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COLOSSAL
CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL

Quadrupole Aerosol Chemical Speciation Monitor (Q-ACSM)

Standard Operating Procedure

Version May 2021

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1. PREAMBLE

This document provides some recommendations for the use of quadrupole-type Aerosol Chemical Speciation Monitors (Q-ACSM) developed by Aerodyne Research Inc. (ARI) for the measurement of the chemical composition of non-refractory submicron particles (NR-PM_1), and more recently of non-refractory particles with aerodynamic diameter below 2,5µm (NR-$PM_{2.5}$).

It is intended to provide key information and good practice relating to operating parameters, maintenance frequencies, as well as data validation steps to be respected.

The reader is also strongly encouraged to refer to the manual supplied by the manufacturer and/or by the distributor for information about the operation of the instrument.

These standard operating procedures were prepared based on documentation and information provided by ARI and its French distributor (ADDAIR) as well as the state of the scientific art and good practice shared in the context of the European Aerosol, Clouds and Trace gases Research InfraStructure (ACTRIS, www.actris.eu), the European COST Action CA16109 for Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL (COLOSSAL, www.costcolossal.eu), and feedback from ACSM operators within French regional monitoring networks.

Information provided herewith reflects consensual agreements reached within these research communities by the time the first version of the present document has been edited in May 2021. A revised version might bring additional and complementary information on a later stage.

How to cite:

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2. DOCUMENTATION AND RESOURCES

Website of the manufacturer Aerodyne:

https://support.aerodyne.com/

User manuals in English for Igor and the data acquisition software DAQ can be downloaded from this website. It is also possible to download useful software for the proper functioning of the instrument (Igor function, pump software, dryer software).

Software:

- DAQ: ACSM driver software
- Igor (Wavemetrics): scientific software for data processing and user interface with the instruments
- Igor Function “ACSM_Local”: raw data processing module
- VS_PumpStats_Pfeiffer: pump driver software.

Website of the University of Colorado and of the Paul Scherrer Institute:

http://cires.colorado.edu/jimenez-group/wiki/index.php?title=ToF-AMS_Main

https://www.psi.ch/acsm-stations/

These sites give very useful information for operating “Aerosol Mass Spectrometer” (AMS) type instruments, including the ACSM, particularly concerning collection efficiency, installation of the sampling line, and data treatment methodologies.

3. INSTALLATION OF THE ACSM ON SITE FOR LONG-TERM OBSERVATIONS

3.1. Sampling system

3.1.1. Cut-off diameter of the sampling line

It is recommended to use a cyclone upstream from the ACSM's sampling line. This cut-off diameter limits obstruction of the critical orifice at the inlet of the ACSM by preventing large particles from passing through. The cyclone cut-off diameter should be higher than the size fraction under investigation to avoid the particle cut-off to be applied twice: once at the sampling line's inlet and again at the inlet of the ACSM.

The $PM_{2.5}$ cyclone recommended by the manufacturer (URG-2000-30ED) is compatible with a PM_1 ACSM sample flow rate of 3 l/min. When using this cyclone upstream from a $PM_{2.5}$ ACSM, the sample flow rate should be reduced to 2 l/min. Otherwise, ensure that the cut point of the cyclone is greater than the cut point of the ACSM lens and the flow rates are in agreement with section 3.1.3.

3.1.2. Sampling line materials

It is recommended to use a sampling line made of a conductive material (stainless steel, copper) in order to reduce particle losses. The use of a stainless-steel line is ideal for long-term observations. The long-term use (i.e. several years) of an annealed copper line must be checked regularly due to potential oxidation.

Flexible black tubes with an interior conductive carbon coating must not be used as they can contaminate the measurement, especially m/z 73 fragment, which is also a marker of biomass burning aerosols.

3.1.3. Flow rate in the sampling line

The ACSM has an internal sample flow rate of around 0.08 l/min, which is fixed by a critical orifice at the inlet of the vacuum chamber.

This flow rate is too low to ensure accurate sampling of ambient air through a sampling system that is several meters long. Consequently, the primary flow rate must be higher to reduce the residence time and, consequently, particle loss through diffusion. An external sampling pump must be used to regulate the flow in the sampling system, at a flow rate consistent with the cyclone as described in section 3.1.1.

The flow rate and sample tube diameter must be adjusted so that the flow remains laminar in the line (Reynold's number Re <2000), which limits losses through diffusion. For example, rates of 1 and 10 l/min passing through a 3/8''-diameter line induce Reynold's numbers Re equal to 922 and 92 respectively, which correspond to a laminar flow in both cases.

The flow rate in the line can generally be set between 1 and 10 l/min as long as the expected cyclone cut-off diameter is respected. However, it should be noted that the split from the ½ inch sampling line to the 1/8 inch inlet tubing at the ACSM inlet is designed to be isokinetic at 3 l/min, so that the latter flow rate is highly recommended here.

The sample flow should be continuously recorded to monitor stability.

The length of sample lines should be minimised. To avoid condensation in the sample line ahead of the dryer, especially when hot / humid air enters an air-conditioned room, the distance between the dryer and the outside should be minimised and / or well insulated.

Finally, it is important to ensure that there is no leak in the sampling system. This can be checked by placing a HEPA filter at the inlet of sampling line and/or by verifying the correspondence of the flow measured both sides of the sampling line.

3.1.4. Drying the collected air

The ACSM sampling line system should routinely be maintained at a relative humidity between 20% and 60%. Principally because collection efficiency (CE) is impacted by the water content of the aerosol that is difficult to predict.

Nafion® membrane dryers are recommended over dryers with silica beads as they require less maintenance. The dryer must have a metallic casing to reduce the loss of charged particles. Recommendations for drying particles are found here: http://www.wmo-gaw-wcc-aerosol-physics.org/files/actris-recommendation-for-aerosol-drying.pdf.

The manufacturer offers a Nafion® dryer which enables all of its parameters (i.e. relative humidity, temperature, dryer's inlet pressure, dryer inlet/outlet differential pressure, and dryer sheath pressure) to be recorded. It functions with a pump which also controls the sample flow (section 3.1.3) as well as the reverse flow in the dryer. It is recommended to compare the humidity sensors on this dryer with a reference sensor annually.

3.1.5. Estimating losses from the sampling line system

As with other instruments that measure the characteristics of aerosols, the losses in the sampling system should be evaluated, taking into account parameters such as the length and diameter of the line, the sample flow, the presence of kinks, the presence of a dryer, etc.). These losses can be modelled with IGOR using the PLC tool (free download available at: http://www.mpch-mainz.mpg.de/~drewnick/PLC/).

Nevertheless, losses in the lines are minimised by following the recommendations described above, specifically avoiding kinks in the sampling line, ensuring a laminar flow in the line and using metallic tubing.

3.1.6. Sampling frequency

Usually, the Quadrupole ACSM are run in ambient air with a time resolution of about 30min (corresponding to 28 sets of 1 open followed by 1 closed measurement scan, at 200ms/amu).

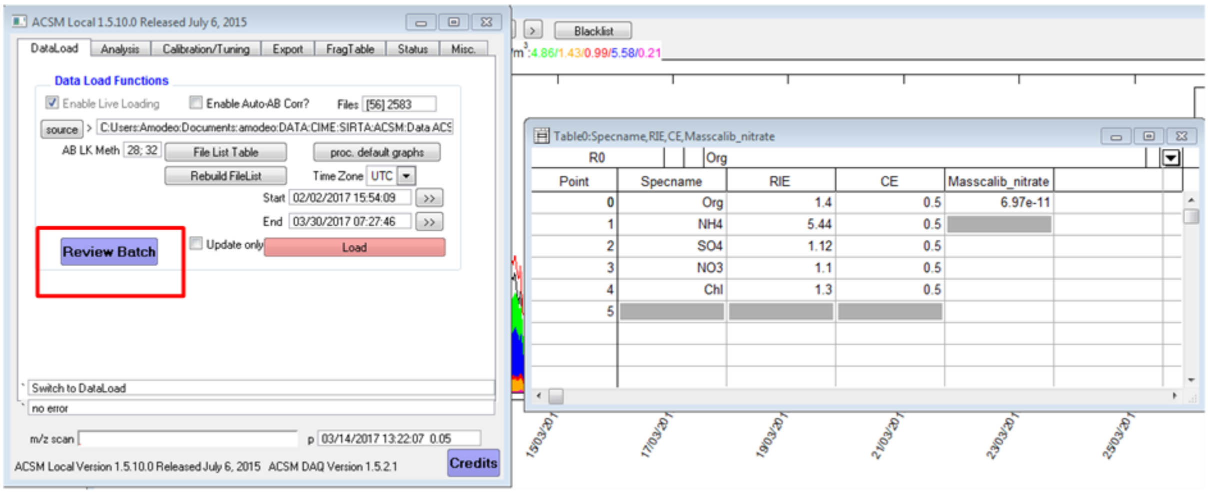
This time resolution may be set to approximately 1h at remote sites displaying very low concentrations. Note that short sampling times can also be re-gridded during post-analysis to generate longer averages if signal-to-noise appears to be too low.

Conversely, a 15min time resolution (or higher) may be better suited when substantial emissions from local sources are expected (e.g., traffic sites).

3.2. “ACSM-local” software

The correct configuration of “ACSM_local” software is necessary to ensure the valid operation of the instrument. This needs to be undertaken periodically and following any system change (e.g. after rebooting), as follows:

- Set RF and RIEs values coherently with results obtained from the last accurate calibration(s) (section 5)
- Set a default Collection Efficiency (CE) value, such as CE=0.5 in case of standard vaporizer and CE=1 in case of capture vaporizer.



ACSM Local 1.5.10.0 Released July 6, 2015

☑ Enable Live Loading
☐ Enable Auto-AB Corr?
Files [56] 2583
source > C:Users:Amodeo:Documents:amodeo:DATA:CIME:SIRTA:ACSM:Data:ACS
AB LK Meth 28; 32
Time Zone UTC
Start 02/02/2017 15:54:09
End 03/30/2017 07:27:46
☐ Update only
Switch to DataLoad
no error
m/z scan
p 03/14/2017 13:22:07 0.05
ACSM Local Version 1.5.10.0 Released July 6, 2015 ACSM DAQ Version 1.5.2.1

m³:4.86/1.43/0.99/5.58/0.21

Table0:Specname,RIE,CE,Masscalib_nitrate

Point	Specname	RIE	CE	Masscalib_nitrate
0	Org	1.4	0.5	6.97e-11
1	NH4	5.44	0.5	
2	SO4	1.12	0.5	
3	NO3	1.1	0.5	
4	Chl	1.3	0.5	
5				

Figure 1: “ACSM_local” software, setting-up RIE, RF and CE values

It is also important to note that these parameters can be updated a posteriori, when reloading and reprocessing raw data files (*.itx) within the "ACSM_local" software (section 6). Therefore, if an erroneous calibration data entry is identified, it is possible to reprocess the data as long as the validation of the technical parameters presented in section 4 is achieved.

3.3. Other recommendations

The ACSM requires 300W of power and operates on 85-264 VAC, 47/63 Hz. An inverter (for example, an uninterruptible power supply (UPS), 2000kV) is recommended in order to protect the instrument from unexpected electrical interruptions. If power is lost to the instrument, venting can be avoided using an automatic shutdown device; this monitors the AC power through an AC/DC converter connected to the same circuit as the UPS (but not the UPS itself) and trigger a timer to shutdown the system if power is not restored in a certain (user configurable) amount of time.

It is imperative that the ACSM is installed in an air-conditioned environment to prevent the turbo pumps or the Prisma detector from failing due to overheating. The maximum operating temperature indicated by the manufacturer is 33°C and the station temperature should be stable and maintained below 25°C. Avoid direct flow of AC system onto the instrument or sampling line (see section 3.1.3 on insulating the sample line which is especially relevant if the AC flow cannot be redirected). The turbo pump and Prisma detector ventilators should be cleaned once a year to avoid cooling problems.

Finally, the ACSM should be connected to the Internet to allow remote access control of the instrument (e.g. via TeamViewer) and to collect data.

4. SERVICING, CHECKS AND MAINTENANCE

4.1. Synthesis of ACSM Diagnostics and Actions

The following table (Table 1) summarises the parameters that influence whether the ACSM functions properly and how frequently these parameters should be checked by the operator. Respecting these checks and maintenance operations enables optimisation of the operating rate and maximizes the quality of available data.

Table 1: Summary table of checks and maintenance

Check and/or maintenance points	Frequency	Requirement		Action in case of non-conformance with the requirement
		PM_1	$PM_{2.5}$	
Verification that the acquisition software or the PC is not "frozen"	Daily	The scanning bar, visible in the DAQ software or in Igor, must be moving. The graphics in Igor and the voltages on the DAQ must be updated.		Reboot the Prisma, then PC and the software
Aerodynamic lens pressure (inlet pressure) in DAQ	Daily	Stable 1.3 ± 15% torr valve open	Stable 3.3 ± 15% torr valve open	Clean the critical orifice, see section 4.2.1. Verify that the pumps (turbo and primary) are working properly within established parameters (these differ for different pumps). Note: these values will also differ at high altitude locations and different critical orifices may be required in these locations.
		0.04 ± 0.04 valve closed		
Vaporizer voltage	Daily	Initial set point		See section 4.2.2
Airbeam	Daily	Must be stable at 10^{-7} (± 15%) amps		Check SEM voltage on, if so tune, see section 4.2.3
SEM voltage	Daily	Activated (ON)		Turn on and tune, see section 4.2.4
Filament emission	Daily	1mA ± 5%		Turn on the filament or change if broken
Concentrations (NO_3, NH_4, SO_4, Org)	Daily	Must be primarily positive (>± LOD)		Long term zero concentrations must lead to an investigation (valve, filament, voltage, acquisition tuning…) Systematically negative concentrations can be caused by an inversion of the particle filter valve see section 4.2.5
Turbo and MD1 pumps	Daily	Correct power and temperature (dependent on pump #)		Investigation, turbo pumps issues can be caused by a leak in the vacuum chamber, fan etc. MD1 pump issues may be due to the diaphragm which can be replaced.
Dryer	Daily	RH 20 - 60%		Verification of the flow rate, integrity of the Nafion® membrane and pump, see section 4.2.6
MD1 backing pressure	3-6 months / every visit	Backing pressure should be ±10% of last check		Change diaphragm or pump
Flow rate of the sampling system	Each visit (or remotely)	Stable and equal to 3 l/min (±0.3 l/min)	Stable and equal to 2 l/min (±0.3 l/min)	Verification of the pump and sample line integrity, see section 4.2.7

Check and/or maintenance points	**Frequency**	**Requirement**		**Action in case of non-conformance with the requirement**
		PM_1	**$PM_{2.5}$**	
	6 months	Check 3 l/min (±0.3 l/min) using independent flow meter	Check 2 l/min (±0.3 l/min) using independent flow meter	Investigate leaks, pump performance
Instrument Blank / Leak Check	6 months or whenever changes are made to the sample line	Install HEPA filter on instrument inlet. Concentrations must be close to the instrument's detection limits (< ± 0.5 µg/m^3)		Concentrations must be close to the instrument's detection limits. Investigation (leak, nafion, vacuum problem, clogged filter …), see section 4.2.8
Reset PrismaPlus baseline	6 months / post SEM replacement	Reset baseline to avoid negative error matrix		See section 4.2.9
Cleaning of the critical orifice	6 months	Clean critical orifice		
m/z calibration	6 months or whenever RF calibration	Check prisma resolution and mass-to-charge (m/z) calibration		Check m/z 28 and m/z 128, see section 4.2.10 Note: m/z calibration before RF calibration
Heater bias voltage	6 months / coincident with calibration / filament change	If checking – within 1V of previous value. Post filament change - tune		Note: post filament change check daily for 1 week and retune once stable, see section 4.2.11
Cleaning the cyclone	6 months or more often in dirtier / more corrosive locations	Cleaning similar to other automatic PM measuring systems with DI water and detergent if required.		
Cleaning the sampling line (from head to the lens)	1 year	Cleaning similar to other automatic PM measuring systems		

Check and/or maintenance points	Frequency	Requirement		Action in case of non-conformance with the requirement
		PM$_1$	PM$_{2.5}$	
Cleaning of pumps' and detector's fans	1 year	These include fans (electronics box, pump1, under prisma, internal to prisma)		Note: may be required more often depending on environment
Replacement of the particle filter	1 year	Preventive replacement, pressure difference should be less and 0.01 Torr between open and closed		
Replacement of the three-way valve	2 years	Preventive replacement		Note: it is recommended that a spare servo is kept and replaced when needed.
Change turbo pump lubricant reservoir	4 years	https://support.aerodyne.com/knowledgebase/articles/KA-01144/en-us		

4.2. Description of main ACSM Diagnostics and Actions

4.2.1. Aerodynamic lens pressure (inlet pressure)

The inlet pressure corresponds to the air flow entering into the ACSM and differs for PM_1 and $PM_{2.5}$ instruments. When the inlet valve is open, this parameter must be between 1.3 ±15% Torr for PM_1 and 3.3 ± 15% Torr for $PM_{2.5}$ in DAQ so as to obtain a sample flow rate in the instrument equal to 0.08 ± 0.015 L/min. When the valve is closed, this parameter drops to a value of approximately 0.04 ± 0.04 Torr. The inlet pressure also varies with atmospheric pressure and can be compared to the variation in atmospheric pressure (available in the dryer output parameters) when troubleshooting.

A gradual or sudden decrease in pressure when the valve is open corresponds to a decrease in the ACSM inlet flow, most often caused by a partial or complete blockage of the critical orifice and is typically returned to normal operation by cleaning (see user manual). An increase in pressure, in particular when the valve is closed, can often be caused by a leak. It is also possible that there is a blockage in the sample line.

4.2.2. Vaporizer

The recommended value of this parameter is 600 (±30°C) for a tungsten vaporiser and 550 (±30°C) for a capture vaporiser. It can be controlled by varying the vaporiser set voltage (Set V) in the DAQ "ionizer settings" menu. If temperature is >650 °C adjust voltage to bring down to 600°C.

A temperature that varies too significantly from its recommended value will induce a modification of the fragmentation processes of the analysed species and thus a bias in the calculation of the concentration of these species (i.e. invalidating of the fragmentation table used for this calculation).

Turning off the vaporiser set voltage will bring about a sudden drop in its temperature, leading to a decrease in the vaporisation of chemical species, starting with the least volatile (Org and SO_4). These species' signal will consequently become almost zero. An ammonium nitrate signal can still persist because it is very volatile.

A significant variation in vaporiser temperature typically indicates that the connection between the temperature sensor (thermocouple) and the vaporiser has weakened or broken. In rare cases it can also be due to an issue in the electronics box.

It is important to note that, according to the manufacturer, the voltage-to-temperature relationship does not vary over time. Therefore, unless the vaporiser has been replaced, **the temperature set voltage should be set at the value initially configured** and found in 'Performance and Calibration' file shipped with your instrument typically titled 'XXX_XXX_performance_and_calibration.odp' and found on the desktop or in a subdirectory of C:\ACSM.

4.2.3. Airbeam (N_2^+ signal)

The Airbeam is the measured signal in amps of m/z=28 in the mass spectrum while the switching valve is in filter position. This is predominantly from N_2^+ from atmospheric N_2. This value is taken as a reference to correct for variations in the ACSM's flow rate as well as changes in instrument sensitivity, typically due to a decrease in the detector effectiveness.

The Airbeam reference value is 10^{-7} amps. This value is controlled by adjusting the SEM voltage of the Prisma detector following the tuning procedure described in the user's manual. This tuning must be done before a calibration. It must be also be done when the value has decreased by more than 15 % from the reference value. It can also be low if the SEM voltage has been switched off.

During data processing, the concentrations measured by the ACSM are corrected, linearly, from the Airbeam variations around its reference value. If the Airbeam deviates more than 30% from its reference value, correction may no longer be valid and the data should be investigated to ensure consistent response. If the deviation is due to drift (SEM), rather than flow, then it may be possible to correct the data with some confidence.

A low value from the Airbeam can be due to a closed inlet valve, a blocked critical orifice, or the SEM detector or filament's power being off. In "acquisition" mode, do not forget to activate the Airbeam's correction function in the tab "time series correction".

4.2.4. SEM Voltage

This parameter corresponds to the voltage applied to the electron multiplier (SEM). There is no set reference value for this parameter. At a constant voltage, the SEM efficiency decreases with the duration that the instrument is in operation, in particular when it is new, thus inducing a decrease in the Airbeam's signal over time.

A drop in the Airbeam can also be linked to a drop in the air flow entering into the ACSM (blockage of the critical orifice) or the filaments being switched off. Before calibrating the SEM's voltage, first verify the inlet pressure (which corresponds to the flow entering into the ACSM) and that the filament is functioning properly.

The SEM voltage must be increased with caution to avoid the rapid deterioration of the SEM (i.e. by increments of maximum 100 Volts). The SEM linearity is ensured up to 3000V according to the manufacturer.

SEM voltage should be tuned before calibration and checked periodically as described in section 4.2.3.Filament emission

The reference value for the filament emission is 1 mA. It should be verified that the real average value varies in a range of the order of ±5%.

This parameter does not degrade; rather it falls to zero when the filament is broken or when the reference voltage has been stopped. If the filament stops, so will ionisation, which corresponds to a significant decrease in the Airbeam and the concentrations detected by the ACSM.

4.2.5. Switching Valve

The switching valve is a servo-actuated 3-way valve that changes the sample entering the ACSM vacuum system between particle-laden air and air that has passed through a particle filter. The instrument is typically configured so the valve switches every 30 seconds. The servo lifetime is variable from system to system, but typically needs to be replaced every two years.

The two most common symptoms of a switching valve issue are: 1. Measured mass loadings are noise about zero which indicates that the valve is stuck in one position, typically because of a failed servo motor 2. Measured pressure between sample and filter position are dramatically different indicating that one of the two positions is not correct. In early versions of the ACSM with electronics board revisions below 7.1, running with a damaged servo for prolonged periods could lead to damage to the electronics. Newer instruments include a fuse in the valve control circuitry which may need to be replaced if a servo motor fails.

4.2.6. Dryer

Drying the particles before measurement is important because the concentration measured by the ACSM is dependent on humidity. Calculation of the corrected collection coefficient according to the method proposed by Middlebrook (CE_dry) considers particles that were first dried. The "Middlebrook method" indicates that the maximum relative humidity is difficult to predict and thus recommends effectively drying the aerosols upstream from the ACSM. Full details are in section 6.2.4.

A relative humidity at the dryer exit of 20-60% is recommended, this should be logged at 5 min. intervals.

4.2.7. Pump operation

The software that monitors the pumps displays the rotation speeds, power and operating temperatures. The rotation frequencies are equal to 650, 1500 and 1000Hz respectively for the three turbo-pumps. The software also allows one to record these parameters in a log. The default log is the following: « c:\ACSM\PumpData.txt ». These parameters should be recorded at 5 to 10 min intervals. These data can be used in the event of an investigation.

4.2.8. Instrument Blank / Leak Check

Place a HEPA filter on the sample inlet and measure in “acquisition” mode for minimum 3 hours. Concentrations must be close to the instrument’s species dependent detection limits (see section **¡Error! No se encuentra el origen de la referencia.**). It may be useful to have a CPC in line for added sensitivity.

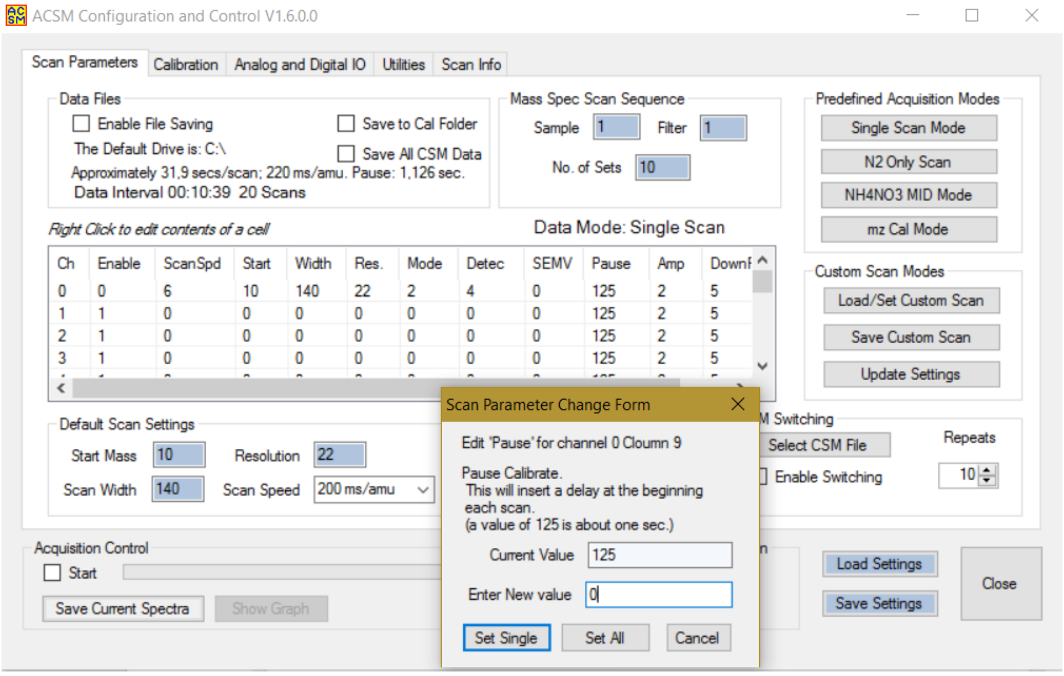
If a leak is suspected in the sampling line: measure through the ACSM filter placed before the aerodynamic lens to help identify the locations.

Important locations to check are the switching valve (ensure it rotates to a fully closed position), switching valve (which can/should be cleaned using compressed air, filter integrity, damage to o-rings, …).

A He leak check may help identify the location:
https://support.aerodyne.com/knowledgebase/articles/KA-01157/en-us

4.2.9. Reset the baseline settings of the PrismaPlus electronics

It is recommended to run the Amplifier Offsets routinely (every 6 months) or after SEM replacement. To do so, first set the scan parameter "Pause" to "0" for all channels in the "Scan Parameters" panel by right clicking in the "Pause" column to bring up the "Scan Parameter Change Form," typing "0" in the "Enter New Value" text box, then clicking "Set All" as shown in Figure 2.



Data Files
☐ Enable File Saving ☐ Save to Cal Folder
The Default Drive is: C:\ ☐ Save All CSM Data
Approximately 31,9 secs/scan; 220 ms/amu. Pause: 1,126 sec.
Data Interval 00:10:39 20 Scans

Mass Spec Scan Sequence
Sample 1 Filter 1
No. of Sets 10

Right Click to edit contents of a cell

Data Mode: Single Scan

Ch	Enable	ScanSpd	Start	Width	Res.	Mode	Detec	SEMV	Pause	Amp	Downf
0	0	6	10	140	22	2	4	0	125	2	5
1	1	0	0	0	0	0	0	0	125	2	5
2	1	0	0	0	0	0	0	0	125	2	5
3	1	0	0	0	0	0	0	0	125	2	5

Default Scan Settings
Start Mass 10 Resolution 22
Scan Width 140 Scan Speed 200 ms/amu

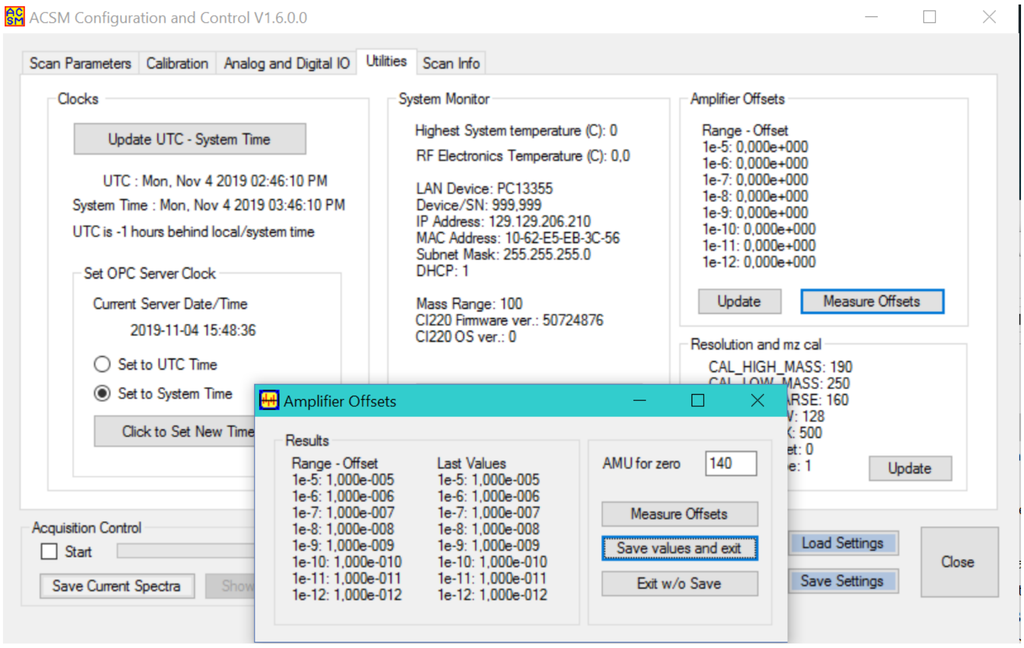
M Switching
☐ Enable Switching
Repeats 10

☐ Start

Scan Parameter Change Form
Edit 'Pause' for channel 0 Cloumn 9
Pause Calibrate.
This will insert a delay at the beginning each scan.
(a value of 125 is about one sec.)
Current Value 125
Enter New value 0

Figure 2: Set the Pause value to "0" in all channels

Then, reset the baseline by clicking "Measure Offsets" and set the "AMU for zero" value to "140 or 145" in the top right of the "Utilities" panel and clicking "Save values and exit" and clicking "Update" when the routine completes as shown in Figure 3.



Clocks
UTC : Mon, Nov 4 2019 02:46:10 PM
System Time : Mon, Nov 4 2019 03:46:10 PM
UTC is -1 hours behind local/system time

Set OPC Server Clock
Current Server Date/Time
2019-11-04 15:48:36
○ Set to UTC Time
● Set to System Time

System Monitor
Highest System temperature (C): 0
RF Electronics Temperature (C): 0,0

LAN Device: PC13355
Device/SN: 999,999
IP Address: 129.129.206.210
MAC Address: 10-62-E5-EB-3C-56
Subnet Mask: 255.255.255.0
DHCP: 1

Mass Range: 100
CI220 Firmware ver.: 50724876
CI220 OS ver.: 0

Amplifier Offsets
Range - Offset
1e-5: 0,000e+000
1e-6: 0,000e+000
1e-7: 0,000e+000
1e-8: 0,000e+000
1e-9: 0,000e+000
1e-10: 0,000e+000
1e-11: 0,000e+000
1e-12: 0,000e+000

Resolution and mz cal
CAL_HIGH_MASS: 190
CAL_LOW_MASS: 250
RSE: 160
V: 128
: 500
et: 0
e: 1

☐ Start

Amplifier Offsets
Results

Range - Offset	Last Values
1e-5: 1,000e-005	1e-5: 1,000e-005
1e-6: 1,000e-006	1e-6: 1,000e-006
1e-7: 1,000e-007	1e-7: 1,000e-007
1e-8: 1,000e-008	1e-8: 1,000e-008
1e-9: 1,000e-009	1e-9: 1,000e-009
1e-10: 1,000e-010	1e-10: 1,000e-010
1e-11: 1,000e-011	1e-11: 1,000e-011
1e-12: 1,000e-012	1e-12: 1,000e-012

AMU for zero 140

Figure 3: Updating the "Amplifier Offsets" by clicking "Measure Offsets" in "Utilities" panel

4.2.10. Prisma resolution and mass-to-charge (m/z) calibration.

The mass-to-charge (m/z) calibration of the quadrupole is based on water, air and naphthalene peaks. The naphthalene fragment ions, with a parent peak at m/z 128 (Figure 5), come from an internal standard that is used to correct for ion transmission loss at high m/z in the quadrupole, as well as to calibrate the m/z scale. Naphthalene molecules are emitted continuously into the vacuum chamber close to ionisation region because this chemical compound has a correct vapor pressure to be used as an effusive source (~ 0,01 torr at 25°C). It is important to note that naphthalene signal is detected whatever the position of the 3-way switching filter valve, that explains there is no naphthalene signal in the MS diff.

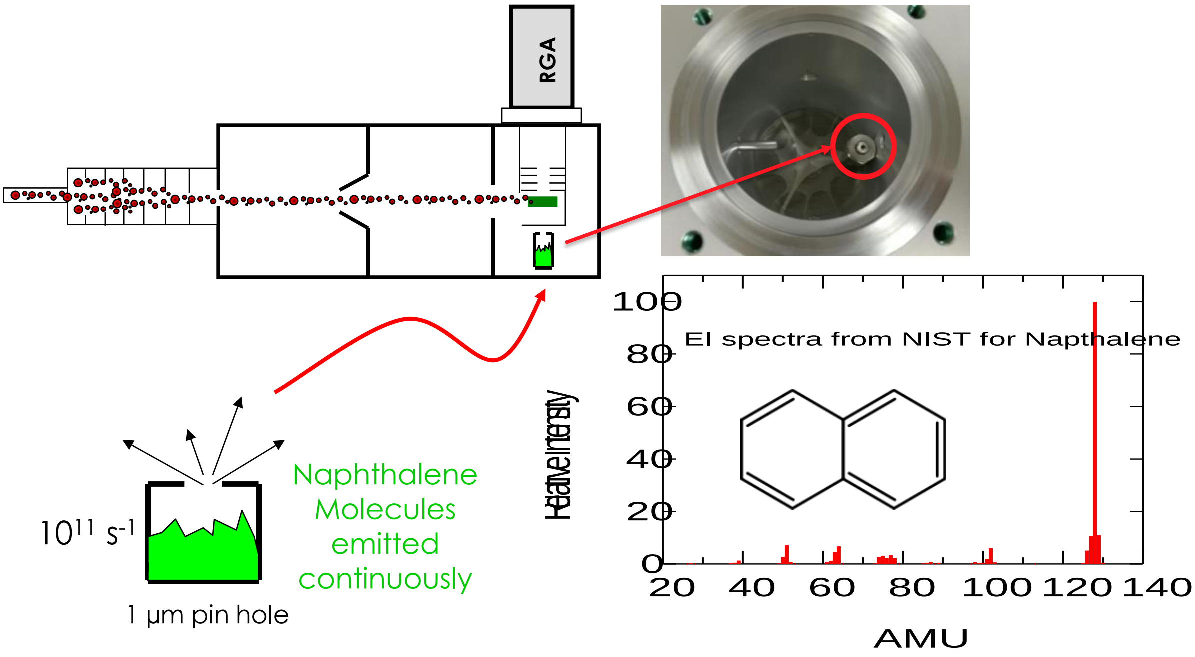
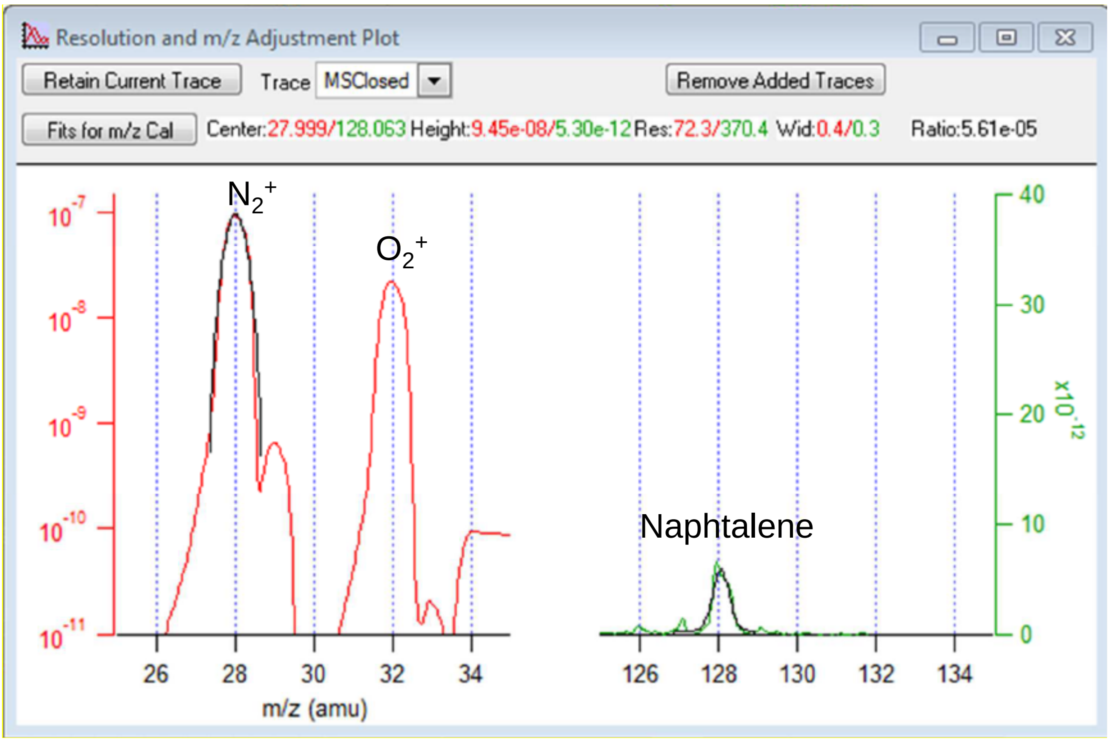


Figure 4: Naphthalene mass spectrum from NIST and localization of the naphthalene source into the vacuum chamber.

In practice, this is a two-point calibration procedure using peaks at *m/z* 28 (N_2^+) and naphthalene peak at *m/z* 128 to "electronically" calibrate the analyzer over the 10-150 amu range. These fragments provide in-situ measurements of ion transmission and thus can impact the RIT correction (see section 6.2.1).

The mass-to-charge calibration can be performed through the 'Control Settings -> Scan Parameters' window in the DAQ menu. Predefined 'mz cal mode' acquisition mode needs to be selected (with sample = 0; filter = 1; Nb of sets = 10 in the mass spec. scan sequence for example) before starting acquisitions with the Igor Automation Server enabled. Results can be viewed in the IGOR 'acsm_local.ipf' procedure through 'Calibration/Tuning' window by selecting 'Resolution and m/z Adjustement Plot'. Nominal mass at m/z 28 and 128 can be compared to centred values obtained by clicking on "fits for m/z cal' button.



Center:27.999/128.063 Height:9.45e-08/5.30e-12 Res:72.3/370.4 Wid:0.4/0.3 Ratio:5.61e-05

Figure 5: m/z calibration results in the ‘acsm_local’ software.

If the amu difference is higher than +/-0.05 (the mass resolving power is 1 for Q-ACSM so it is not critical that the mz calibration is set perfectly), make m/z offset and slope adjustments on the Calibration tab of the Configuration and Control window of ACSM DAQ (v1.6.0.0 and higher) or using the OPC Browser (prior to 1.6.0.0) until the N_2^+ and naphthalene peaks are centred at their nominal mass value. The slope parameter is set to 1.000 and the offset parameter is set to 0.000 by default. Both are quite sensitive and need to be adjust with caution in steps of 0.001. The adjustment procedure is described in the user manual. For more information, see also the specific technical note ‘TN_012’ from the manufacturer describing empirical calibration of the OPC Slope and OPC offset relationships.

Even if m/z calibration is not supposed to change over time, it is important to check amu calibration once per half-year and after each maintenance into the vacuum chamber. There is no reference value for naphthalene signal, which varies from one instrument to the other but the signal needs to be enough intense to be detected on each MS to reduce measurement uncertainties when ion transmission is corrected. Please refer to section 4.2.3 for airbeam signal values.

4.2.11. Heater Bias Voltage

This voltage optimises the throughput of ions generated in the ion source to the mass spectrometer, calibration is therefore very important.

There is no reference value for this parameter, which varies from one instrument to the other. However, its optimum is typically within several volts of the Ion Reference voltage. It should be adjusted to maximise the Airbeam signal for a given SEM voltage. In normal operation, these voltages must remain close from one calibration to the next.

As with the SEM voltage, this calibration is semi-automatic via the instrument's operating software through the "tuning" function and is described in the user manual. The calibration of these two parameters must also be done sequentially, calibration of the heater bias voltage always preceding calibration of the SEM voltage.

Heater bias voltage should be checked periodically as described in Table 1 but only adjusted if a change in the Airbeam signal varies by greater than 15% from value 7 days before.

5. RESPONSE FACTOR AND RELATIVE IONIZATION EFFICIENCY CALIBRATION

The Response Factor (RFRF) of NO_3, and Relative Ionisation Efficiencies (RIE) of NH_4 and SO_4 are determined from measurement of 300 nm diameter particles of NH_4NO_3 and $(NH_4)_2SO_4$ respectively. The determination of RIEs for chloride and MSA may be necessary in some environments (see sections 5.5 and 5.6). Experimental setup is detailed on the following Figure.

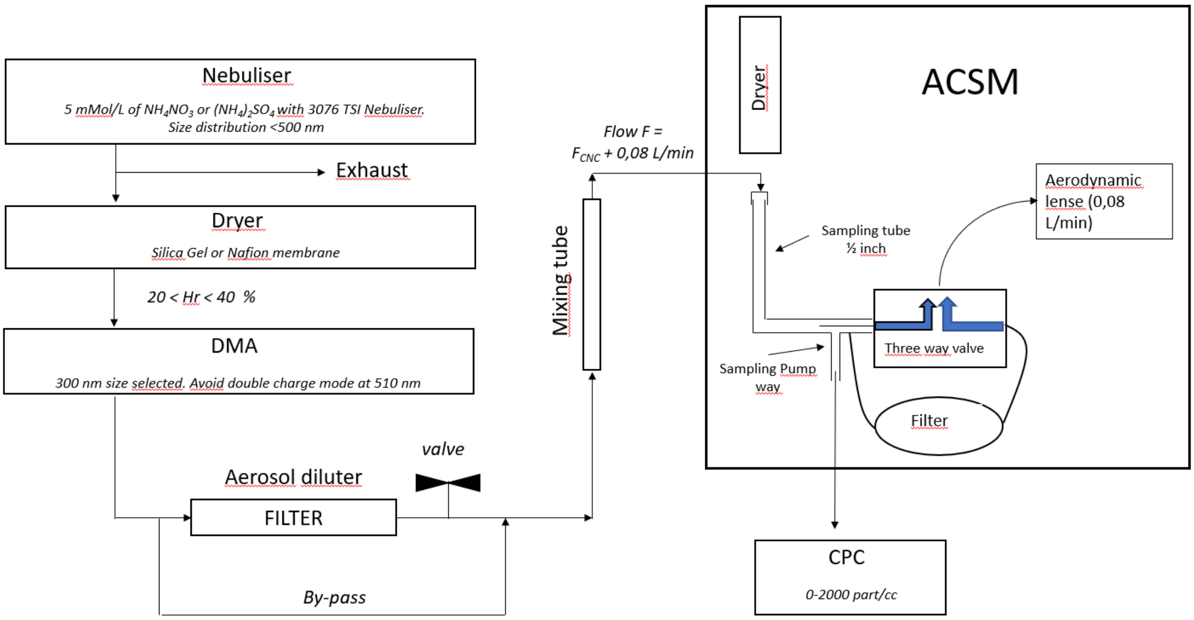


Figure 6: Typical ACSM calibration setup

- First, particles are generated from nebulizing of solutions of ammonium nitrate or ammonium sulfate (see section 5.1).
- Particles are dried before size-selection. After the dryer, the relative humidity should ideally be kept between 20 and 40%.
- 300 nm particles are size-selected using a Differential Mobility Analyzer (DMA).
- An aerosol diluter allows the user to dynamically change the aerosol concentration to provide a concentration range during calibration. The use of a mixing tube downstream of the aerosol diluter is necessary to ensure the aerosols and diluting air are fully mixed before they reach the ACSM and CPC inlet.
- The outlet of the generation setup can be connected on the ½ inch sampling tube located downstream the dryer to mimic the sampling setup.
- A CPC is used to measure the number concentration of 300 nm particles. It should be connected to the ACSM sampling pump connector. The length of the tube should be minimized to avoid particle loss.

5.1. Aerosol generation

It is important that the calibration solution not be too highly concentrated to avoid artefacts from double-charged particles (located at 510nm when 300 nm particles are generated). For example, an optimum concentration value of 5 mM has been obtained using a TSI nebulizer model 3076. If another type of nebulizer were used, it could be necessary to check the concentration of 510nm particles generated. Ratio of number concentration of 510nm on 300 nm particles should be minimized, and at least, less than 2%

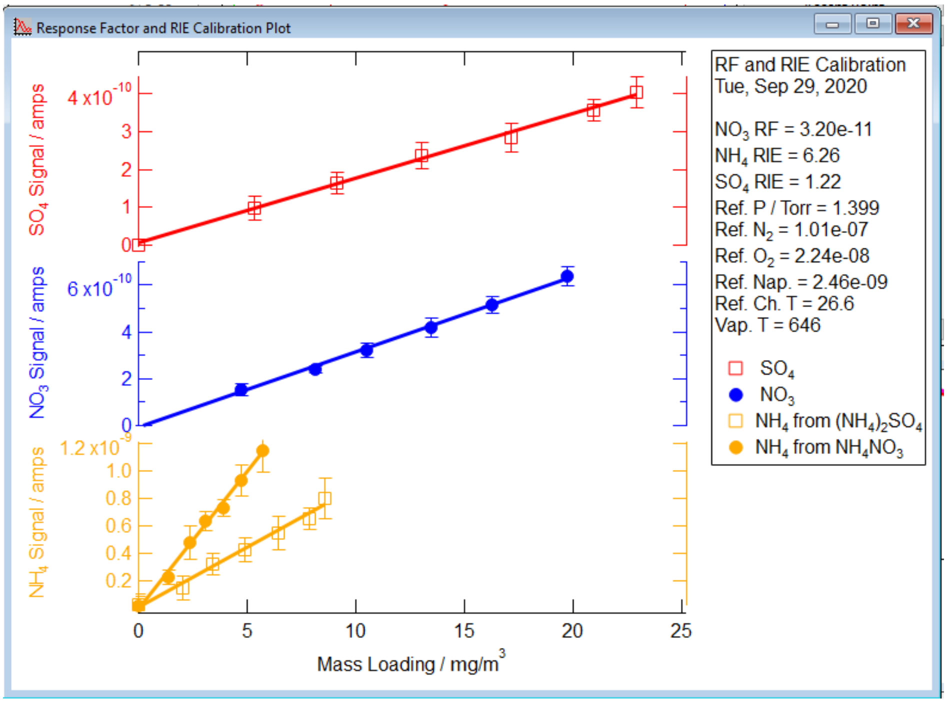
Devices such as Centrifugal particle Mass Analyser (CPMA) or Aerodynamic Aerosol Classifier (AAC) can be used to remove double charge particles at 510nm. In that case, there is less need to control the concentration of the solution precisely. When used, such a device must be installed between DMA and aerosol diluter on the scheme.

5.2. Software configuration

The instrument should be tuned directly prior to the calibration.

The user should use the custom file for calibration from the Aerodyne ACSM webpage: "ACSM_Calibration_NH4NO3.scn" and calibrate ACSM using the "ambient air mode" (i.e. full scan mode).

For calibration with ammonium sulphate, use the respective custom scan file also available on the Aerodyne webpage: ACSM_Calibration_NH42SO4.scn



RF and RIE Calibration
Tue, Sep 29, 2020

NO_3 RF = 3.20e-11
NH_4 RIE = 6.26
SO_4 RIE = 1.22
Ref. P / Torr = 1.399
Ref. N_2 = 1.01e-07
Ref. O_2 = 2.24e-08
Ref. Nap. = 2.46e-09
Ref. Ch. T = 26.6
Vap. T = 646

Figure 7: Example of usual RF and RIE calibration results using the dedicated "ACSM-local" software panel

It is recommended that each calibration curves includes at least 6 data points, equally distributed over the expected concentration range in the investigated ambient air and starting from zero (**¡Error! No se encuentra el origen de la referencia.**). Near-future updates of this calibration panel are planned to include some statistics on the linearity of the calibration curves, which might then be used to assess the validity of obtained calibration results.

5.3. RF and ammonium RIE

RF is determined by measuring ions for NO_3^+ (m/z 30, 46) obtained from measurement of 300nm ammonium nitrate particles. The signal of NO_3^+ (m/z 30, 46) in Amps, is linked with the mass concentration injected into the ACSM. The particle number concentration (measured by the CPC) is converted to mass concentration using the density of ammonium nitrate (in g/cc) and a shape factor of 0.8.

C_{mass} = density x Shape factor x 4/3 x πr^3

RIE of NH_4^+ is then calculated from mass balance between NH_4^+ and NO_3^- in ammonium nitrate.

5.4. Sulfate RIE

The RIE of SO_4^{2-} should be measured immediately following an RF NO_3 and RIE NH_4 from nitrate calibration.

RIE of SO_4^{2-} is determined from $(NH_4)_2SO_4$ particles generated by the set up and sampled with the ACSM.

The RIE of SO_4^{2-} can be calculated from mass balance with NH_4^+, since the RIE of NH_4^+ is known from the ammonium nitrate calibration. This method is not biased by particle bounce. Indeed, ratios of NH_4 from nitrate and NH_4 form sulphate are used to estimate the collection efficiency of sulfate during 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.

5.5. Ammonium Chloride

It is advisable to calibrate for ammonium chloride if this is the dominant form of chloride in your environment[1].

5.6. Methanesulfonic acid (MSA)

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

---

[1] Tobler, A. K., Skiba, A., Wang, D. S., Croteau, P., Styszko, K., Nęcki, J., Baltensperger, U., Slowik, J. G., and Prévôt, A. S. H.: Improved chloride quantification in quadrupole aerosol chemical speciation monitors (Q-ACSMs), Atmos. Meas. Tech., 13, 5293–5301, https://doi.org/10.5194/amt-13-5293-2020, 2020.

6. ACSM DATA REPROCESSING AND VALIDATION

The quality assurance regime described here is designed to be applied to ACSM instruments operating in long term deployments but could equally applied to instruments operating on campaigns. It comprises a two-stage process consisting of regular 'validation' checks during the instrument operation to ensure the instrument is working correctly. This is followed periodically (every 3/6 months or at the end of the campaign) by a final ratification step which reviews the QA/QC information, cleans data for anomalies not identified in the first step and applies the quality assurance data over a longer timescale. Both these steps utilise a set of diagnostics that are important for assessing the correct operation of the instrument; these are shown in section 6.1.

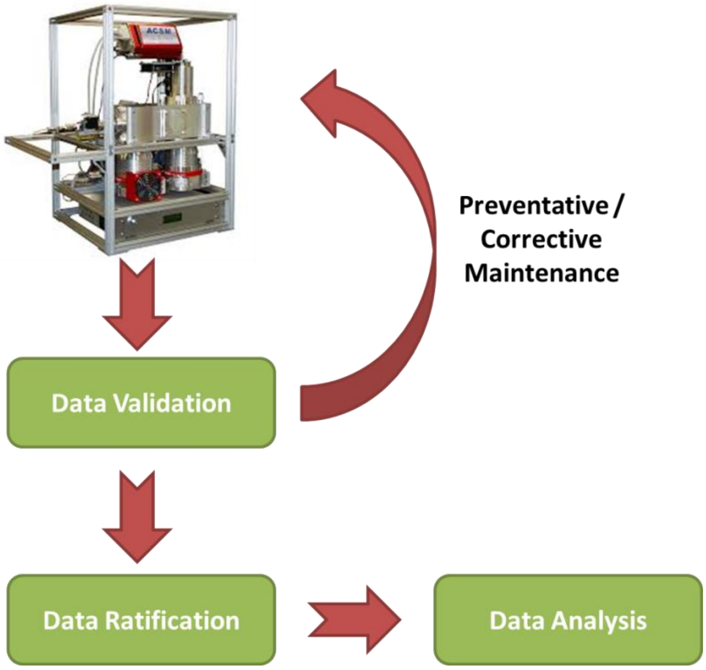


Figure 8: Data Reprocessing and Validation Schematic

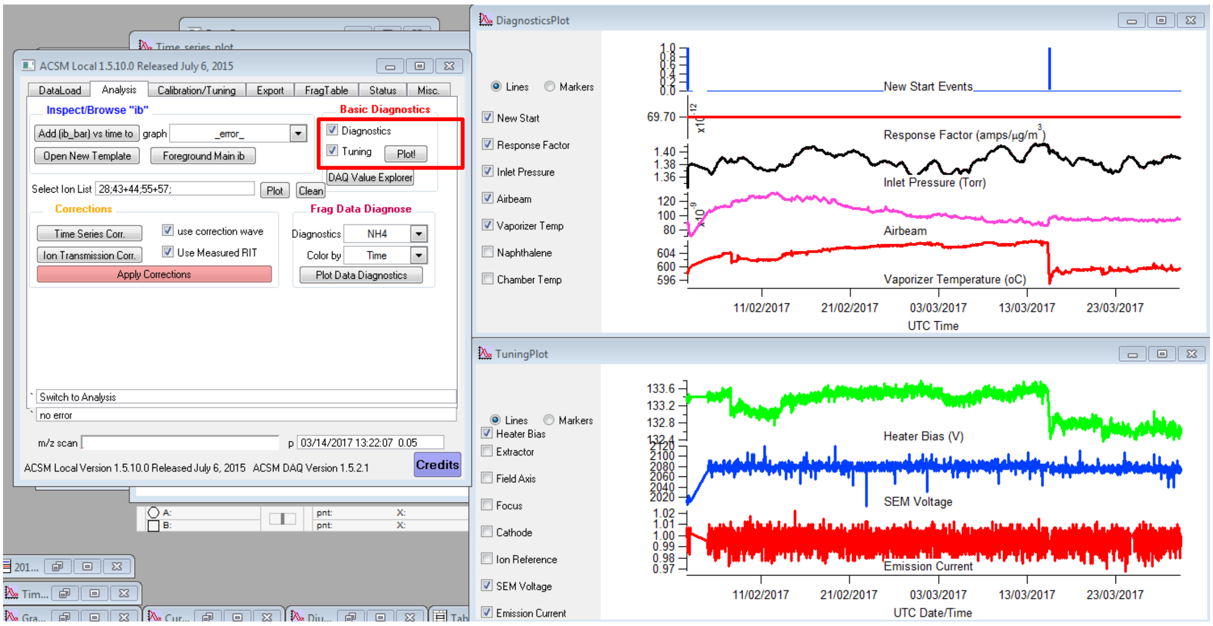
6.1. Data Validation Scheme

For each data point, check the following technical parameters and ensure they are consistent with the values in Table 2 using the *.csv file exported to the acquisition PC or by opening the ACSM's raw files with the Igor software.

Table 2: Summary table of data validation criteria

Diagnostic	Criterion		Action when criteria are not met	Reference
	PM1	$PM_{2.5}$		
Aerodynamic lens pressure (inlet pressure)	1.3 ± 0.2 torr	3.3 ± 0.2 torr	Investigate data validity if outside criteria range or large deviations / sudden changes and flag / reject if necessary	4.2.1
Vaporizer voltage	Check set point maintained			4.2.2
Airbeam	Must be close to 10^{-7} ± 30% amp		Investigate data validity if less than 70% and flag / reject if necessary	4.2.3
SEM Voltage	No sudden variations other than those induced by tuning		Investigate data validity and flag / reject if necessary	4.2.4
Heater Bias Voltage	No sudden variations		Investigate data validity and flag / reject if necessary	4.2.11
Filament Emission	No sudden variations, >0mA		Investigate data validity and flag / reject if necessary	0
Dryer	RH 20% to 60%		Investigate data validity and flag / reject if necessary	4.2.6
Validity of RIEs	Verification of the ionic balance: The fit between the measured NH_4 and the predicted NH_4 should be linear and its slope should be close to 1 (±0.1) and linear		If slope not close to 1, verify that the RIEs are correct and consider recalibration. If the relationship is not linear, and below 1, this may indicate the presence of acidic aerosol.	5.3 5.4
Total concentration of ACSM	Positive and not close to zero / negative for long periods		Investigate (valve closed, filter valve switching, filament off, detector voltage, acquisition settings, RF and RIE configuration, inlet clean, leaks...)	4.2.8

A "diagnostic" tab allows all of these parameters to be visualised. The window represented in Figure 9 allows an overview of certain significant time series, including the flow rate into the ACSM (pressure), the Airbeam (N_2), as well as the RF set during measurements.



ACSM Local 1.5.10.0 Released July 6, 2015

Add (ib_bar) vs time to graph _error_

☑ Diagnostics

☑ Tuning

Select Ion List 28;43+44;55+57;

☑ use correction wave

☑ Use Measured RIT

Diagnostics NH4

Color by Time

Switch to Analysis

no error

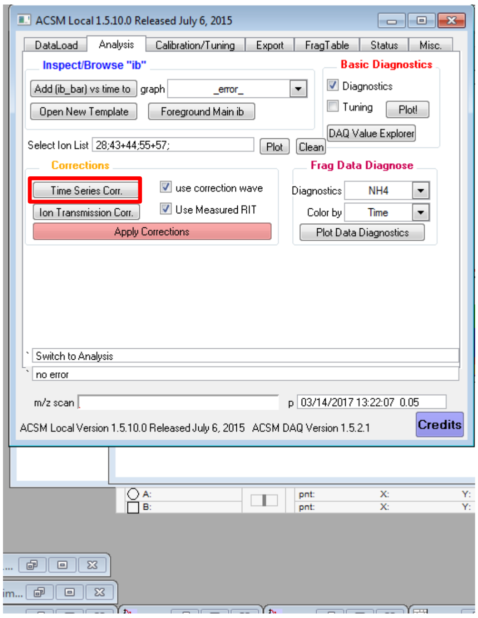
p 03/14/2017 13:22:07 0.05

ACSM Local Version 1.5.10.0 Released July 6, 2015 ACSM DAQ Version 1.5.2.1

Figure 9: Visualisation of the ACSM's technical parameters with the ACSM_local data visualisation software.

6.2. Data Ratification Scheme

This second step consists of checking, for each data point, the correct configuration of the calibration coefficients (RF, RIE), the collection efficiency (CE), reference values enabling correction of the Airbeam's measurement variations, as well as the relative ion transmission efficiency (RIT) for naphthalene (Figure 10).



ACSM Local 1.5.10.0 Released July 6, 2015

Add (ib_bar) vs time to graph _error_

☑ Diagnostics

☐ Tuning

Select Ion List 28;43+44;55+57;

☑ use correction wave

☑ Use Measured RIT

Diagnostics NH4

Color by Time

Switch to Analysis

no error

p 03/14/2017 13:22:07 0.05

ACSM Local Version 1.5.10.0 Released July 6, 2015 ACSM DAQ Version 1.5.2.1

Figure 10: Configuration of the reference parameters to take into account corrections of Airbeam pressure variations and calibration coefficients

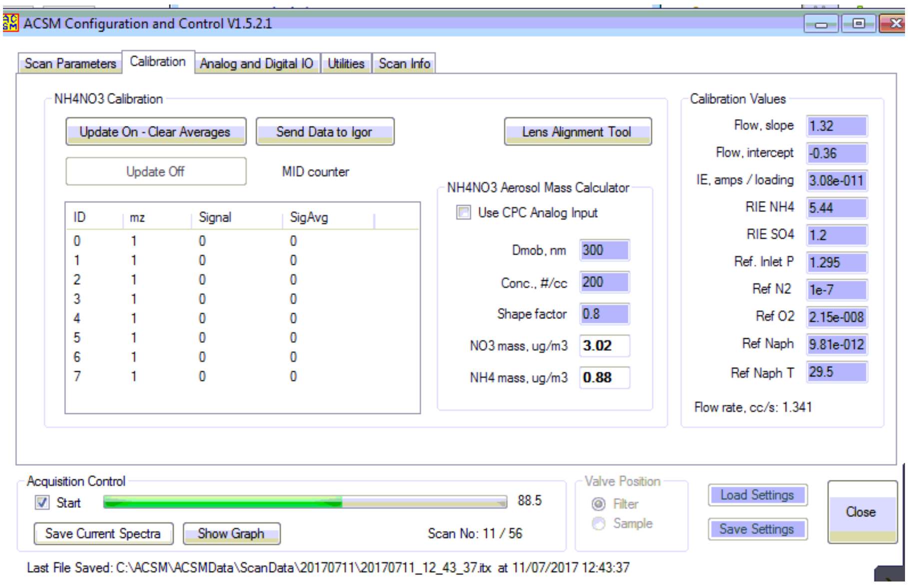
The windows represented in Figure 11 shows on the righthand side the ACSM's "reference" technical parameters (N_2 signal, O_2 signal, Ar signal, naphtalene signal, RF, aerodynamic lens pressure, temperature), i.e. as they were measured during calibration RF. All of these reference parameters shown here can be modified by the operator, and the configured parameters on the righthand side of this window must be those recorded during calibration of the RF applicable to the considered data series.

The reference parameters that have most significant impacts on data are: the flow rate (when using this to correct in time series window) into the instrument (reference P), the Airbeam (reference N2) and the RF. Each of these three parameters impacts directly and linearly the concentrations measured by the ACSM. More specifically, an RF value must always be associated with a Pref and N2 ref value.

Note 1: It is important to validate the RF value in this window as this value will be used in the calculations, in priority over that of the "review batch", of which the start-up value can be different.

Note 2: If an RF change is visible on the graph on the bottom of Figure 3, corresponding to the fact that a calibration was done, the default reference values will be those corresponding to the oldest data. Therefore, the operator should modify the reference values if necessary.

Note 3: Following a calibration, new reference values are saved in the DAQ software and can be consulted in the "calibration" tab. Each saved raw *.itx file are stored, and calibration results are saved in an Igor file in c:\\ACSM\settings » under the name « ACSM_NO3CalPlot_yyyymmdd_hhmmss.pxp



ID	mz	Signal	SigAvg
0	1	0	0
1	1	0	0
2	1	0	0
3	1	0	0
4	1	0	0
5	1	0	0
6	1	0	0
7	1	0	0

☐ Use CPC Analog Input

Dmob, nm 300
Conc., #/cc 200
Shape factor 0.8
NO3 mass, ug/m3 3.02
NH4 mass, ug/m3 0.88

Flow, slope 1.32
Flow, intercept -0.36
IE, amps / loading 3.08e-011
RIE NH4 5.44
RIE SO4 1.2
Ref. Inlet P 1.295
Ref N2 1e-7
Ref O2 2.15e-008
Ref Naph 9.81e-012
Ref Naph T 29.5
Flow rate, cc/s: 1.341

☑ Start 88.5
Scan No: 11 / 56

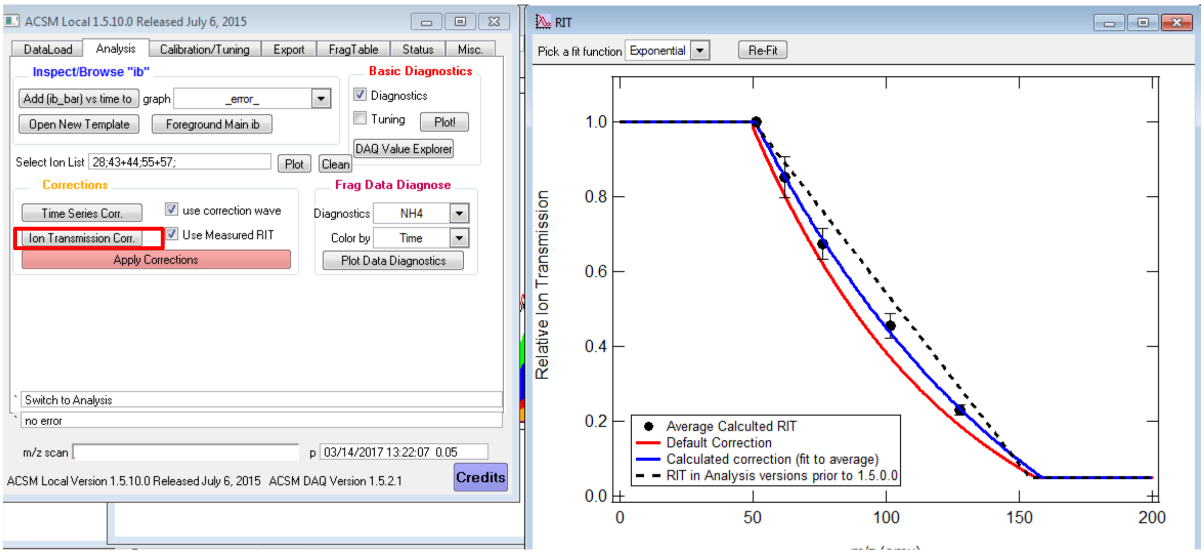
● Filter
○ Sample

Last File Saved: C:\ACSM\ACSMData\ScanData\20170711\20170711_12_43_37.itx at 11/07/2017 12:43:37

Figure 11: Calibration tab of the ACSM driver software in which the reference values of the last calibration are shown.

6.2.1. *Verification that the ACSM's transmission efficiency correction (RIT) is activated*

This correction can be accessed in the window of the "ACSM_local" software shown in Figure 12 and should be consistent with the relationship shown. It corresponds to the assessment of the ACSM's transmission efficiency, which decreases for greater masses.



ACSM Local 1.5.10.0 Released July 6, 2015

Add (ib_bar) vs time to graph _error_

☑ Diagnostics

☐ Tuning

Select Ion List 28;43+44;55+57;

☑ use correction wave

☑ Use Measured RIT

Diagnostics NH4

Color by Time

Switch to Analysis

no error

m/z scan

p 03/14/2017 13:22:07 0.05

ACSM Local Version 1.5.10.0 Released July 6, 2015 ACSM DAQ Version 1.5.2.1

Pick a fit function Exponential

Figure 12: Mass spectrometer transmission efficiency correction function (RIT)

This option must be activated and the mathematical adjustment (exponential, power, etc.) must be selected by the operator so that the correction function is the closest possible to the experimental points.

After verification of the four preceding points, the operator should activate "time series correction" and "RIT" by selecting the button "Apply Corrections".

Note: there are some cases where it is not working = not a good fit. Then clean the system closing the valve, and then check if the fit is better. If not, do not apply (then the red line will be applied).

6.2.2. *Fragmentation diagnostic plots*

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.

Potential issues around blocked filter causing pressure drop can lead to non-zero intercept.

Nitrate and sulfate diagnostics: Check for (1) linearity; (2) intercept at origin.

6.2.3. *Ion balance*

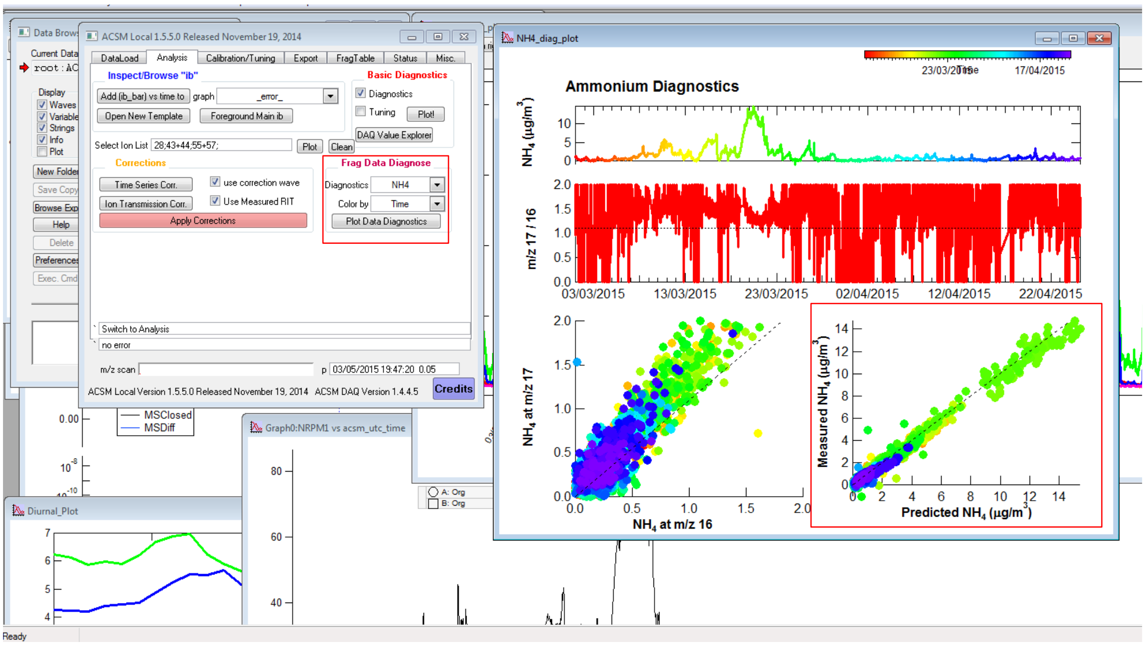
This step enables validation of the NH_4 and SO_4 RIE values. It is a question of verifying that the ammonium concentration measured by the instrument is close to "predicted ammonium" concentrations. This is determined with NO_3, SO_4 and Cl measurements, since in the atmosphere, these species are most often associated with ammonium in the form of NH_4NO_3, $(NH_4)_2SO_4$ and NH_4Cl.

Thus:

NH_4predicted = $[NO_3]/62 + 2\,[SO_4]/96 + [Cl]/35.45$

NH_4measured = $[NH_4]$

This diagnostic can be carried out by applying the above calculations to the exported data in the *.csv file. It is also available in the "ACSM_local" under the "Analysis" tab.



ACSM Local 1.5.5.0 Released November 19, 2014

Select Ion List 28;43+44;55+57;

☑ use correction wave

☑ Use Measured RIT

Diagnostics NH4

Color by Time

Switch to Analysis

no error

p 03/05/2015 19:47:20 0.05

ACSM Local Version 1.5.5.0 Released November 19, 2014 ACSM DAQ Version 1.4.4.5

Figure 13: Ion balance diagnostics in IGOR.

An NH_4measured/NH_4predicted close to 1 means that the relative distribution of the four inorganic species (NO_3, NH_4, Cl, SO_4) measured by the ACSM is correct within the instrument's uncertainty limits.

Hence, the slope of a series of data must be equal to 1 ± 10%. It is preferable to evaluate this slope with a relatively continuous time series (several weeks) and inorganic particle concentrations that are not too low (> 5 µg m^{-3}).

This relationship can be temporarily lowered during certain pollution episodes when there is a presence of $(NH_4)HSO_4$ instead of $(NH_4)_2SO_4$-type acid aerosols, or in the presence of SO_4 or NO_3 linked to organic matter (organo-nitrate, organo-sulfate). In these two examples, the predicted ammonium would be overestimated and the NH_4measured/NH_4predicted relation decreased.

Hence, one should monitor the evolution of this relationship over time in order to observe any drift. A continuous and significant deviation over time can indicate that the calibration of the NH_4 and SO_4 RIEs must be checked. A one-time deviation that returns to normal should be interpreted in terms of atmospheric chemistry.

An operator error in RIE calibration can lead to an error in the slope.

Finally, it should be noted that feedback shows that RIE values fluctuate very little over time in metropolitan urban-background stations.

6.2.4. Collection efficiency adjustment

Standard operation procedures to be applied for accurate ACSM operation are given elsewhere[2]. Furthermore, an important parameter to be considered is the collection efficiency, which translates how efficiently the sampled particles eventually reach and are impacted onto the vaporizer. For online ACSM data acquisition and for instrument equipped with a standard vaporizer, a default collection efficiency of 0.5 (CE=0.5) is commonly set on the instrument software (so-called "ACSM_local"). This collection efficiency should be adjusted *post hoc* to take into account its variation over time, notably depending on the chemical composition and mixing state of the sampled aerosols. Middlebrook et al. (2015) proposed a procedure to accurately estimate CE under various conditions[3]. This procedure is assumed as state-of-the-art. Its use is then highly recommended.

Note: For ACSM equipped with so-called capture vaporizer, a constant CE value of 1 should be used.

For standard vaporizers, time-dependent CE values mainly fluctuate with the ammonium nitrate mass fraction (ANMF), aerosol's acidity, and relative humidity. This can be calculated using Igor functions given in Annex 1 of the present document, which is a modification from Middlebrook et al., 2015. Annex 1 refers to the calculation of CE_dry values,

The logic behind the calculations is to use a constant default CE when the ANMF is not very high, and to use a variable CE that depends on the ANMF, when it is higher. For low concentrations below DL, the CE is set to the default value.

$$CE_{corr} = \min\left(0.45,\ \max\left(1, \begin{cases} 0.5\ si\ NH_4 < LOD_{NH_4} \\ 1 - 0.73 \cdot \frac{NH_4}{NH_4^{predicted}}\ si\ \frac{NH_4}{NH_4^{predicted}} < 0.75 \\ 0.0833 + 0.9167 \cdot ANMF\ si\ \frac{NH_4}{NH_4^{predicted}} \geq 0.75 \end{cases}\right)\right)$$

Depending on the version used for this CE correction procedure (which needs to be previously imported into the computer's Igor folders), time-dependent CE may be obtained via the command window, as follows:

```
CalcCE_dry(NH4_DL,CE_lowNH4)  or CalcCE_fPhase(NH4_DL,CE_lowNH4,RH_SL)
```

where NH4_DL is the detection limit for ammonium, CE_lowNH4 is the CE that should be used when measured NH4 is below the detection limit (typically 0.5), and RH_SL is the measured relative humidity if not kept below 60%.

The detection limit for ammonium (NH4_DL in the procedure) should be determined for each measurement site and period. To do so, a filter should be placed in the ACSM inlet line and measurements should be collected. Averaging the mass concentrations for each species using CE=0.5 and multiplying the resulting standard deviations by 3 would result in the determined detection limits.

---

[2] Current SOP version available from COLOSSAL website

[3] Middlebrook et al. (2012) Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Science and Technology, 46:3, 258-271.

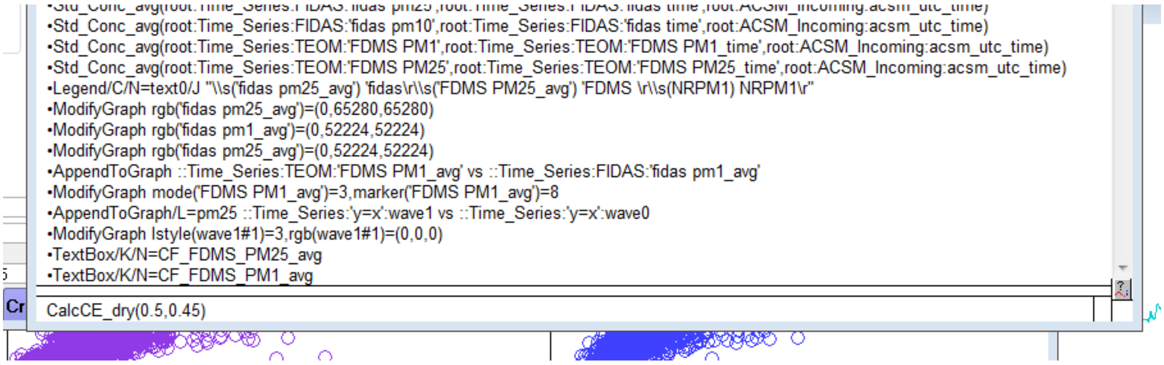
When this is not done, a default detection limit of 0.284 ug/m3 can be used for ammonium (Ng et al., 2011).

The CE that should be used when measured NH4 is below the detection limit (CE_lowNH4 in the procedure) is dataset specific. If a dataset corresponds to a polluted place and most likely it is never ammonia-deficient, hence ammonium concentrations below DL indicate low concentrations in general of all species and hence the default CE should be set to 0.5, since the calculation of the ANMF would have too high uncertainty. If a dataset can have acidic aerosol, then ammonium concentrations below DL may show acidic aerosol and hence default CE should be set to 1. The DL of sulfate may be used instead to determine when the concentrations are low.

An example of the input can then be

CalcCE_dry(0.45,0.5) or CalcCE_dry(0.45,1), depending on the site

Once calculated, time-dependent CE corrected values can automatically be reported in the exported *.csv data files using an Igor function, "Auto_ACSM_export.ipf", which is currently available on request at acmcc@lsce.ipsl.fr and should hopefully be implemented in the ACSM software in the near-future.



```
•Std_Conc_avg(root:Time_Series:FIDAS:'fidas pm10',root:Time_Series:FIDAS:'fidas time',root:ACSM_Incoming:acsm_utc_time)
•Std_Conc_avg(root:Time_Series:TEOM:'FDMS PM1',root:Time_Series:TEOM:'FDMS PM1_time',root:ACSM_Incoming:acsm_utc_time)
•Std_Conc_avg(root:Time_Series:TEOM:'FDMS PM25',root:Time_Series:TEOM:'FDMS PM25_time',root:ACSM_Incoming:acsm_utc_time)
•Legend/C/N=text0/J "\\s('fidas pm25_avg') fidas\r\\s('FDMS PM25_avg') 'FDMS \r\\s(NRPM1) NRPM1\r"
•ModifyGraph rgb('fidas pm25_avg')=(0,65280,65280)
•ModifyGraph rgb('fidas pm1_avg')=(0,52224,52224)
•ModifyGraph rgb('fidas pm25_avg')=(0,52224,52224)
•AppendToGraph ::Time_Series:TEOM:'FDMS PM1_avg' vs ::Time_Series:FIDAS:'fidas pm1_avg'
•ModifyGraph mode('FDMS PM1_avg')=3,marker('FDMS PM1_avg')=8
•AppendToGraph/L=pm25 ::Time_Series:'y=x':wave1 vs ::Time_Series:'y=x':wave0
•ModifyGraph lstyle(wave1#1)=3,rgb(wave1#1)=(0,0,0)
•TextBox/K/N=CF_FDMS_PM25_avg
•TextBox/K/N=CF_FDMS_PM1_avg
CalcCE_dry(0.5,0.45)
```

Finally, it should be noted that the CE might also be significantly influenced by the type of sampled aerosols. For instance, Alfarra et al. suggested CE value equal to 0.7 when high relative contributions of organic matter from biomass combustion are present.[4] Comparisons of individual chemical species concentrations with external data can support the identification of the optimal CE value.

---

[4] Alfarra et al. (2007) Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions. Environ. Sci. Technol., 41, 5770-5777

Annex 1 Igor function to calculate time-dependent CE under various RH conditions (courtesy of David Green, modified from Middlebrook et al., 2015)

```
Function CalcCE_fPhase(NH4_DL,CE_lowNH4)
Variable NH4_DL,CE_lowNH4
// NH4_DL = ammonium detection limit
// CE_lowNH4 = CE for points where ammonium is below its detection limit
// Prior to running this procedure, all species must be calculated using CE=1.
// The sampling line relative humidity (if measured) should be named "RH_SL"
wave SO4, NH4, NO3, Chl, org, RH_SL
// Create waves of each species to smooth for the calculations.
duplicate/o SO4 SO4_CE1
duplicate/o NH4 NH4_CE1
duplicate/o NO3 NO3_CE1
duplicate/o Chl Chl_CE1
duplicate/o org org_CE1
Smooth 1, SO4_CE1,NH4_CE1,NO3_CE1,Chl_CE1, org_CE1
Variable i
Duplicate/o SO4 PredNH4_CE1, NH4_MeasToPredict, ANMF
Duplicate/o SO4 CE_dry,CE_fPhase
CE_dry=nan
CE_fPhase=nan
// Equation 3
PredNH4_CE1=18*(SO4_CE1/96*2+NO3_CE1/62+Chl_CE1/35.45)
NH4_MeasToPredict=NH4_CE1/PredNH4_CE1
// Equation 5
ANMF=(80/62)*NO3_CE1/(NO3_CE1+SO4_CE1+NH4_CE1+Org_CE1+Chl_CE1)
// Calculate the dry collection efficiency, CE_dry
For (i=0;i<(numpnts(SO4_CE1)+1);i+=1)
// Nan negative NH4_MeasToPredict points
If (NH4_MeasToPredict[i]<0)
//NH4_MeasToPredict[i]=nan
NH4_MeasToPredict[i]=1 //DG mod to eliminate nan CE
EndIf
// Nan ANMF points if negative or more than 1
If (ANMF[i]<0)
ANMF[i]=nan
ElseIf (ANMF[i]>1)
ANMF[i]=nan
EndIf
If (PredNH4_CE1[i]<NH4_DL)
// In general, do not calculate CE for these points.
CE_dry[i]=nan
// In the CE paper, applied CE for low ammonium mass
// CE_dry[i]=CE_lowNH4
ElseIf (NH4_MeasToPredict[i]>=0.75)
// Apply Equation 4
CE_dry[i]= 0.0833+0.9167*ANMF[i]
```

```
ElseIf (NH4_MeasToPredict[i]<0.75)
// Apply Equation 6
CE_dry[i]= 1-0.73*NH4_MeasToPredict[i]
EndIf
EndFor
// Make CE_dry between 0.45 and 1
CE_dry=min(1,(max(0.45,CE_dry)))
If (WaveExists(RH_SL)==1)
// Apply Equation 7
CE_fPhase=(5*CE_dry-4)+(1-CE_dry)/20*RH_SL
For (i=0;i<numpnts(CE_fPhase)+1;i+=1)
If (RH_SL[i]<80 || numtype(RH_SL[i])==2 )
CE_fPhase[i]=CE_dry[i]
EndIf
EndFor
Else
CE_fPhase=CE_dry
EndIf
KillWaves SO4_CE1,NH4_CE1,NO3_CE1,Chl_CE1, org_CE1, PredNH4_CE1
End Function
```