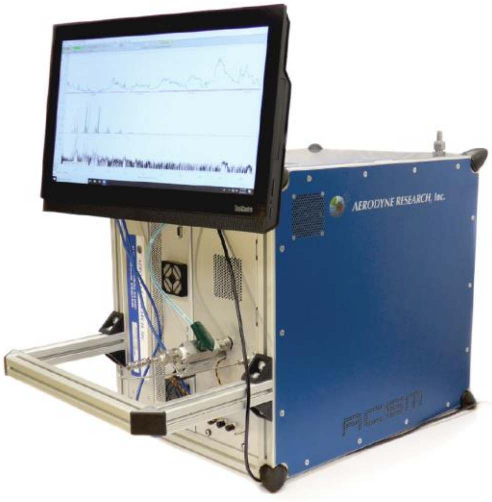
COLOSSAL

Chemical On-Line cOmpoSition and Source Apportionment of fine aerosoL



TOF- ACSM Standard Operating Procedures

Version 1, March 2022

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1. PREAMBLE

This document provides recommendations for the use of Time of Flight Aerosol Chemical Speciation Monitors (TOF-ACSM) developed by Aerodyne Research Inc. (ARI) and TOFWERK AG 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 2,5 µm (NR-$PM_{2.5}$). The reader is strongly encouraged to refer to the TOF-ACSM User Guide, available at support.aerodyne.com, and/or provided by the distributor, for information about the operation of the instrument. The present document is intended to provide key information and good practice relating to operating parameters, maintenance frequencies, as well as data validation steps to be followed.

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.

2. DOCUMENTATION AND RESOURCES

Website of the manufacturer Aerodyne:

https://support.aerodyne.com/

Software and manuals in English can be downloaded from this site.

Software:

- DAQ: Acquility and TofDaq (KA-01182), runs in Igor 7
- Data Analysis: Tofware 3 for TOF-ACSM (KA-01180), runs in Igor 7 or 8

Igor and updates can be downloaded from www.wavemetrics.com. See the PerformanceandDocumentation.odp file on the instrument computer for Igor licence keys.

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 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 being 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 the m/z 73 fragment, a widely used marker for 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. With a 100 micron critical orifice, pressure at the inlet should be between 1.6 and 2.0 mbar for the standard lens and between 4 and 4.8 mbar for the PM2.5 lens. Depending on the operating altitude it may be necessary to use a larger diameter orifice to attain these pressures.

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 in the sampling system 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 minimized. 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 minimized and / or well insulated.

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 in a way 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

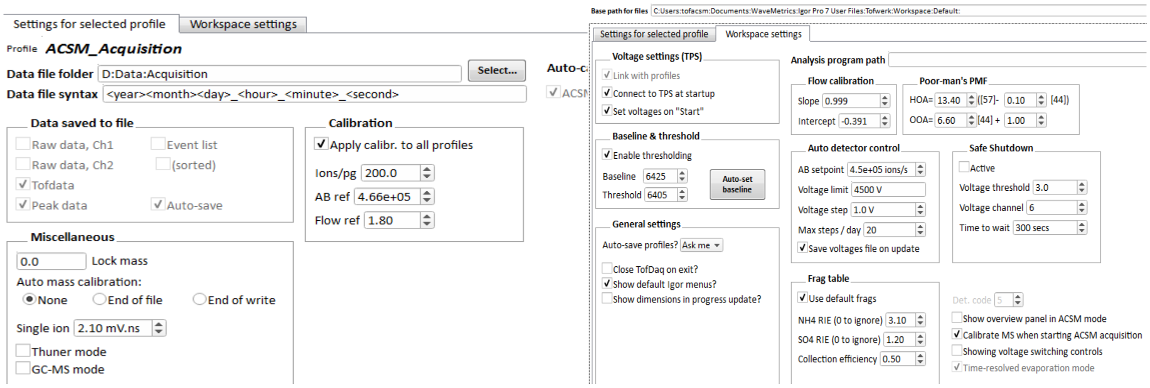
Details of the sampling time is under "DAQ Windows/Timing and Dimensions (F9)". Data is acquired every 40 s, with 20 s in filter and 20 s in sample. Multiple sets of 40s can be averaged together to decrease time resolution and to decrease the size of the data files.

3.2. TOFWARE Acquility 2.3.9 software

The correct configuration of "Acquility" software is necessary to ensure the valid operation of the instrument. All calibration values are automatically read into the software following calibration. However, these values can be verified or edited in the workspace editor. It is recommended to verify these values *This needs to be undertaken periodically and following any system change (e.g. after rebooting).* Under the "Settings for selected profile" tab, the latest calibration values are saved from the last accurate calibration(s) (ions/pg and airbeam and flow ref values) (Section 5).

Under the "Workspace settings", the NH4 RIE and SO4 RIE as well as the collection efficiency are saved. Additional parameters for the detector, flow calibration, and safe shutdown options can be viewed here. These will be discussed in more detail in Section 5.

The default Collection Efficiency (CE) value should be 0.5 for the standard vaporizer and 1 for the capture vaporizer.



Profile **ACSM_Acquisition**
Data file folder D:Data:Acquisition
Data file syntax <year><month><day>_<hour>_<minute>_<second>

Data saved to file
☐ Raw data, Ch1
☐ Raw data, Ch2
☑ Tofdata
☑ Peak data
☐ Event list
☐ (sorted)
☑ Auto-save

Calibration
☑ Apply calibr. to all profiles
Ions/pg 200.0
AB ref 4.66e+05
Flow ref 1.80

Miscellaneous
0.0 Lock mass
Auto mass calibration: ● None ○ End of file ○ End of write
Single ion 2.10 mV.ns
☐ Thuner mode
☐ GC-MS mode

Base path for files: C:Users:tofacsm:Documents:WaveMetrics:Igor Pro 7 User Files:Tofwerk:Workspace:Default:

Voltage settings (TPS)
☑ Link with profiles
☑ Connect to TPS at startup
☑ Set voltages on "Start"

Baseline & threshold
☑ Enable thresholding
Baseline 6425
Threshold 6405

General settings
Auto-save profiles? Ask me
☐ Close TofDaq on exit?
☑ Show default Igor menus?
☐ Show dimensions in progress update?

Analysis program path

Flow calibration
Slope 0.999
Intercept -0.391

Poor-man's PMF
HOA= 13.40 ([57]- 0.10 [44])
OOA= 6.60 [44] + 1.00

Auto detector control
AB setpoint 4.5e+05 ions/s
Voltage limit 4500 V
Voltage step 1.0 V
Max steps / day 20
☑ Save voltages file on update

Safe Shutdown
☐ Active
Voltage threshold 3.0
Voltage channel 6
Time to wait 300 secs

Frag table
☑ Use default frags
NH4 RIE (0 to ignore) 3.10
SO4 RIE (0 to ignore) 1.20
Collection efficiency 0.50

Det. code 5
☐ Show overview panel in ACSM mode
☑ Calibrate MS when starting ACSM acquisition
☐ Showing voltage switching controls
☑ Time-resolved evaporation mode

Figure 1: “Acquility” software, workspace editor to verify RIE, IE and CE values. Profile tab (left) contains IE, ABref, Flow ref, and single ion strength. Workspace settings tab (right) contains RIEs and CE.

It is also important to note that these parameters can be updated a posteriori, when reloading and reprocessing raw data files (*.h5) within the Tofware data analysis 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. Assessment of Limits of Detection

It is recommended to place a filter in front of the sampling line approximately every 3 months, for at least three hours so as to acquire a sufficient number of data points that can then be used to calculate the limit of detection (LoD) of the instrument. Analyze the data in Tofware. Three times the standard deviation of the mass loading will give you an estimate of the detection limit. The detection limit depends on the electronic noise and on the cleanliness of the vacuum chamber.

3.4. Other recommendations

The ACSM requires 350W of power (600W max) and operates on 90-260 VAC, 50:60 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 triggers a timer to shut down 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 data acquisition card from failing due to overheating. The maximum ambient operating temperature indicated by the manufacturer is 26°C and the station temperature should be stable and maintained below 25°C. Avoid direct flow of the 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). Fans on the TPS and instrument panels should be cleaned once a year, or more frequently if operating in a dusty environment, 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 download data.

4. SERVICING, CHECKS AND MAINTENANCE

4.1. Synthesis of ACSM Diagnostics and Actions

The following table (Table 1) summarizes 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 optimization of the operating rate and maximizes the quality of available data.

Table 1: Summary table of checks and maintenance

Check +/Maintenance points	Frequency	Requirements	Action in case of non conformance
Sampling inlet flow rate (c.f. Section 4.2.1)	Weekly	PM1: Check 3 l/min (±0.3 l/min) using independent flow meter PM2.5: Check 2 l/min (±0.3 l/min) using independent flow meter	Check/adjust pump
Instrument Blank / Leak Check	6 months or after sampling line changes	Install HEPA filter on instrument inlet. Concentrations must be close to the instrument's detection limits (< ± 0.5 µg/m^3)	Investigate (leak, nafion, vacuum problem, clogged filter), see Section 4.2.9
Cleaning of the critical orifice	6 months or more often in dirty/corrosive environments.	If flow rate drops 5% from starting value.	Clean critical orifice

Cleaning the cyclone	6 months or more often in dirty/corrosive environments	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 yr	Cleaning similar to other automatic PM measuring systems	
Cleaning of TPS and panel fans	1 yr	These include all fans on the PC and instrument.	Note: may be required more often depending on environment
Replacement of the particle filter	1 yr or if pressure difference between filter and sample	Preventive replacement, pressure difference should be less than 0.01 Torr between sample and filter	
Replacement of the three-way valve (c.f. Section 4.2.6)	2 years	Preventive replacement	Note: it is recommended that a spare servo is kept and replaced when needed.
Service split flow pump	4-5 years	Contact Pfeiffer or ARI.	

4.2. Description of main ACSM Diagnostics and Actions

4.2.1. Aerodynamic lens pressure (inlet pressure)/flow rate

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 1.6 and 2.0 mbar for the standard lens and between 4 and 4.8 mbar for the $PM_{2.5}$, corresponding to a sample flow rate into the instrument equal to 0.08 ± 0.015 L/min. When the valve is closed, this parameter drops to a value of approximately 0.05±0.05 mbar. 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. The flow rate into the ACSM is calculated from the inlet pressure using a calibration curve. See the User Guide for details.

The filament and detector must be turned off while the inlet valve is being opened in order to avoid damage. It is recommended to use the automatic (servo-actuated) inlet valve to open as this will automatically lower the filament and detector voltage prior to opening the inlet. Once the pressure is stable, the detector and filament voltages will ramp up to their set point values. A gradual or sudden decrease in pressure while 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 Guide). An increase in pressure, in particular when the valve is closed, can often be caused by a leak.

4.2.2. Vaporizer temperature

The recommended value of this parameter is 600 (±30°C) for a standard vaporizer and 550 (±30°C) for a capture vaporizer. It can be controlled by varying the heater power in the Heater section of the Instrument Control panel.

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

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

If the vaporizer temperature has decreased over time for a constant heater power setting, this typically indicates that the connection between the temperature sensor (thermocouple) and the vaporizer 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 power-to-temperature relationship does not vary over time. Therefore, unless the vaporizer has been replaced, the vaporizer power should be set at the value initially configured and found in 'Performance and Documentation' file shipped with the instrument typically titled 'TOFACSM-XXX_PerformanceAndDocumentation.odp' and found in the calibrations folder.

4.2.3. Airbeam (N2+ signal)/Single Ion

The Airbeam is the measured signal 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.

A typical Airbeam is 2 to 5 x 10^5 ions/s. The Airbeam value is not set directly. Instead, the magnitude of a single ion is set to 1.3 to 1.5 mV.ns (for the Magnetof detector) by adjusting the detector voltage. This is done immediately before calibration or if the Airbeam has dropped by more than 20%.

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 detector drift, 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 detector or filament's power being off.

4.2.4. Detector Voltage

This parameter corresponds to the voltage applied to the detector. There is no set reference value for this parameter. At a constant voltage, the detector 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 detector voltage, first verify the inlet pressure and that the filament is functioning properly.

The detector voltage must be increased with caution to avoid the rapid deterioration of the detector (i.e. by increments of maximum 100 Volts). The detector linearity is ensured up to 4000V according to the manufacturer.

Detector voltage should be tuned before calibration and checked periodically as described in Section 4.2.3.

4.2.5 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 less than ± 1%.

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 ionization, which corresponds to a significant decrease in the Airbeam and the concentrations detected by the ACSM.

4.2.6. 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 20 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, and 2. Measured pressure between sample and filter position are dramatically different indicating that one of the two positions is not correct.

4.2.7. 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. More details are in Section 6.2.4. A relative humidity at the dryer exit of 20-60% is recommended and this should be logged at 5 min intervals.

4.2.8. Pump operation

Pump operation can be monitored in the Pumps section of the Instrument control panel. The parameter to monitor is “Turbo power” because an increase in Turbo power, compared to normal for the specific instrument, can indicate a leak in the vacuum chamber. Turbo power should be below 140 W with the inlet valve open and below 50 W with the inlet valve closed. More details about pump operation are shown in the Vacuum panel. Pump operational parameters are saved in the datafiles and can be checked in Tofware.

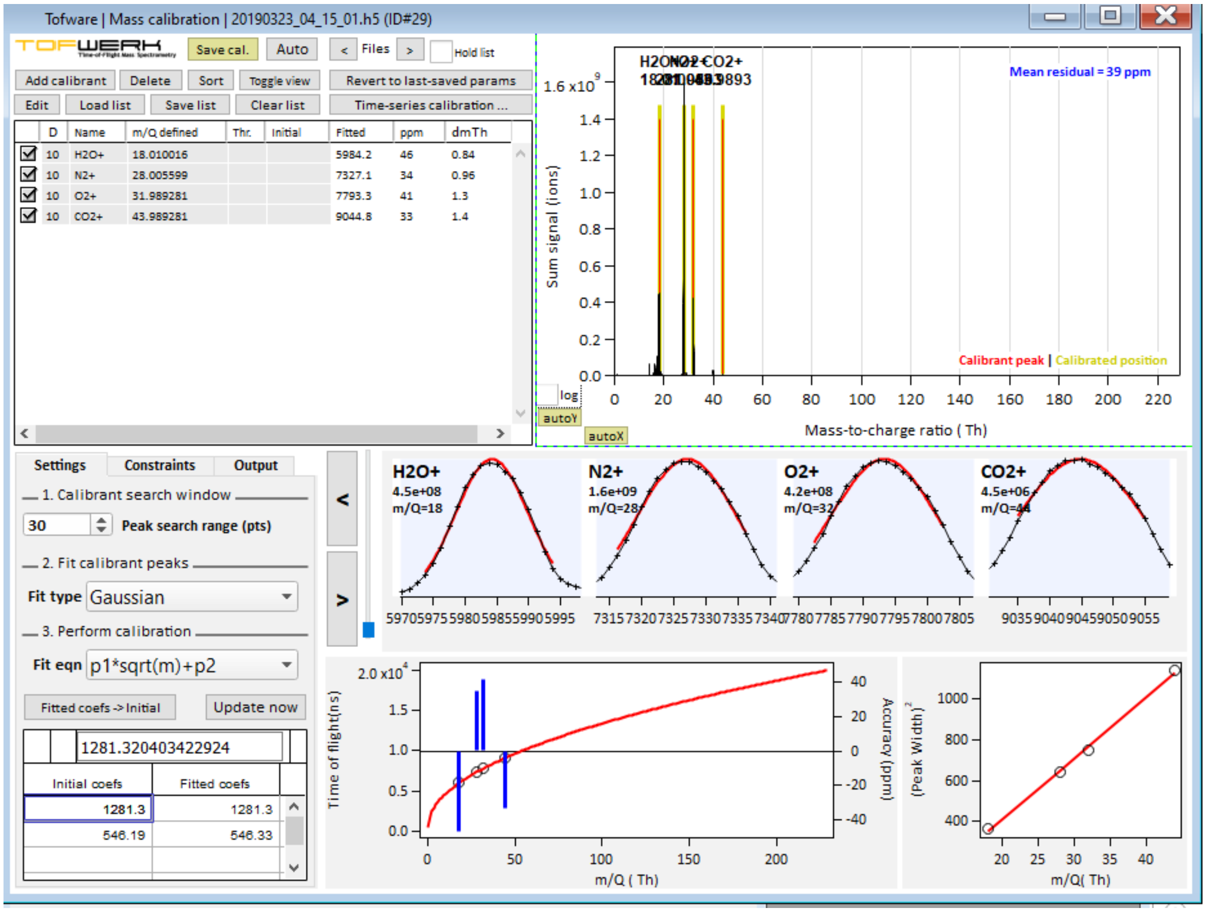
4.2.9. Instrument Blank / Leak Check

Place a HEPA filter on the sample inlet and measure in “ACSM_Acquisition” mode for minimum 3 hours. Concentrations must be close to the instrument’s species dependent detection limits (see Section 3.3). It is useful to have a CPC in line to confirm that particle counts are zero.

If a leak is suspected, important locations to check are the switching valve (ensure it rotates to fully between positions, ensure that swagelok connectors with teflon ferrules are finger tight, ensure that tubes are fully seated in connectors), inlet valve (ensure that Ultratorr connectors are tight), critical orifice holder (ensure that both o-rings are present and in good condition and nut is finger tight), and filter (replace if there is a pressure difference between filter and sample).

4.2.10. TOF MS mass-to-charge (m/z) calibration.

The mass-to-charge (m/z) calibration of the time-of-flight mass spectrometer is based on the peaks at water (H_2O^+, m/z 18), nitrogen (N_2^+, m/z 28), oxygen (O_2^+, m/z 32) and carbon dioxide (CO_2^+, m/z 44). This calibration is performed through the mass calibration panel (Figure 2), found in the DAQ Windows dropdown or by pressing F6. Acquility fits each of these four peaks with a Gaussian to find the ion time of flight. Time of flight versus m/z is fit with a two-parameter equation. The difference between the measured time of flight and the fit is shown with blue bars as accuracy (ppm). The expected accuracy is < 100 ppm.



	D	Name	m/Q defined	Thr.	Initial	Fitted	ppm	dmTh
☑	10	H2O+	18.010016			5984.2	46	0.84
☑	10	N2+	28.005599			7327.1	34	0.96
☑	10	O2+	31.989281			7793.3	41	1.3
☑	10	CO2+	43.989281			9044.8	33	1.4

1. Calibrant search window

30 Peak search range (pts)

2. Fit calibrant peaks

Fit type: Gaussian

3. Perform calibration

Fit eqn: p1*sqrt(m)+p2

1281.320403422924

Initial coefs	Fitted coefs
1281.3	1281.3
546.19	546.33

Figure 2: The mass-to-charge (m/z) calibration of the time-of-flight mass spectrometer is based on the peaks at water (H_2O^+, m/z 18), nitrogen (N_2^+, m/z 28), oxygen (O_2^+, m/z 32) and carbon dioxide (CO_2^+, m/z 44).

4.2.11. Heater Bias Voltage

This voltage optimizes the throughput of ions generated in the ion source to the mass spectrometer and adjustment is therefore very important.

There is no reference value for this parameter, which varies from one instrument to the next. However, its optimum is typically within several volts of the Ion Reference voltage. Heater bias voltage should be adjusted to maximize the Airbeam signal for a given detector voltage, while minimizing the signal at m/z 39 due to K^+ surface ions from the vaporizer. This procedure is described in the User Guide.

Heater bias voltage should be checked periodically as described in Table 2. In normal operation, the heater bias voltage should not change by more than a few tenths of a volt. It might change by a larger amount following a filament change.

5. IONIZATION EFFICIENCY AND RELATIVE IONISATION EFFICIENCY CALIBRATION

The ionization efficiency calibration is recommended to be carried out at least every 6 months. The Ionization Efficiency (IE) of NO_3 in ions/pg and Relative Ionization 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 5.4 and 5.5). Experimental setup is detailed in the following figure.

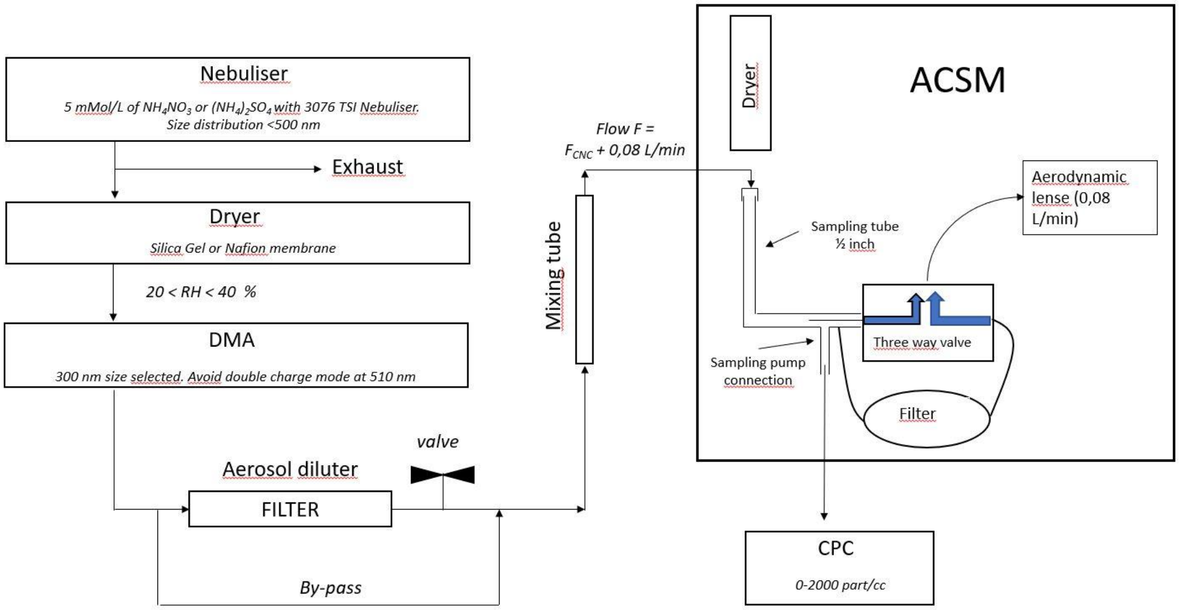


Figure 3: Typical ACSM calibration setup.

Particles are generated from nebulizing solutions of ammonium nitrate or ammonium sulfate (see Section 5.1). These particles are dried prior to 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). No impactor is required.

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 to the ½ inch sampling tube, bypassing the ACSM sampling line dryer.

A CPC is used to measure the number concentration of 300 nm particles. It should be connected to the ACSM sampling pump connector and typically set at an aerosol flow rate of 0.3 lpm. 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 more concentrated than recommended (5 mM) to avoid artefacts from multiply-charged particles (located at 510 nm when 300 nm particles are generated). This concentration value of 5 mM has been obtained using a TSI nebulizer model 3076. If another type of nebulizer were used, it is necessary to check the presence of 510 nm (doubly charged

300 nm particles). Ratio of number concentration of 510 nm to 300 nm particles should be minimized, and at least, less than 2%

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

5.2. Software configuration

Heater bias voltage tuning should be checked directly prior to the calibration.

Connect the analog output of the CPC to analog input #3 on the front panel of the ACSM in order to relate the averaged number concentration to the ion signal in Acquility. If analog output is not available, the CPC number concentration can be entered manually during the calibration.

Use Calibration mode in Acquility. The timing for this mode can be modified in the Timing and Dimensions panel. The default setup consists of 40 bufs * 1 cube * 8 (or 10) writes and thus a 320 (or 400) second file.

In calibration mode, 4 steps are outlined in the checklist on the left of the calibration mass spectrum window: 1/ Calibrate mass axis, 2/ Set base line, 3/ Single Ion, 4/ Acquire file. Follow the four steps to obtain the first point. Subsequent points can be acquired by pressing “Start” once the particle concentration is stable at a new value.

5.2.1 Measure single ion

Start acquisition of the single ion value, then wait for detector stabilisation. Signal should be recorded during several thousand extraction points. Single ion value should be 1.3 to 1.5 mV.ns (for the Magnetof detector) or 2 mV.ns (for the older Fasttof detector). If necessary, adjust the detector voltage to reach the proper value of single ion. Note that the maximum value of the new detector is 4000 V (after 2018) and 4500 V for the older one. Please refer to the TOF-ACSM User Guide for more details.

5.2.2 Acquire file

Use the normal "Start" button to record a calibration file. At the end of the file, Acquility will ask for the mobility diameter and for the chemical species used (AN or AS).

It is recommended that each calibration curve includes at least 6 data points, equally distributed over the expected concentration range in the investigated ambient air. Please refer to the TOF-ACSM User Guide for more details.

The AB value and flow rate obtained during the IE calibration are the reference values used for correcting data for changes in detector sensitivity and flow rate. The AB set point for automatic detector gain adjustment should be set to the reference AB value.

5.3. Ionisation efficiency and ammonium RIE

Ionisation efficiency is determined by measuring ions for NO^+ (m/z 30) and NO_2^+ (m/z 46) obtained from measurement of 300 nm ammonium nitrate particles. The signal for NO^+ (m/z 30) and NO_2^+ (m/z 46) in ions/s is divided by the mass concentration injected into the ACSM in pg/s. The particle number concentration (measured by the CPC) is converted to mass concentration using the density of ammonium nitrate (1.72 g/cc) and a shape factor of 0.8.

C_{mass} = density * Shape factor * 4/3 * 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 IE 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 same set up, after carefully cleaning the nebulizer, and sampled with the ACSM. It is 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.

For the calibration with ammonium sulfate, start with small concentrations and increase slowly. Due to slow evaporation of ammonium sulfate, hysteresis effects can influence the calibration if done starting with a high concentration.

5.5. Ammonium Chloride

It is advisable to calibrate for RIE of Cl with ammonium chloride if this is the dominant form of chloride in your environment. Calibration of RIE for Cl is not yet part of the Calibration mode in Acquility. To perform this calibration, collect data in ACSM_Acquisition mode for several concentrations of NH4Cl particles. Analyse the data in Tofware and determine the RIE of Cl from the mass balance with NH4.

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.

6. ACSM DATA REPROCESSING AND VALIDATION

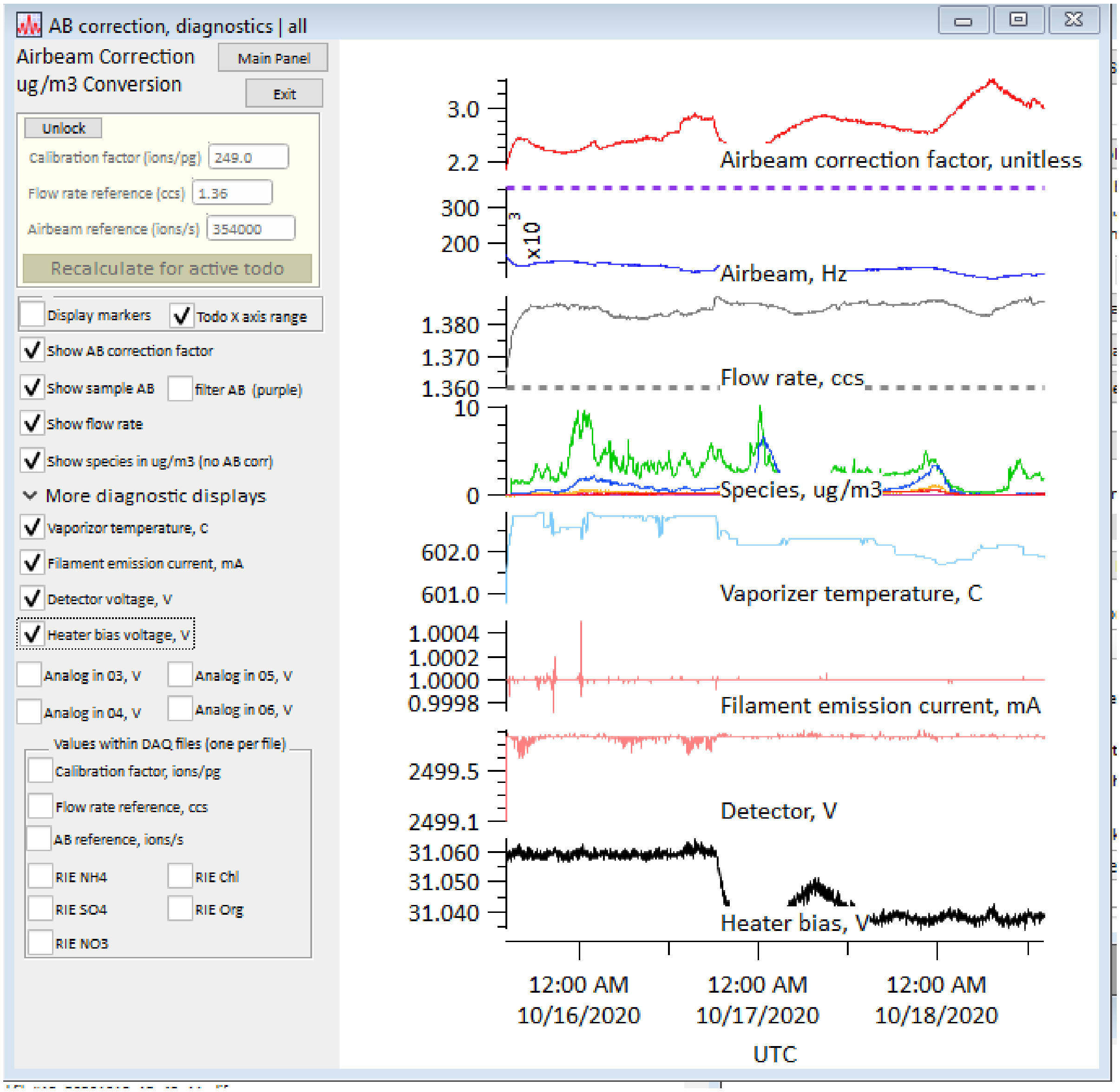
The quality assurance regime described here is designed to be applied to ACSM instruments operating in long term deployments but could equally be applied to instruments operating on campaigns. It comprises a two-stage process consisting of regular (weekly) ‘validation’ checks during the instrument operation 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 utilize a set of diagnostics that are important for assessing the correct operation of the instrument; these are shown in Section 6.2.

6.1. Data Validation Scheme

Data from the TOF-ACSM is analyzed in the Igor-based program Tofware for TOF-ACSM. Data analysis occurs in two parts. In the first part, the raw mass spectra are integrated to provide unit mass resolution (UMR) values at each m/z for each 1 s data point. Next, the average values during sample and filter are calculated and saved in files with “_dif” added to the filename.

In the second part, the “_dif” files are loaded and used to calculate mass loadings and mass spectra. A composition dependent collection efficiency (CDCE, Middlebrook et al., 2011) can be calculated and applied to the data. 2D matrices of mass spectra vs time and the corresponding errors can be exported for use in PMF/ME-2/SoFi analysis.

Data validation parameters are displayed after clicking the yellow “Airbeam correction, diagnose, and Hz unit conversion” button. These can be displayed for all loaded data (All) or for a subset defined by a “todo”. Figure 3 shows the panel with the diagnostic parameters for a sample data set. The different parts are described in Table 2. Click on the More diagnostic displays carrot to see the parameters in the bottom half of Table 2 (Figure Z3).



Calibration factor (ions/pg) 249.0
Flow rate reference (ccs) 1.36
Airbeam reference (ions/s) 354000

☐ Display markers ☑ Todo X axis range
☑ Show AB correction factor
☑ Show sample AB ☐ filter AB (purple)
☑ Show flow rate
☑ Show species in ug/m3 (no AB corr)

More diagnostic displays
☑ Vaporizer temperature, C
☑ Filament emission current, mA
☑ Detector voltage, V
☑ Heater bias voltage, V
☐ Analog in 03, V ☐ Analog in 05, V
☐ Analog in 04, V ☐ Analog in 06, V

Values within DAQ files (one per file)
☐ Calibration factor, ions/pg
☐ Flow rate reference, ccs
☐ AB reference, ions/s
☐ RIE NH4 ☐ RIE Chl
☐ RIE SO4 ☐ RIE Org
☐ RIE NO3

Figure 4. Diagnostic panel of ACSM technical parameters with the TOFWARE software.

Table 2: Summary table of data validation criteria in AB correction panel in Tofware

Diagnostic	**Criterion**	**Action when Criteria are not met**	**Reference**
Airbeam	Should be between 2 to 5 x 10^5.	Check single ion and adjust detector voltage more frequently.	4.2.3
Flow rate	Should be within 5% of reference flow rate and relatively stable.	Sudden decreases may indicate clogged critical orifice or problem with sampling line. Investigate data. Flag/reject if necessary.	4.2.1
Species (CE not applied)	Check that values are positive, roughly make sense.	Consistently negative values, or zeros where expect some signal, suggest closer examination of the data.	
Parameters in more diagnostics			
Vaporizer T	Should not fluctuate more than ± 5 C.	Check heater power. If T is dropping, but power is constant, then thermocouple may be detaching. Use previous T measurement. If large, regular fluctuations up and down, then room T may be fluctuating. Try to stabilize room T.	

Filament Emission Current	No sudden variations, >0 mA	Investigate data validity and flag / reject if necessary	4.2.5
Detector Voltage	No sudden variations other than those induced by increasing detector V, either automatically or while checking single ion.	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	4.2.10

Table 3: Summary table of data validation criteria in main analysis panel in Tofware

Diagnostic	Criterion	Action when criterion not met	Reference
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 is 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.	6.2.3
Total mass loading	Positive and not close to zero / negative for long periods	Investigate (inlet valve closed, filter valve switching, filament off, detector voltage, acquisition settings, IE and RIE configuration, inlet clean,	

		leaks…). Flag / reject bad data if necessary	
Dryer (Import data with DryerDataLoader.ipf)	RH 20% to 60%	Investigate data validity and flag / reject if necessary	

6.1.1. Black List Measurements

Where measurements need to be excluded from the dataset due to diagnostic information outside the criteria laid out in Tables 2-4, create a todo that does not include these points. See Tofware for TOF-ACSM User Guide.

6.2. Data Ratification Scheme

This second step consists of checking, for each data point, the correct configuration of the calibration coefficients (IE, RIE), the collection efficiency (CE), and the AB correction.

The yellow box in the upper left corner of the AB panel (Figure 3) shows the IE, flow rate and AB recorded in the first datafile based on the most recent calibration that preceded that datafile. If subsequent calibrations have been performed, those values will be recorded in the following datafiles. The time series of values saved in the datafiles can be displayed by checking the boxes in the lower left corner of the AB panel. If the calibration values vary with time, the user needs to decide whether to apply a single average value to the entire set or to apply a time-varying correction factor. If the calibration values vary by less than ± 20%, the manufacturer recommends using the average value. The average values can be entered in the yellow box by clicking Unlock. These values will be applied to the entire dataset. A correction factor for time-varying calibration values needs to be developed manually by the user.

6.2.2. Fragmentation diagnostic plots

Fragmentation diagnostics plots are accessed through the “Species & frag diagnostics panel” button on the main workflow panel. The first tab shows the species table (RIE and CE for each species) and the second tab shows the Frag 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

In the Frag diagnostics plots tab, choose NH4 meas vs pred and click the yellow button to create the plot. 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 = $[NO_3]*18/62 + [SO_4]*2*18/96 + [Cl]*18/35.45$, NH_4measured = $[NH_4]$

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 with NH_4 above its LOD (measured for your instrument). (Section 3.3)

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 acidic aerosols, or in the presence of SO_4 or NO_3 linked to organic matter (organo-sulfate, organo-nitrate,). 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.

6.2.4. Collection efficiency adjustment

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 instruments equipped with a standard vaporizer, a default collection efficiency of 0.5 (CE=0.5) is commonly set on the instrument software. 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. (2012[1]) proposed a procedure to accurately estimate CE under various conditions. This procedure is assumed as state-of-the-art. Its use is then highly recommended.

Note #1: For ACSM equipped with 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 acidity, and relative humidity. This can be calculated using the "Composition dependent collection efficiency (CDCE)" button in the main Tofware panel. 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. Similar logic is applied for very acidic aerosol. For low concentrations below the DL of NH_4, the CE is set to the default value (CE=0.45) for the CDCE parameterization. Note that the default CE in the CDCE parameterization (CE=0.45) is different from the recommended default CE=0.5 when not using the CDCE parameterization (see Middlebrook et al. (2012[1]) for details.)

The CE that should be used when measured NH_4 is below the detection limit (CE_lowNH_4 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.

Finally, it should be noted that the CE might also be significantly influenced by the type of sampled aerosols. For instance, Alfarra et al. 2007[2] suggested CE value equal to 0.7 when high relative contributions of organic matter from biomass combustion are present. Comparisons of individual chemical species concentrations with external data can support the identification of the optimal CE value.

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[1] [1] 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.
[2] Alfarra et al. (2007) Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions. Environ. Sci. Technol., 41, 5770-5777.