines should be limited to reduce diffusive particle losses. This can be accomplished with (1) a pump (e.g. split from the Nafion dryer pump below) and/or (2) connecting other instrumentation (e.g. SMPS) near the ACSM inlet. Required flowrate depends on sampling lines, generally 1 to 10 L/min up to the dryer inlet. This flowrate should be continuously monitored and recorded.

The combination of tube width and sampling flow should be selected to maintain laminar flow ( $Re < 1000$ ) to avoid particle losses from turbulent flow.

Important to test sampling line for leaks (e.g. filter on or near sampling inlet).

### *Nafion dryer*

ACSM bounce collection efficiency is affected by relative humidity in ways that are difficult to predict. Note that it is the RH at the ACSM inlet that matters, not the ambient RH, and thus this effect is also influenced by outdoor/indoor temperature gradients. It is **strongly recommended to dry the sampled aerosol** (25 to 50% RH) before the ACSM inlet. This allows the collection efficiency to be estimated from the particle composition, and also facilitates comparisons with co-located instrumentation (e.g. SMPS).

Nafion dryers are preferred over silica gel dryers because they require less maintenance (silica gel dryers may require daily gel changes). The dryer should have a metal casing to reduce charged particle losses. The PermaPure MD series dryers work well:

<http://www.permapure.com/products/dryers/md-gas-dryers/>

The aerosol should be plumbed through the inner path, and a pump with critical orifice connected to the outer path to reduce the outer path pressure to  $\sim 0.1$  atm. When connecting the inner path, care should be taken with the fittings to avoid breaking the internal seals on the Nafion membrane, introducing a leak to atmosphere. This can be checked by placing a filter at the dryer inlet and measuring zero particles at the dryer outlet with a CPC.

More information on dryer setup and operation is available at:

[http://cires.colorado.edu/jimenez-group/wiki/index.php/Field\\_ToF-AMS\\_Operation#Dryer\\_Set\\_Up](http://cires.colorado.edu/jimenez-group/wiki/index.php/Field_ToF-AMS_Operation#Dryer_Set_Up)

## **2. Spare parts and support equipment**

On-line uninterruptible power supply (UPS, 2000 kV)

Servo motor for inlet assembly

Filter for valve body assembly. Filter should be changed when a pressure drop is observed across the filter (see diagnostics plot in ACSM analysis software).

SEM (monitor the required voltage as a function of time to anticipate failure).

Filaments (2 sets of 2). At any time, 2 filaments are installed in the instrument. Should compare their performance after installation.

Critical orifice

Turbo pump

Diaphragms for backing pump and tool for changing diaphragms

Part numbers can be found at:

<https://sites.google.com/site/ariacsm/support-information>

### **3. Maintenance/Calibration Schedule**

**Continuously monitor instrument flowrate, signals for m/z 28, and turbo pump speeds/currents/temperatures.** Stability of these parameters generally indicates stable ACSM operation. However, it is still advisable to regularly perform calibration/maintenance activities, particularly for a new instrument, at the beginning of a new deployment, or following venting of the instrument. For an instrument for which long-term stability has been confirmed, the calibration schedule can be reduced.

#### *Daily*

Monitor inlet pressure (~flowrate), m/z 28 and naphthalene signals. Significant changes indicate maintenance is needed.

Monitor turbo pump speeds, currents, and temperatures. This helps to anticipate pump failure.

#### *2x per week*

Check and record detector amplification (use N2 signal as reference: 1e-7 amps), adjust if needed (if change >15%).

Detector amplification should be checked on a daily basis if possible at the start of a campaign or after venting the instrument, until stable operation is observed. For new instruments the detector voltages have to be adjusted more frequently.

#### *Every month (or as needed; this is highly site-dependent)*

Clean dust from turbo pump fan filters & fan in the Prisma head.

Check flow rate, clean orifice with isopropanol, check flow rate again.

#### *Every 2 months*

IE calibration with ammonium nitrate & RIE calibration with ammonium sulphate. This should be done more frequently (weekly) at the start of a campaign or after the instrument has been vented, until stable results (i.e. airbeam to IE ratio) are obtained.

*Every 3 months*

Collect data with (1) valve closed to check background (2) valve open with filter in-line. Several data points are needed, suggest collecting for at least 1-2 hrs at 15-min time resolution.

Check inlet pressure with valve open and closed to evaluate vacuum/pumping integrity.

Keep DAQ software updated (~6 months or following crucial update). DAQ is available from Aerodyne's ACSM users' site.

*Other*

Evaluate stability of m/z calibration and resolution. Normally this is stable, but should be individually confirmed.

**4. Calibrations***Flow calibration*

**Critical to record the ambient pressure and temperature at which flow calibration is performed.**

Necessary to adjust critical orifice size if instrument is operated at altitude.

*Ionization efficiency*

All IE calibrations should be immediately preceded by tuning of detector voltage and heater bias voltage.

It is important that the  $\text{NH}_4\text{NO}_3$  calibration solution not be more concentrated than recommended (5 mM) to avoid artifacts from multiply-charged particles.

Confirm that particles are **dried** before size-selection.

Measure ions for  $\text{NO}_3^+$  (m/z 30, 46),  $\text{NH}_4^+$  (15, 16, 17), and air. These are the standard settings if the custom scan file for calibration with  $\text{NO}_3\text{NH}_4$  from the Aerodyne ACSM webpage are used. For calibration with ammonium sulphate use the respective custom scan file also available on the Aerodyne webpage.

Ratio of m/z 28 to IE should be **logged and monitored**. This serves as a reference point for sensitivity corrections during data analysis.

*Relative ionization efficiency*

$\text{SO}_4^{2-}$ : Should be measured immediately following an IE calibration, where the RIE of  $\text{NH}_4^+$  has just been calculated from mass balance between  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . Nebulize  $(\text{NH}_4)_2\text{SO}_4$  and sample with the ACSM. The RIE of  $\text{SO}_4^{2-}$  can then be calculated from mass balance with  $\text{NH}_4^+$ , since  $\text{NH}_4^+$ 's RIE is known. This method is not biased by particle bounce.

Make sure, that the ammonium nitrate calibration is performed before the ammonium sulphate calibration. For the calibration with ammonium sulphate start with small concentrations and increase

slowly. Due to partly slow evaporation of ammonium sulphate hysteresis effects can influence the calibration if done otherwise.

Methanesulfonic acid (MSA): It is advisable to calibrate for MSA if sampling near the ocean. This species has been observed in previous ACSM/AMS measurements but the RIE is not well known.

## **5. Operation and analysis**

### *Sampling time*

30 minute time resolution is generally recommended (e.g. 1 open 1 closed 28 sets at 200ms/amu). Maximum of 1 hr for sites with very low concentrations. 15 minutes can be very helpful if local sources are important. Note that short sampling times can easily be re-gridded during post-analysis to generate longer averages if signal-to-noise is problematic.

### *Collection efficiency (from particle bounce)*

Uncertainties due to bounce collection efficiency ( $E_b$ ) can be **greatly reduced** by installing a Nafion dryer as discussed above.

Bounce collection efficiency should be estimated using the composition-based estimate given in Middlebrook et al. (2012). Further investigation by comparison with external instruments (e.g. SMPS) is strongly recommended. Note that the Middlebrook et al. method was developed using AMS data, but applies equally to the ACSM. It requires (1) an estimate of the ammonium detection limit, and (2) when ammonium is below detection limit, an estimate of minimum collection efficiency ( $E_b = 0.45$  is recommended).

Middlebrook, A.M., Bahreini, R., Jimenez, J.L., and Canagaratna, M.R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, *Aerosol Sci. Technol.*, 46, 258-271, doi:10.1080/02786826.2011.620041, 2012.

[http://cires.colorado.edu/jimenez/Papers/2011\\_AST\\_Middlebrook\\_CE.pdf](http://cires.colorado.edu/jimenez/Papers/2011_AST_Middlebrook_CE.pdf)

When investigating collection efficiency by comparison with co-located instruments, care should be taken to assess assumptions/approximations used to perform such inter-comparisons! Note also that other instruments have their own uncertainties, and disagreements with the ACSM may not necessarily be due to collection efficiency. **Collection efficiency should not be a catch-all for disagreements between instruments!**

A few points relating to comparisons of ACSM with SMPS (or similar instruments):

- (1) Particles should be dried for both instruments
- (2) Transmission ranges of the ACSM and SMPS should be synchronized, especially at large particle sizes (can be done during SMPS analysis, as long as the large-size SMPS cutpoint exceeds that of the ACSM)

- (3) Refractory species (black carbon, dust, sea salt, etc.) must be negligible or measured by other methods with comparable size transmission.

#### *Sensitivity/gain corrections during analysis*

Recommended to use m/z 28 signal (rather than naphthalene) for gain/sensitivity corrections due to better signal-to-noise. Recommended m/z 28 reference value =  $1 \times 10^{-7}$  amps.

#### *Post-Analysis (PMF, ME2, etc.)*

Filter outliers/bad points out of data before analysis (e.g. using continuously monitored data in section 3).

#### *Fragmentation diagnostics*

Org44 vs. Org43: Org44 has potential air interferences, while Org43 is an approximate (interference-free) surrogate for total organics. The Org44/Org43 plot should have an intercept at the origin. Otherwise fragmentation tables may need adjustment.

Nitrate and sulfate diagnostics: Check for (1) linearity; (2) intercept at origin. If these criteria are not met, fragmentation tables may require adjustment. Older versions of the DAQ software may have some nonlinearity (especially for nitrate) due to detector settings; fixed in newer software.

#### *PMF Matrix*

Use software version 1.5.3.5 or newer to create PMF matrices (older versions have bugs in the calculation of the error matrix).

PMF matrices should not include m/z > 120 because of large ion transmission corrections and naphthalene interferences.

The dwell time requested by export routine is the total integration time for a single m/z within a single saving interval (i.e. can include multiple scans of the mass spectrum). It is calculated as:

Dwell time = (number of MS scan sets) \* (integration time for 1 m/z in 1 scan) \* (stick integration width)

Where:

1 MS scan set = open MS + closed MS

Integration time for 1 m/z in 1 scan is determined from scan speed setting in DAQ

Stick integration width = 0.1 amu (written in procedure as 2\*ka\_amu\_window)

Recommendations for ACSM PMF analysis can be found in:

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijälä, M., Alastuey, A., Artiñano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-

Estève, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prévôt, A. S. H.: ACTRIS ACSM intercomparison – Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, *Atmos. Meas. Tech. Discuss.*, 8, 1559-1613, doi:10.5194/amtd-8-1559-2015, 2015.