

Aerosol Chemical Speciation Monitor (ACSM) Instrument Handbook

TB Watson

August 2017

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Acronyms and Abbreviations

ASCII	American Standard Code for Information Interchange
ACSM	Aerosol Chemical Speciation Monitor
AOS	Aerosol Observing System
ARM	Atmospheric Radiation Measurement
C	Celsius
cc	cubic centimeters
cm	centimeters
DAQ	data acquisition control
DMA	differential mobility analyzer
ENA	Eastern North Atlantic
g	grams
HR-ToF-AMS	High-Resolution Time-of-Flight Aerosol Mass Spectrometer
I/O	input/output
kg	kilograms
lbs	pounds
LPM	liters per minute
MAOS	Mobile Aerosol Observing System
min	minutes
nm	nanometer
OD	outside diameter
OPC	Openness, Productivity, Collaboration
PILS	particle-into-liquid sampler
PMF	positive matrix factorization
RF	response factor
RGA	residual gas analyzer
RIE	relative ionization efficiency
sec	seconds
SEM	secondary electron multiplier
SGP	Southern Great Plains
SMPS	scanning mobility particle sizer
SPA	Sulfate Particulate Analyzer
VAC	volts of alternating current
W	watts

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1.0 General Overview

The Aerodyne Aerosol Chemical Speciation Monitor (ACSM) measures particle mass loading and chemical composition in real time for non-refractory sub-micron aerosol particles. The ACSM is designed for long-term unattended deployment and routine monitoring applications.

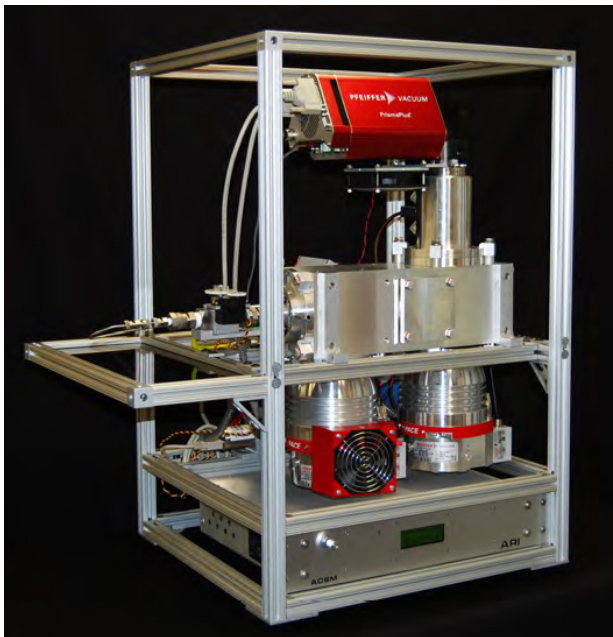


Figure 1. The bench top configuration of the ACSM.

2.0 Mentor Contact Information

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4.0 Measurements Taken

The Aerosol Chemical Speciation Monitor (ACSM) routinely characterizes and monitors the mass and chemical composition of non-refractory submicron particulate matter in real time. Under ambient conditions, mass concentrations of particulate organics, sulfate, nitrate, ammonium, and chloride are obtained with a detection limit $<0.2 \mu\text{g}/\text{m}^3$ for 30 min of signal averaging. The ACSM is capable of routine stable unattended operation for months with minimal maintenance or calibration.

5.0 Definitions and Relevant Information

Non-refractory, in the context of the ACSM, is any particulate material that cannot be vaporized at 600 °C.

5.1 Data Object Description

The ACSM generates two types of raw data files. These are designated a1 in the Atmospheric Radiation Measurement (ARM) Climate Research Facility Data Archive. They both contain data in different formats.

The first format is specific to Igor. They are known as Igor text files and are named with the form `yyyymmdd_hh_mm_ss.itx`. For example: `20140916_00_24_07.itx`. These are generated after completion of the number of scans in each averaging period and are the average over these scans. This is usually 30 minutes, which results from 28 scans of aerosol sample and 28 scans of filtered background. These files are used with the Igor-based data analysis software supplied by Aerodyne to reprocess the data.

The second format is ASCII. These files are named with the convention `XXXacsmC1.a0_bnl.yyyymmdd.hhmmss.asc`. For example: `sgpacsmC1.a0_bnl.20140916.121150.asc`. These files contain the following columns:

Table 1. ASCII file structure.

Org	total organic
NH4	ammonium
SO4	sulfate
NO3	nitrate
Chl	chloride
acsm_local_time	Seconds since January 1, 1904
acsm_utc_time	Seconds since January 1, 1904
Vaporizer_T_C	nominally 600 °C
Emission_Current_mA	nominally 1mA
Flow_Rate_ccs	nominally 1.4 cc sec^{-1} (calculated from calibration and inlet pressure)
Inlet_P_Closed_Torr	nominally 0.03 torr
Inlet_P_Open_Torr	nominally 1.3 torr

5.2 Data Ordering

<http://www.arm.gov/xdc>

6.0 Technical Specification

Data Rate:

30 minutes averaging

Sample Flow:

85 cc min⁻¹ (volumetric flow)

Operating Pressure:

Ambient

Data Acquisition (DAQ) Control:

Ethernet based

Size/Weight:

Bench top, 21" x 19.5" x 34", 140 lbs

[53.34 cm x 49.53 cm x 86.36 cm , 64 kg]

Electric Power:

300 W; 85-264 VAC, 47-63 Hz

Software:

Custom acquisition and analysis routines.

Specialized routines for positive matrix factorization (PMF) analysis of the organic fraction.

6.1 Units

μg m⁻³

6.2 Range

Aerosol Size range:

40 nm to 1 μm (vacuum aerodynamic diameter)

Mass range (m/z):

10 to 200 amu

6.3 Accuracy

Accuracy of the ACSM has been determined from intercomparison with other instruments measuring similar parameters such as the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), the Particle-into-Liquid Sampler (PILS), and the Sulfate Particulate Analyzer (SPA). Correlation plots of ACSM results versus HR-ToF-AMS for all measured species and for Sulfate versus the PILS and SPA from data taken during the Queens College Air Quality Study are given in Tables 2 and 3 (Ng, et al. 2011). Data from this and other studies place the accuracy of the ACSM measurements at ± 30%.

Table 2. Slope and correlation coefficient for plots of ACSM data versus data from HR-ToF-AMS during Queens College Air Quality Study.

Species	slope	r ²
Organic	0.76	0.89
Sulfate	0.95	0.91
Nitrate	1.01	0.88
NH ₄	0.82	0.88
Chloride	0.95	0.81

Table 3. Slope and correlation coefficient for plots of ACSM data versus sulfate data from PILS and SPA during the Queens College Air Quality Study.

Instrument	slope	r ²
PILS	0.69	0.77
SPA	0.69	0.85

6.4 Precision

Error in the mass spectra is a function of averaging time and is related to the number of counts recorded at each mass value.

$$e_c = a\sqrt{S}$$

where:

e_c \equiv the error in the mass signal in counts

a \equiv is a constant determined empirically, 1.2 in this case

S \equiv the number of counts at a particular m/z

Since the ACSM data are the result of the subtraction of the background signal from the sample signal, the error is given by the sum in quadrature of the two errors:

$$e_d = \sqrt{(e_o)^2 + (e_c)^2}$$

where:

e_d \equiv the error in the difference of the open and closed signals

e_o \equiv the error in the open signal

e_c \equiv the error in the closed signal

or

$$e_d = \sqrt{(a\sqrt{S_o})^2 + (a\sqrt{S_c})^2}$$

where:

S_o \equiv is the number or counts when the sample is collected

S_c \equiv is the number or counts when the background is measured

However, The ACSM signal is a measurement of current at the secondary electron multiplier (SEM), not ion counts. Application of the ion counting statistics requires that the signal in amperes be converted to counts. This is accomplished by estimating the number of electrons measured at each m/z scanned by the quadrupole and assuming that the number of ions at each m/z is equal to the number of electrons measured at that mass value.

$$S = \left(\frac{A}{\epsilon}\right) \left(\frac{D}{G}\right)$$

Where:

$A \equiv$ the signal in amperes (Coulombs per second)

$\epsilon \equiv$ the charge of the electron in Coulombs = 1.60×10^{-19} C

$D \equiv$ the dwell time on each m/z value used to determine the signal

$G \equiv$ the SEM gain, nominally 20,000

The dwell time is the time over which data is averaged to calculate the mass spectrum and is the product of the size of the integration window at each m/z, the scan rate of the quadrupole, and the number of points collected per amu.

The error in amperes can be expressed as:

$$\delta A = a \sqrt{\left(\frac{A_o + A_c}{6.24 \times 10^{18}}\right) \left(\frac{G}{D}\right)}$$

And this can be converted to μgm^{-3} using the measured NO_3 calibration. This value is typically $1\text{-}10 \times 10^{-11}$ (amps/ μgm^{-3}).

A plot of synthetic data for signals of 0.1 to 100 μgm^{-3} is given in **Error! Reference source not found.**

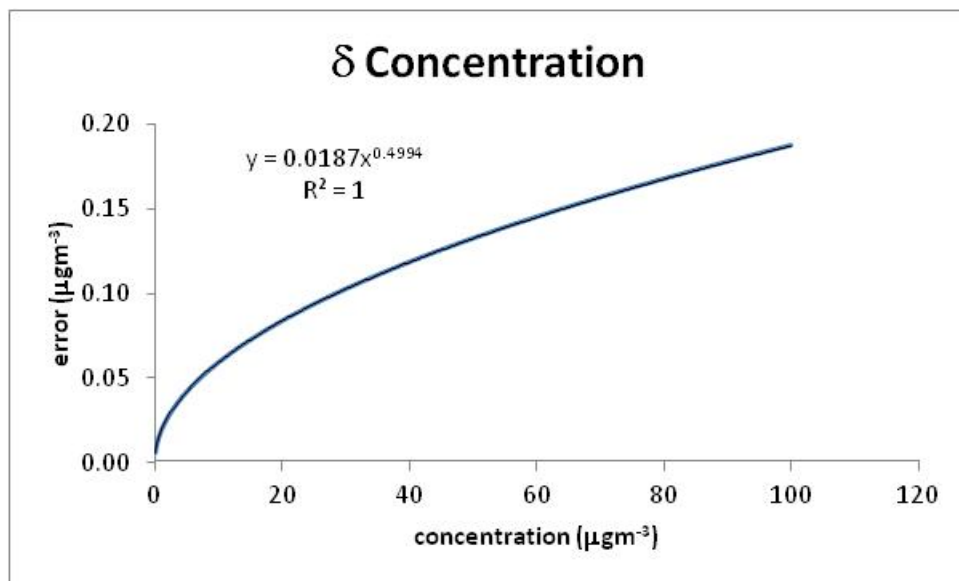


Figure 2. Plot of error in concentration for synthetic data ranging from 0.1 to 100 μgm^{-3} .

6.5 Sensitivity

($\mu\text{g m}^{-3}$, 30 minute, 3σ):

Organic: 0.3
 Sulfate: 0.4
 Nitrate: 0.2
 NH₄: 0.5
 Chloride: 0.2

7.0 Instrument System Functional Diagram

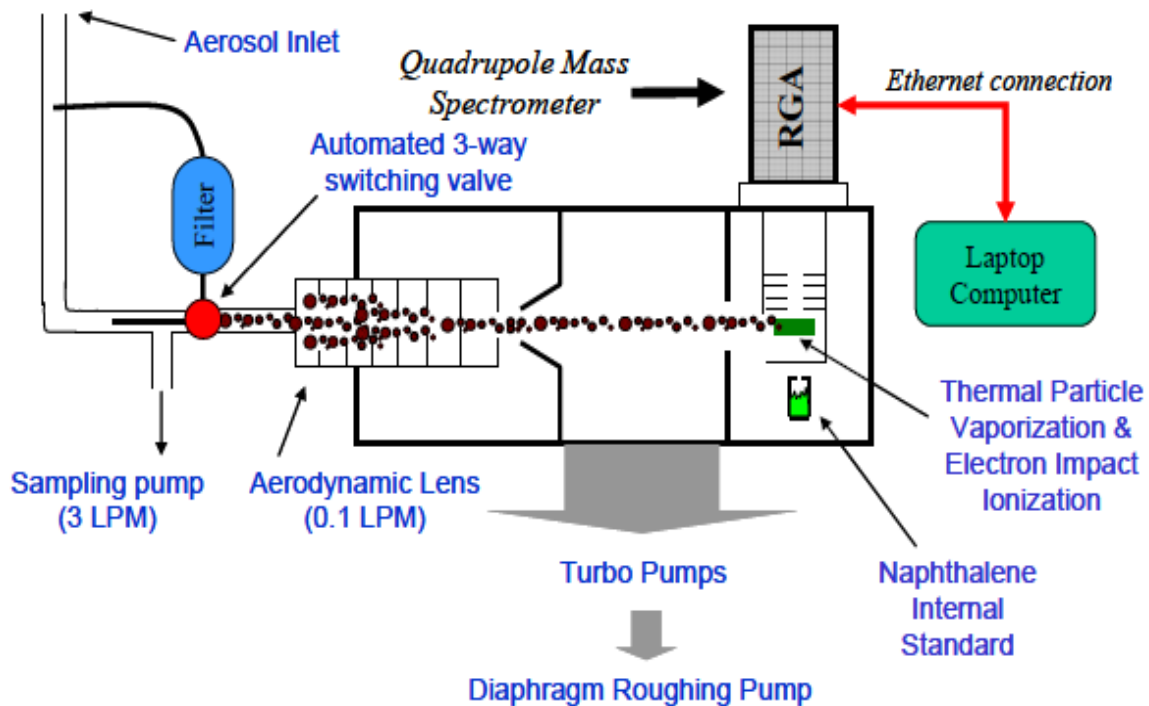


Figure 3. ACSM schematic.

8.0 Instrument/Measurement Theory

A schematic of the ACSM is shown in **Error! Reference source not found.** The vacuum chamber couples the particle aerodynamic lens with the thermal particle vaporization source and the mass spectrometer. The aerodynamic lens creates a beam, approximately 1 mm in diameter, of particles that is directed at the resistively heated particle vaporization source typically operated at 600 °C. The vaporizer is mounted inside the electron impact ionization source, which ionizes any vaporized particulate material. The ions formed are then analyzed, with the quadrupole mass spectrometer providing composition information. Three turbo molecular pumps provide differential pumping to efficiently separate the gas from the particle beam. A small oil-free diaphragm pump is used to back the turbo pumps. An aerosol inlet system couples the particle lens flow to a larger sample flow. The flow into the ACSM through the particle lens is ~0.1 LPM fixed by a 100 μm -diameter critical aperture. This rather small flow is sub-

sampled from the main aerosol inlet system flow that is designed to be 3 LPM for near isokinetic sampling conditions. Since the ion source operates continuously, there is always a background mass spectra (present in the absence of any particles) which must be measured and subtract from the particle mass spectra. This is done routinely during data acquisition by drawing the sample thru an aerosol inlet system that combines a 3-way valve and a particle filter. The position of the 3-way valve is alternately switched between filter position and sample position at the completion of each full mass scan.

This results in a “particle” mass spectrum and a “particle-free” mass spectrum. The difference between these two spectra contains the particle composition information. The frequent zero measurement adds to the long-term stability on the ACSM data sets. The ACSM also incorporates a small effusive source of naphthalene that is mounted in the detection region. This source provides a reference for calibrations such as mass-to-charge for the amu scale, instrument stability and ion transmission through the quadrupole mass filter.

The ACSM is designed around the Pfeiffer Vacuum Prisma Residual Gas Analyzer (RGA), which operates with the Prisma Plus electronics. The RGA is a 6-mm-diameter quadrupole rod system with a thermal particle vaporization and electron impact ionization source that allows universal ionization of non-refractory aerosol components. The mass analyzer covers a scan range of 0-200 amu. The Prisma electronics supports Ethernet connectivity with an OPC interface. OPC is a standard software interface that enables data communication between applications of different manufacturers. OPC stands for Openness, Productivity, Collaboration (formerly Windows OLE for Process Control). The Prisma Plus contains an embedded computer with a Windows CE Operating system that runs a Pfeiffer application called QMStart.exe, which executes at power on. The Pfeiffer electronics and QMStart application supports digital and analog input/output (I/O) which is used to control various aspects of the ACSM. All of the features and operation of the Prisma RGA are controlled via OPC commands.

9.0 Operation

There are currently three ACSM systems operating in ARM installations. One is located at the Southern Great Plains (SGP) ARM site in Oklahoma, one in the Mobile Aerosol Observing System (MAOS), and the third in the mobile facility currently located at the Eastern North Atlantic (ENA) site, Graciosa Island, Azores, Portugal.

10.0 Calibration

10.1 Sample Flow Rate Calibration

The sample flow rate calibration is used to determine the sample flow rate into the instrument based on the pressure at the inlet. The Igor data processing software uses the pressure measurement to calculate the sample flow rate based on this calibration and to calculate the mass concentrations. This calibration is performed by measuring the sample flow rate versus inlet pressure for a range of flow rates using a Gilibrator, or other flow measurement device, and the inlet pressure measured by the instrument. The slope and intercept of a linear fit to the data are entered in the software and the program uses the measured pressure to determine the sample flow rate. The sample flow rate is used to calculate the concentrations.

10.2 NO₃ Response Factor (RF) Calibration and NH₄ and SO₄ Relative Ionization Efficiencies (RIE)

This calibration determines the instrument response to nitrate (NO₃) and the relative ionization efficiencies of sulfate (SO₄) and ammonium (NH₄). These values are used in the conversion of mass spectrometer response to mass loadings. The NH₄NO₃ data are used to calculate the NO₃ Response Factor and the NH₄ Relative Ionization Efficiency. The response at m/z 28, 32, and 128 are also measured to obtain reference values for N₂, O₂, and naphthalene, which are used to correct the data for changes in response factor. The (NH₄)₂SO₄ data are used to calculate the SO₄ apparent response factor (RF_{app}) and the NH₄/SO₄ Relative Ionization efficiency (RIE). The SO₄ RIE is calculated based on the NH₄/NO₃ RIE and the NH₄/SO₄ RIE values.

The calibration is performed by using an aerosol generator and a Scanning Mobility Particle Sizer (SMPS), and a dilution system generate a 300 nm aerosol at a range of concentrations from approximately 100 to 1000 particles per cc. The Differential Mobility analyzer of the SMPS (DMA) is set to select 300 nm particles because this diameter particle is passed with 100% efficiency by the particle lens in the ACSM. Calibration points are collected over a range of approximately 100 to 1000 particles cm³, as indicated on the CPC. The calibration software converts the particle concentration to μg m⁻³. An example of calibration curves is given in **Error! Reference source not found.**

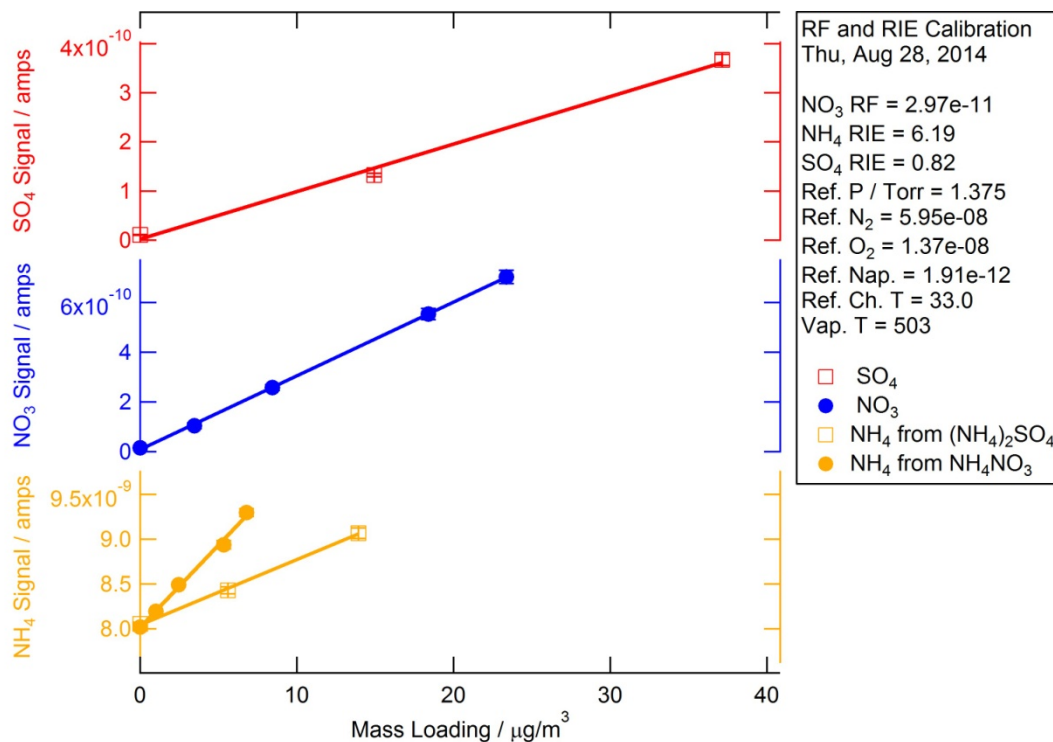


Figure 4. Results of calibration using NH₄NO₃ and (NH₄)₂SO₄.

10.3 Calibration Frequency

The manufacturer has indicated in recent discussions that the ideal calibration frequency is once a month. The SMPS is a cumbersome and expensive instrument that requires a sealed radioactive source or an x-ray generator to reduce static charge on the aerosol. This instrument is not available at all locations where the ACSM is deployed. A dedicated calibration SMPS has been procured by ARM, but this instrument must service ACSM in three locations as well as other particle measurement instruments. These locations are distributed across the globe in locations that have included Finland and Antarctica. Monthly calibrations are not practical. We are developing a calibration schedule to maximize frequency of calibration for all instruments. We are also developing procedures to evaluate instrument performance by monitoring the air beam signal present in all measurement because of the constant presence of peaks at m/z 28 resulting from nitrogen. This peak is used to adjust the mass concentrations for changes in detector sensitivity caused by aging. It has been suggested that recalibration should be performed when the air peak decreases by 10%. This as well as other diagnostics will be evaluated going forward.

11.0 Inlet System

Ambient aerosol-laden air is brought to the instruments through an 8"-diameter external stack nominally 10 m above the roof (**Error! Reference source not found.**) of the enclosure at 800 lpm. Inside the stack, sample air flows through a 2"-diameter stainless steel pipe in the center of this larger flow at 120 lpm. This flow is split inside the enclosure into four 30-lpm sample lines, one of which supplies the ACSM. The ACSM is connected to this line with a "T" and pulls sample through insulated 3/8-inch OD copper tubing connected to a separate vacuum system (**Error! Reference source not found.**). This line is insulated to prevent condensation in the line in the air-conditioned interior of the instrument enclosure. A critical orifice connected to the vacuum line maintains a flow of approximately 3 lpm past the instrument inlet. A water trap is installed at the point where the line is exposed to remove any liquid water that may condense as the line is cooled. The sample stream is dried with a Nafion dryer immediately after the trap. The sample entering the ACSM for analysis is pulled from the dry sample stream at 0.1 lpm controlled by a 100 μm critical orifice.

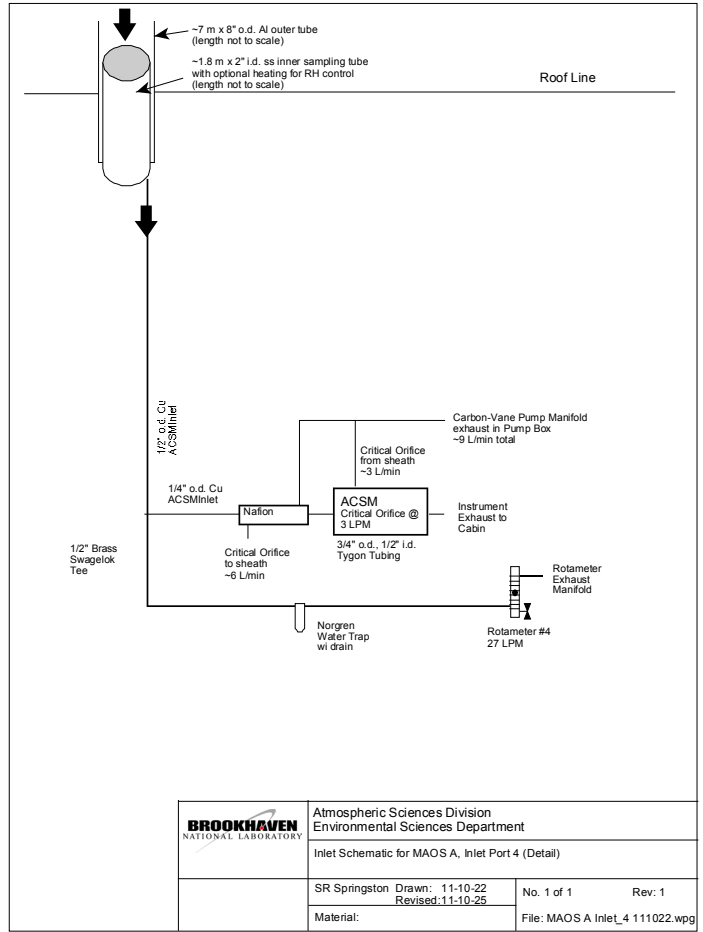


Figure 5. Schematic of inlet system.



Figure 6. Aerosol Observing System (AOS) instrument enclosure with 10 m sampling stack.

12.0 Software

12.1 ACSM Data Acquisition Software (DAQ)

Two software applications are used with the ACSM system:

- A Visual Basic (.NET) application that handles the communications with the Prisma electronics, instrument configuration, and saving of raw mass spec files
- An Igor procedure provides a user interface for real-time viewing and processing of the recorded data.

The Igor procedure uses routines to convert the mass spectra to chemical species by applying fragmentation table calculations and generating time series. The Igor procedure also prepares data matrices for positive matrix factorization (PMF) analysis. The primary role of the .NET application is to configure the mass analyzer, write raw data to the hard drive, and push data to Igor. Within the Igor interface the user can manipulate and transform the data without having any impact on the core acquisition activity that runs in the background. As data are loaded into Igor, the Igor procedure files

process the mass spectra for aerosol mass loading and prepare them for PMF analysis. The ACSM Igor application can be run at any time to process new or existing data sets.

Acquisition Computer Directory Structure

The ACSM DAQ program should be installed under the root director of drive C at C:\ACSM\ACSM_DAQ. There are several subdirectories that are accessed and used by ACSM DAQ; these are:

- C:\ACSM\ACSMDData
 - The directory where the ACSM raw data files are written.
- C:\ACSM\ACSMSSettings
 - This directory contains files that store program variables or configuration information. ACSM DAQ will automatically create these files if they do not exist. Files would include:
 - ACSM_Ionizer.dat (stores ionizer settings)
 - ACSM_Param.dat (stores scan and save settings)
 - ACSM_IPConfig.dat (stores information for connecting to Prisma)
 - ACSM_eMail.dat (stores SMTP settings for email notifications)
 - ACSM_LensAlign.dat (stores lens alignment data)
 - DAQVal_Descriptor.itx (stores text values that describe DAQVals contained in the raw data files)
- Under the program root directory, C:\ACSM, three log files are created automatically which record various instrument events.
 - ErrorLog.dat (contains a history of error messages flagged by ACSM DQ)
 - PwrFailLog.txt (contains history of instrument power failures.
 - OPCErrorLog.txt (contains a history of OPC errors flagged by ACSM DAQ)
 - To operate the Igor data analysis routines, the following Igor procedure files are required which are located at C:\ACSM\ACSM_Igor\ :
 - ACSM Local.ipf: performs data loading and processing for display.
 - GlobalUtilities.ipf :A set of helper functions used by ACSM_Local.ipf
 - To export ASCII files as well as the *.itx Igor data files, the file C:\ACSM\ACSM_Igor\acsm_local_1530_w_exporf.ipf is also necessary.
 - In addition, ACSM_Local.ipf requires some auxiliary data to process the mass spectra to chemical species. These files must be located at:
 - C:\ACSM\FragmentDataDirectory\frag\
 - This directory contains many files necessary for calculating the mass concentration from the mass spec signal.

13.0 Maintenance

13.1 Critical Orifice Replacement

The critical orifice at the inlet can become clogged with particulate material, sespecially if a 10 μ cyclone impactor is not used in the inlet stream. The inlet pressure, displayed in the “ACSM Configuration and Control” window, “Analogue and Digital IO”, will drop from the nominal value of 1.3 torr if the orifice is clogged. A new orifice can be installed or the old orifice can be cleaned in an ultrasonic bath containing distilled water and reinstalled to fix this problem.

13.2 Turbo Pump Failure

Turbo molecular pumps can fail after months of continuous operation. The symptom of this failure is a loss of vacuum and the shutdown of the vacuum system. This problem can be diagnosed by restarting the backing pump by clicking on MD1 in the pump control window software and starting the turbo pumps individually. The good pumps will start and the failed pump will shut down. When the failed pump shuts down it will turn off the other pumps. It is usually the small turbo pump, pump 3, that fails. This problem can be fixed by installing a new turbo pump.

13.3 Switch Ionizer Element

The ionizer element will burn out after several years of continuous operation. The ionizer element failure error message will appear and the element “on” check box will be unchecked in the “Vaporizer and Ionizer Control” window (**Error! Reference source not found.**). If the “on” box is rechecked, the ionizer will shut down. There are two ionizer filaments in the ACSM. Filament 2 can be selected by clicking on the button to the right of the “on/off” check box so that the green dot appears. The values to the right of the “Emiss, mA” and Max, amps boxes will increase if the filament is operating.

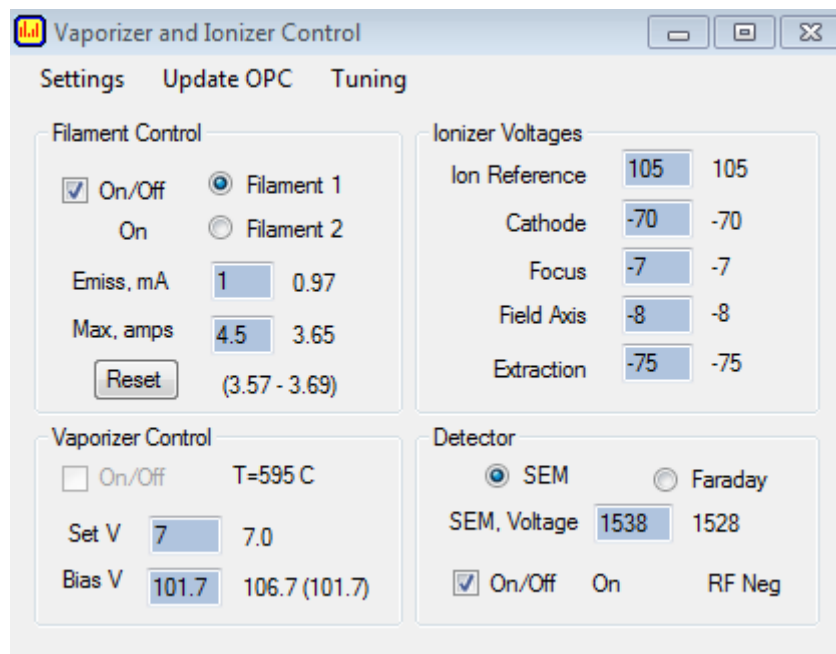


Figure 7. “Vaporizer and Ionizer Control” panel. The “Filament 1” and “Filament 2” selection buttons are indicated.

13.4 Prisma Computer Lockup

If the data acquisition stops because the Prisma computer locks up, it is necessary to reboot Prisma computer. The symptoms of this problem are:

- The loss of active status of the “ACSM Configuration and Control”,

- a failure to update the status of the mass spectrometer values in the “Vaporizer and Ionizer Control” “Filament Control” amperage readings, and the “ACSM Configuration and Control” window, “Analogue and Digital IO” “Inlet (torr)” reading.

To reboot the Prisma computer:

- From software, selecting Prisma reboot from the configuration pull-down menu in the ACSM Main Panel.
- Wait 5 minutes for the Prisma computer to stabilize and click on the “Connect” button in the “ACSM Main Panel”

If the “failure to connect” error message appears, a hard reboot is necessary. To do this:

- Unplug the power cable from the Prisma electronics head, then plug in power, wait 5 minutes and try to connect again.

14.0 Safety

Standard safety protocols should be followed for working on the ACSM. The instrument should be disconnected from all power before attempting to service any element.

15.0 Shipping

- Remove Prisma head and pack it carefully using bubble wrap or another suitable packing material.
- Place container in the box provided by the manufacturer with the computer.
- Make sure that an air-ride truck is used for transport.

16.0 Citable References

Budisulistiorini, SH, MR Canagaratna, PL Croteau, WJ Marth, K Baumann, ES Edgerton, SL Shaw, EM Knipping, DR Worsnop, JT Jayne, A Gold, and JD Surratt. 2013. “Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the Aerodyne aerosol chemical speciation monitor.” *Environmental Science and Technology* 47(11): 5686–5694, [doi:10.1021/es400023n](https://doi.org/10.1021/es400023n).

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