Sunset Carbon Evaluation Project

Quality Assurance Project Plan (QAPP)

QA Level IV

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Ambient Air Monitoring Group

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Sunset Carbon QA Project Plan
QAPP Approval Signatures
Category IV QAPP

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DISTRIBUTION LIST

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1.0 Introduction

This is a level IV Quality Assurance Project Plan (QAPP) that covers an Environmental Data Operation (EDO) conducted by the EPA's Office of Air Quality Planning and Standards (OAQPS) Ambient Air Monitoring Group (AAMG) and State and local monitoring agencies to collect field data at seven (7) sites across the United States. The selection of participating sites is in progress, and to date, monitoring agencies at 3 sites have agreed to participate. These sites are located in St. Louis, Chicago, and Washington D.C. EPA AAMG will operate one site at the Ambient Air Innovation and Research Site (AIRS) monitoring station on the EPA campus located in Research Triangle Park (RTP), NC. This project is an instrument evaluation and feasibility study of the Sunset Semi-Continuous Organic and Elemental Carbon (OC/EC) monitor will be conducted as well as a data comparison with the URG 3000N. At sites where the Magee Scientific Aethalometer is located, data from the Aethalometer will also be compared to the Sunset Semi-Continuous analyzer. The QAPP is a formal document describing necessary Quality Assurance (QA), Quality Control (QC) and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria and objectives. The OAQPS utilizes a four-tiered project category approach to its QA Program. This project falls into Category IV, which is defined as *"Projects involving EDOs to study basic phenomena or issues, including proof of concepts, screening for particular analytical species, etc. Such projects generally do not require extensive detailed QA/QC activities and documentation."* Such projects include those producing results that are used to evaluate and select options for interim decisions or to perform feasibility studies or preliminary assessments of unexplored areas for possible future work. Level IV projects include monitoring, modeling, and/or analyses involving one time studies or local scale monitoring; monitoring, modeling, emission inventories, and assessments; field testing of performance test methods and source monitoring procedures; evaluating formal requests to allow the use of alternative methods; and investigating the feasibility of new or modified performance test methods or source monitoring procedures.

Note that $PM_{2.5}$ filters will be collected using the URG 3000N and analyzed (chemically and physically) by existing, EPA-approved, methods given in the QAPP and accompanying Standard Operating Procedures (SOPs) in use under the EPA/OAQPS Chemical Speciation Network (CSN) contract EP-D-09-010. The Sunset Instrument and Aethalometer are continuous/semi-continuous instruments that do not require further laboratory analysis. They will be operated in the field using the SOPs provided in Appendices H & J of this QAPP.

1.1 Project/Task Description

One of the major areas of interest in air monitoring is the evaluation of continuous monitoring technologies that could feasibly be used to reduce the frequency and amount of filter based technologies. In the CSN alone, over 180 sites are collecting 24-hr filter based samples that are analyzed for mass, trace elements, major ions, and carbon. Carbon (OC/EC) samples are collected on to quartz filters every third or sixth day and shipped to Research Triangle Institute (RTI) for analysis. The cost of sample preparation, shipping and analysis for the carbon network is approximately $2M per year. In an effort to move towards continuous, higher time resolution sampling and reduce the need for expensive, time consuming, filter based sampling, OAQPS is committed to the evaluation of new, continuous monitoring technologies for implementation at routine monitoring networks. For this reason, the AAMG purchased eight Sunset Semi-Continuous OC/EC instruments for deployment to monitoring agencies.

The data gathered from the Sunset Evaluation Project may be used to update EPA's SOP for the instrument. The study will take place at seven (7) CSN monitoring sites across the United States for up to three years, in order to provide enough data to evaluate the instrument in different seasons and meteorological conditions. These study data are **not** being collected for compliance purposes. Sunset field instruments will be operated for the purposes of:

- Evaluating instrument performance in various geographic/climatic/source regimes across the country, during different seasons
- Gaining proficiency in the proper operation and maintenance of the instrument
- Evaluating collocated instrument precision
- Evaluating comparability of the Sunset thermal OC/EC with the URG 3000N thermal OC/EC
- Evaluating comparability of the Sunset optical EC with the Aethalometer optical black carbon (BC), where present
- Evaluating ease of use, level of effort to maintain, and operation in a routine monitoring network setting
- Refining the QC procedures based on the findings and developing training materials
- Determining if implementation across a larger number of CSN sites is appropriate

Table 1 provides the major milestones and deliverables for the study. A final report on the comparability of the analyzers and recommendations for future implementation is expected to be completed in 2015.

Table 1 – Major Milestones and Deliverables

Task Description	Person(s) Responsible	Deliverable Date
Shipment of Equipment to Participating Sites	Landis, Ricks	Fall 2011
Instrument Setup and Training	Sunset Personnel – Josh Dixon	Winter 2011
Field Operation	Site Leads	Winter 2011 – 2014
Updated Sunset SOP, QC Procedures & Checklists	Landis	Ongoing
Data Summary Report	Landis	2015

1.2 Study Objectives

The primary objectives of the study are to evaluate Sunset instrument performance in various locations and conditions, determine how well the Sunset compares with the URG 3000N and the Aethalometer, and determine if integration of the Sunset OC/EC instrument across a larger number of sites is appropriate for long-term monitoring in the CSN.

As a secondary objective, the information from the study will be used to inform and gain insight regarding the questions below:

- What are the space considerations for operating the Sunset analyzer in a shelter? Do any special considerations need to be made for control of shelter temperature and relative humidity? What interferences exist that may be problematic for implementation?
- What important parameters should be tracked or documented for QC purposes (e.g. Laser Correction Value, Oven Temperature, Pressures, etc.)? How should the data be validated? What is the Sunset instrument data capture rate?
- How often should sucrose standard injections be performed? What is the typical value of nightly blanks?
- What are the capital costs, including additional equipment, for operating each analyzer? What level of effort and training are necessary for routine operation?

1.3 Evaluation Project Sample Analysis and Data Reporting

Filter-based samples and semi-continuous monitoring data for the Sunset Evaluation Project will be collected by the local monitoring agencies at the participating locations in Chicago, Washington DC, Houston, Los Angeles and St. Louis and by AAMG staff in RTP, NC. One additional location will be added as an agreement for participation can be secured. The EPA will provide the Sunset instrument (including the organic denuder, site computer and software, $PM_{2.5}$ inlet head, sampling pump, two spare heating coils, and a spare main oven insert) as well as a two-day training and installation from the manufacturer. Participating sites are currently running the URG 3000N according to its SOP under the $PM_{2.5}$ Chemical Speciation Network (CSN) program. RTI currently services the sites with prepared filters, loaded into cassettes, for the URG 3000N filter-based method. This service includes quality assurance checks, such as providing filters for field blank determination and organic artifact assessments. RTI provides data sheets for manual entry of essential field information. These data sheets will be completed by field personnel and returned to the RTI laboratories with the appropriate sample. Following analysis, RTI will upload the data to the EPA's Air Quality System (AQS) along with applicable uncertainties and method detection limits. Local monitoring agencies will be responsible for uploading their Sunset data to AQS and EPA's secure AIRNowTech data system (www.airnowtech.org).

1.4 Standard Operating Procedures (SOPs)

A SOP for the Sunset has been developed based on findings from the AIRS Sunset Carbon Evaluation Project and using vendor provided documents as guidance. For operation of the Magee Scientific Aethalometer, an existing SOP developed by the Office of Research and Development will be used. The SOP for the operation of the URG 3000N is covered under the $PM_{2.5}$ Chemical Speciation Network (CSN) program Quality Assurance Project Plan (QAPP). The SOP for the analysis of the URG 3000N filters by Desert Research Institute (DRI) is also covered under the CSN program QAPP.

The field sampling and analysis method SOPs and operating manuals to be used for this project are referenced in Appendices H, J, L & M.

2.0 Quality Objectives and Criteria for Measurement Data

Formal Data Quality Objectives (DQOs) are not required for Category IV QAPPs; however, project objectives and goals have been defined in section 1.2 and Measurement Quality Objectives (MQOs) are defined below. To maintain the quality of the data over the course of the study, QC objectives have been defined and are listed in Table 4. The primary focus of this project is to assess the performance of the Sunset OC/EC instrument.

- **Precision -** a measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions. This is the random component of error. Precision is estimated by various statistical techniques typically using some derivation of the standard deviation. A MQO of 15% Coefficient of Variation (CV) has been established for collocated precision of Total Carbon (TC) for the CSN. Collocated precision will be estimated initially at EPA's AIRS site in RTP, NC. As the project progresses, the collocated instrument may be moved to another sampling location. We will not be running collocated precision experiments for the Aethalometer and URG 3000N as part of this project, thus we will use the precision estimates provided in Table 2 for these two instruments. Precision will be calculated in the following way:

  <u>Coefficient of Variation</u>

  CV = coefficient of variation $CV = 100 * \left(\frac{\sigma}{\mu}\right)$

  σ = standard deviation $\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2}$

  μ = mean $\mu = \frac{1}{N}\sum_{i=1}^{N} x_i$

- **Comparability** - a measure of the confidence with which one data set or method can be compared to another, considering the units of measurement and applicability to standard statistical techniques. An Expert Panel was convened by the EPA in 1998 to provide advice on the establishment and implementation of the CSN. The Expert Panel provided recommendations on the species and methods used for the CSN, but did not provide any criteria for acceptability or comparability of the measurements. However, the Four-City Study Report (prepared by ORD in 2001) to evaluate speciation samplers for the CSN suggested that the ratio-of-means criteria for OC and EC be 1 ± 0.15 (Reference in Appendix H). Thus, an MQO of 1 ± 0.15 has been established as the target or goal for comparability of OC and EC across methods. Definitions for comparability also used for evaluation of in situ carbon measurements have been suggested by Watson and Chow. The criteria for comparability (Watson and Chow 2002) were (i) a slope that was 1 ± 3 standard errors; (ii) an intercept equal to 0 ± 3 standard errors; and (iii) a correlation (R) ≥ 0.9. These will all be used as the MQO target for the linear least squares regression test. Comparability of datasets is critical to evaluating their measurement uncertainty and usefulness. The OC and EC data from the Sunset, URG 3000N and Aethalometer will be compared, as they are making similar carbon measurements, in the following ways:

Linear Least Squares Regression
A linear least square regression will be done at the site level to provide slope, intercept, R (coefficient of linear correlation – measures the strength of association between x and y) and R^2 (coefficient of determination – measures the quality of the regression line as a means of predicting y from x) values when making the comparison between two different instruments.

Comparison of the Means including Variability
The different instruments will also be compared by looking at their mean values including variance (precision). If the mean value for one instrument falls within the range of the mean value ± the variance (precision) of another instrument, the two instruments can be deemed comparable. As we will not be running collocated precision experiments for the Aethalometer and URG 3000N, we will use the precision estimates provided in Table 2 for these two instruments. Collocated precision will be calculated for the Sunset (as described above) at AIRS.

Ratio of the Means
As a quick way to compare the different instruments, the ratio of the mean Sunset OC/URG OC, Sunset EC/URG EC, Sunset Optical EC/Aethalometer BC will be calculated.

- **Detection Limits -** the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated level of probability (a measure of the smallest signal an instrument can produce). The detection limit of the Sunset instrument will be assessed by injecting low concentration sucrose standards and taking the standard deviation of seven replicates in accordance with 40 CFR Part 136 Appendix B. It will also be estimated using collocated data (Hyslop and White, 2008, Appendix K). These estimates will be compared to the values provided by the vendor (see Table 2). Based on vendor estimates, an MQO of 0.4 µg/m^3 has been established for Total Carbon.

- **Completeness -** the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions. The targeted completeness for each experiment in this study is 80%.

- **Bias -** the systematic or persistent distortion of a measurement process which causes error in one direction. Bias is typically determined by estimating the positive and negative deviation from the true value as a percentage of the true value. However, there are no Federal Reference Methods or reference materials for carbon measurements to assess bias. Nevertheless, known amounts of Sucrose, ≥99.5% from Sigma Aldrich (Product #S9378), will be injected into the Sunset instruments bi-weekly to assess bias relative to the current calibration curve. An MQO target of 5% bias has been established by the vendor for the sucrose injections. The flows will also be measured with a National Institute of Standards and Technology (NIST) traceable flow meters (tetraCal and Bios), that are verified annually, to assure that the Sunsets, URG 3000N and Aethalometer are performing within specifications. The temperature and pressure sensors on the URG

3000N will also be checked with the same NIST traceable meter (tetraCal). See Table 4 for the Measurement Quality Objectives for flow, temperature and pressure for the instruments.

The analyzer operating conditions and performance are provided in Table 2 below.

Table 2 –Analyzer Operating Conditions and Performance

Make/Model	Flow Rate	Sample Cycle	Measurement Range	Detection Limits	Precision Estimates
Sunset OC/EC Model 4	8LPM	1 hour	OC: 0.4-200 µg C/m^3 EC: 0.2-40 µg C/m^3	OC: 0.4 µg C/m^3 EC: 0.2 µg C/m^3	[B]MQO for TC: CV ≤ 15%
Magee Scientific Aethalometer	5LPM	5 min	None Provided	BC: 0.05 µg C/m^3	[C]CV ~ 15% (5 min) [C]CV ~ 3.5% (24 hour)
URG 3000N	22LPM	24±1 hour	[A]0.05-750 µg C/cm^2	OC: 0.064 µg C/m^3 EC: 0.064 µg C/m^3	[D]OC (CV) ~ 17.7% [D]EC (CV) ~ 28.8%

[A] Analytical measurement range for DRI Model 2001 carbon analyzer for a typical punch size of 0.5 cm^2 (DRI SOP)
[B] Measurement Quality Objective (MQO) for Total Carbon (TC) from the Strategic Plan for the Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trends Sites (Appendix H)
[C] CV from the Environmental Technology Verification Report for the Aethalometer (Appendix H)
[D] CV provided by RTI and calculated from 2011 CSN Data Summary Report (Appendix H)

2.1 Field Measurements

Field measurements will ultimately occur at seven sites. Currently, five sites have agreed to participate (Chicago, IL, St. Louis, MO, Los Angeles, CA, Houston, TX and Washington DC) and one site has been established in RTP, NC. The following equipment will be installed and operated at the participating sites, also listed in Table 3:

- Semi-Continuous OC/EC Instruments (Sunset Model 4) – thermal OC/EC and optical EC;
- Particulate Speciation Carbon Filter Samplers (URG 3000N) – thermal OC/EC; and
- Aethalometers (Magee Scientific) – optical BC at 880nm

Meteorological equipment is not required for the monitoring sites; however, on-site meteorological measurements (e.g., wind speed, wind direction, temperature, barometric pressure and relative humidity) are useful to determine the reasons for variability in measurements from day to day (rain or other weather events; calms; steady winds from a particular direction, etc.). If equipment for meteorological measurements is present at the site, it should be checked for accuracy and proper operation by the local operating agency according to the local monitoring agency's quality assurance monitoring plan. The meteorological data may be used to make inferences but will not be relied upon for definitive statements unless adequate data quality information is available.

Table 3–Site Equipment

Site	AQS ID	Sunset(s)	URG 3000N	Aethalometer
AIRS – RTP, NC	37-063-0099	2	1	1
Com Ed - Chicago, IL	17-031-0076	1	1	Not available
Deer Park – Houston, TX	48-201-1039	1	2*	1
Rubidoux – Los Angeles, CA	06-065-8001	1	2*	Not available
McMillan Reservoir – DC	11-001-0043	1	1	1
Blair Street – St. Louis	29-510-0085	1	1	1

*One URG 3000N samples 1:3 and the other samples 1:6

Operational acceptance limits for the sampling devices are presented in Table 4 below.

Table 4– Measurement and Quality Control Objectives

Instrument	Requirement	Frequency	Acceptance Criteria	Corrective Action
Sunset *(SOP in Appendix H)*	Midnight Blanks	Daily (as possible)	<±0.3 µg C (TC)	^{1}Check for leaks, ^{2}Check system pressure, ^{3}Check oxygen trap, ^{4}Check gas lines to be sure no Teflon is used
	Laser Correction Value	Weekly	>0.90	^{1}Check if filter is still in vertical position, ^{2}Check filter for holes/tears, ^{3}Change filter and record any findings in log
	Flows manually set to 0	Weekly	±0.5 cc/min	Perform autozero, note in log
	Precision Calculation	Weekly	CV ≤ 30%	Contact Sunset for troubleshooting assistance
	Single-point External Standard Verification	Bi-Weekly	±5%	^{1}Carefully prepare and re-run two standards, ^{2}Check gas flows, ^{3}Check for leaks, ^{4}Check system temperatures, ^{5}Remake stock solution and rerun samples, ^{6}Perform multipoint calibration and update calibration parameter file
	Multi-point External Standard Verification	Semi-Annually & after changing cal gas tank	±5%	
	Flow check	Semi-Annually & after 1 month of sampling	±2% (He1, HeOx & Cal Gas), ±5% (He Purge)	Perform a flow sensor calibration
URG 3000N *(SOP in Appendix H)*	Date and Time checks	Monthly & Daylight Savings Time Changes	±5 min	Correct Date/Time, note in the log
	Leak Check	Monthly	Vacuum drop <225 mm Hg in 35 seconds	^{1}Reseat cassette and reattempt, ^{2}Replace the cassette and reattempt, ^{3}Inspect o-rings on cyclone for tears or damage, ^{4}Inspect temperature probe plug o-rings for tears or damage, ^{5}Inspect o-rings in inlet tee for tears or other damage, ^{6}Contact URG for further assistance.
	Temp. Control Check	Monthly	±2°C	Perform a temperature calibration, note in log
	Pressure Control Check	Monthly	±10 mm Hg	Perform a pressure calibration, note in log
	Flow Rate Control Check	Monthly	±10%	Perform a flow calibration, note in log
	Temp. Control Audit*	Semi-Annually	±2°C	Perform a temperature calibration, note in log
	Pressure Control Audit*	Semi-Annually	±10 mm Hg	Perform a pressure calibration, note in log
	Flow Rate Control Audit*	Semi-Annually	±10%	Perform a flow calibration, note in log
Magee Scientific Aethalometer *(SOP in Appendix J)*	Date and Time checks	Weekly	±5 min	Correct Date/Time, note in the log
	Verify Flow on Display	Weekly	5± 0.2 LPM	Verify setting was not accidentally changed
	External Flow check	Monthly	±10%	Contact Magee – may need to perform a flow calibration, note new scale factor in log

* Standard independent of that used for monthly check

The field site managers will ensure that the sites have adequate power, space and infrastructure necessary to support the project. The filter-based samplers will run every 3rd day, from midnight- to- midnight on local standard time for the entire study period (three years). The current three day monitoring schedule can be found at www.epa.gov/ttnamti1/calendar.html. The Sunset and Aethalometer will also be operated on local standard time. A summary of required field operations and maintenance tasks, which are more fully explained in the SOPs in Appendices H & J, is presented in Table 5 below.

Table 5– Maintenance Activities for Instrumentation

Instrument	Frequency	Requirement(s)
Sunset *(SOP in Appendix H)*	Weekly	• Verify Carrier Gas Pressures - Order new if primary <1000 PSI, replace if primary <500 PSI, verify secondary ~30 PSI for collocated and ~12 PSI for single • Check that Instrument Gas Flows are relatively stable • Verify Back oven Temperature (~870°C during analysis and ~500°C during sampling) • Change Filter, Shutdown Software, Restart Computer & Download Data • Check Trap below "Drop Out Tee" • Check PSIG in Idle Mode
	Biweekly	• Change the file name (if not writing to a new file daily and on 1 hour sample period) – *restart computer after renaming*
	Monthly	• Change the file name (if not writing to a new file daily and on 2 hour sample period) – *restart computer after renaming* • Change denuder filter strips • Clean inlet cyclone
	Semi-Annually	• Clean inlet tubing
URG 3000N *(SOP in Appendix H)*	Every Visit	• Check o-rings on each filter cassette for wear, damage & proper seat • Clean off any moisture around the outside of the sampler and controller modules
	Monthly	• Clean the interior of the sample and controller modules with KimWipe tissues or paper towel • Clean sampler inlet surfaces
	Quarterly	• Check all Tygon® tubing & vacuum lines; replace if necessary • Inspect electrical line connections • Clean sampler inlet tube (using slightly moistened paper towel and wooden dowel) – allow to dry • Rotate quartz filter cassettes on the "AUDIT" cartridge
Magee Scientific Aethalometer *(SOP in Appendix J)*	Weekly	• Check filter tape supply • Re-tension tape roll take-up spool if necessary • Inspect borders of visible spots on the used filter tape
	Monthly	• Clean inlet cyclone • Replace SD Memory Card
	Semi-Annually	• Perform flow calibration • Perform self test • Perform optical test
	Annually	• Clean or replace inlet probe line • Determine residence time

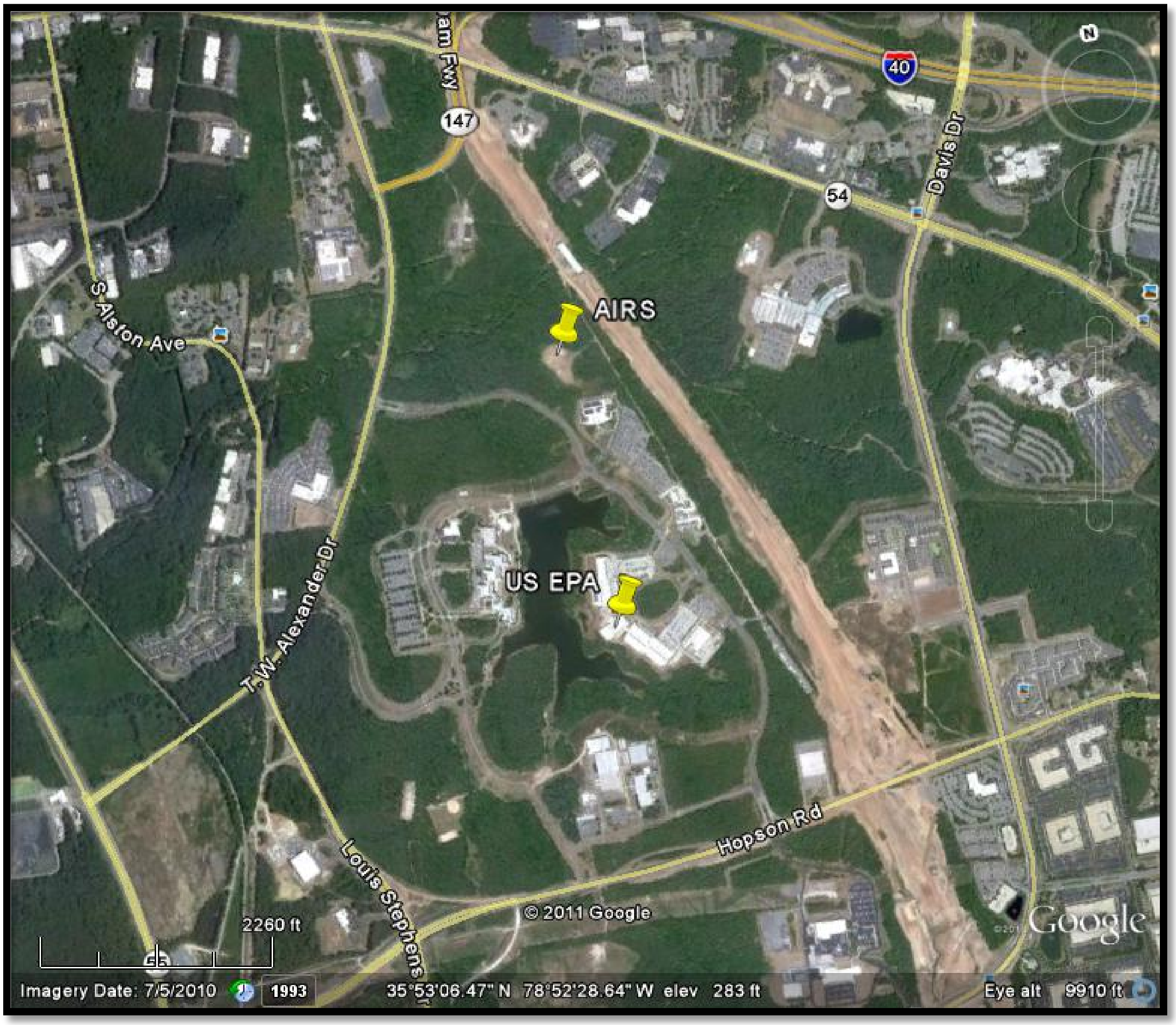
Maintenance activities for the Sunset are described in the “Standard Operating Procedure (SOP) for the Analysis of Organic and Elemental Carbon (OC/EC) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer” by Sunset. The URG 3000N maintenance needs are in the field SOP for the URG-3000N Sequential Particulate Speciation System (Interim Version 1.0), Revision 1. The maintenance requirements for the Aethalometer are discussed in the SOP for the Magee Scientific Aethalometer Models AE-22 & AE-31, Version 1.4 by EPA ORD/NERL.

Operators of individual field sites will maintain field records. Each field site operator will maintain a field notebook and a binder to keep documents in order and readily accessible for review if needed. The notebooks will be uniquely numbered and associated with the Sunset Evaluation Project. Generally, all data from all routine field operations with the URG 3000N will be entered on the field data forms to be supplied by RTI (Appendix D). It is also necessary that the site operator electronically download the data from the sampler’s memory card before shipping the memory card and sample back to RTI. Carbon copies of the URG 3000N field data forms will be maintained by the site operator in a project specific binder. Field data and calibration forms for the Sunset and Aethalometer (Appendix A, B, C, F & G) will also be stored in the project binder. The field notebook will be used to record additional information about field related operations, such as information regarding weather conditions and activities in the area that may influence sample content and concentration (e.g. wind or electrical damage to equipment, construction or mowing activities in the area, welding, wildfires, bad weather, vandalism, power failure, unique traffic disruption, etc.). Some organizations may have the capability of substituting electronic communications (i.e., electronic site notebooks) for the field notebook. This is appropriate as long as it is used consistently.

Field measurements will ultimately occur at seven sites. Currently, five sites have agreed to participate (Chicago, IL, St. Louis, MO, Houston, TX, Los Angeles, CA and Washington DC) and one site has been established in RTP, NC. Details on each of these sites are provided below.

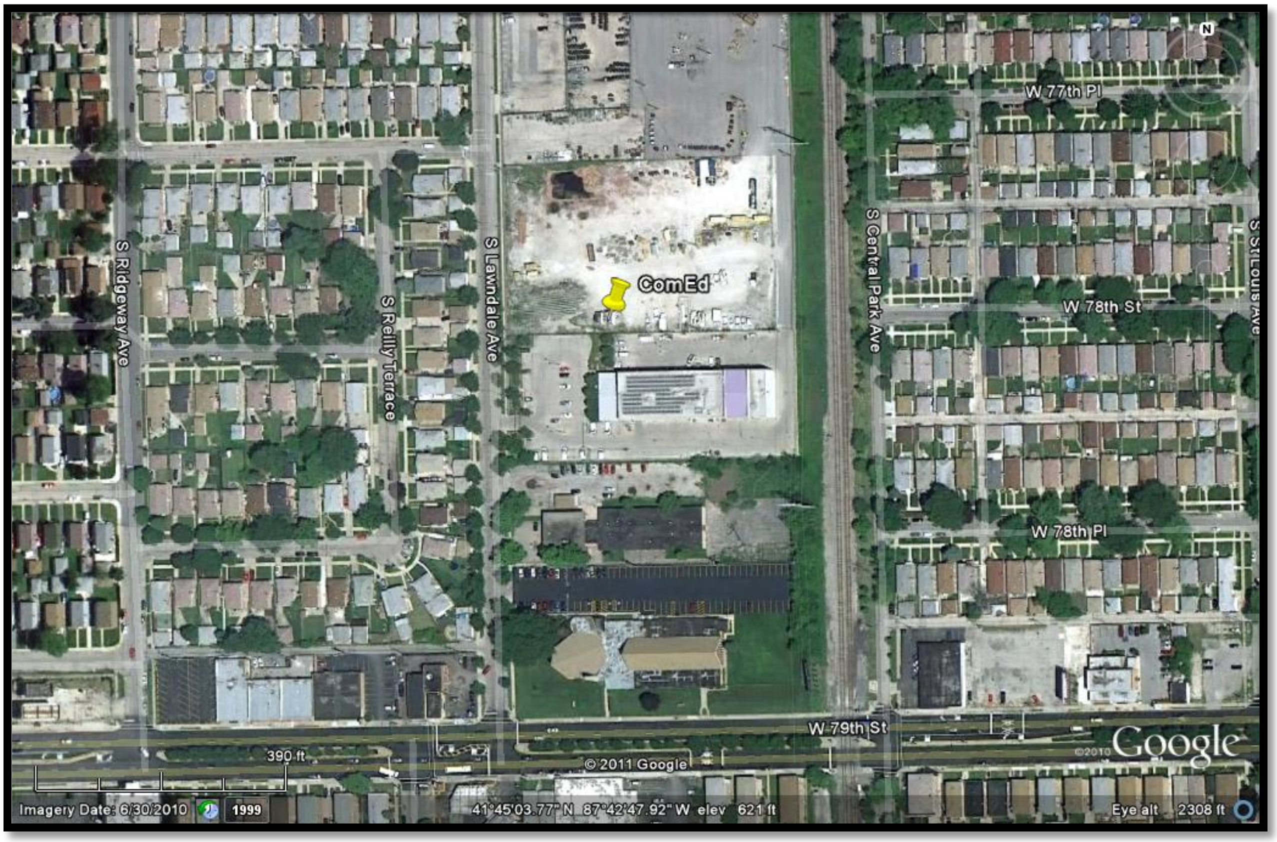
The RTP site (AIRS) is located at on EPA's Campus at 109 TW Alexander Drive, Research Triangle Park, NC 27709. The AIRS site is classified in AQS (ID 37-063-0099) as commercial land use in a suburban location. Day-to-day operations at AIRS will be managed by the AAMG of OAQPS.

Figure 1 – Google Earth Image of AIRS Monitoring Site



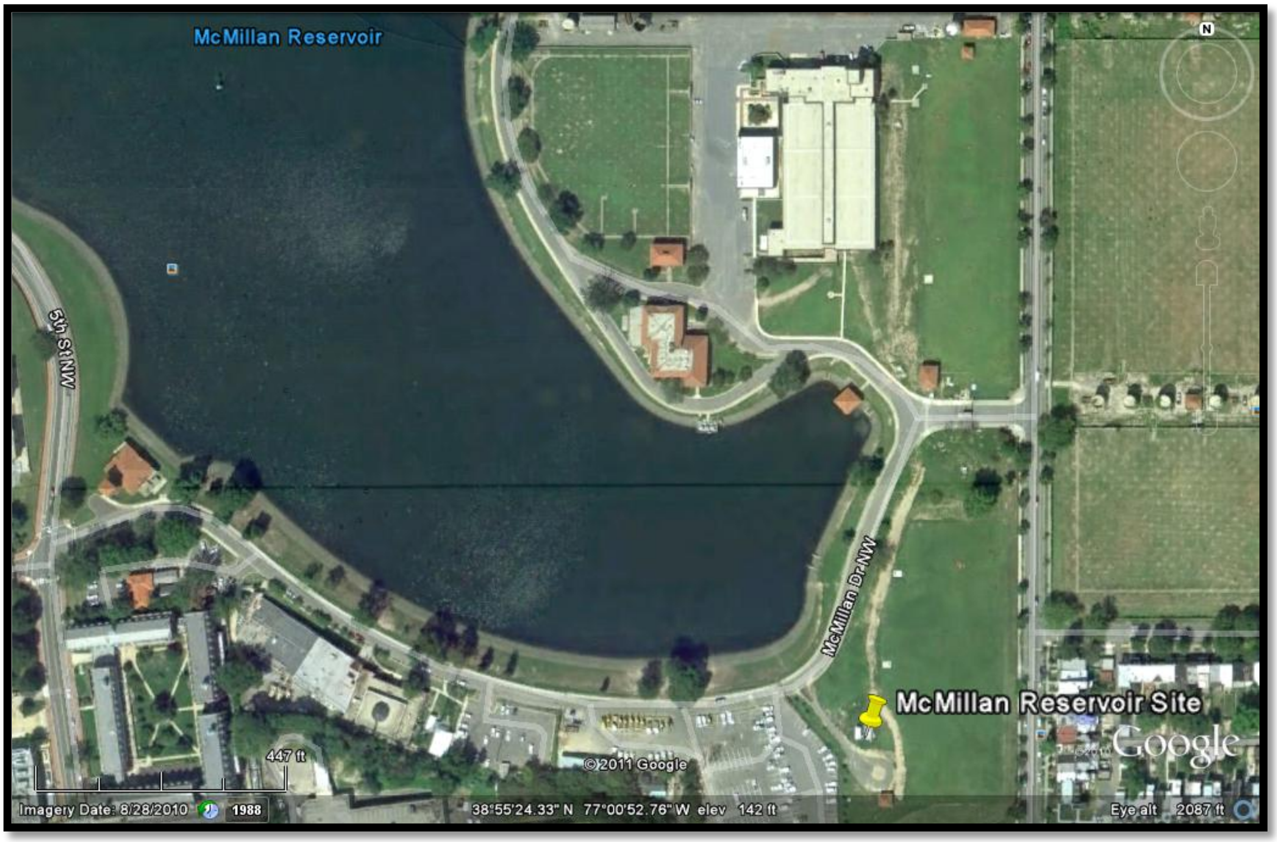
The Chicago, IL site (Com Ed) is located at the Com Ed Maintenance Building at 7801 Lawndale, Chicago, IL 60652. The Com Ed site is classified in AQS (ID 17-031-0076) as residential land use in a suburban location. Day-to-day operations at Com Ed will be managed by the Cook County Department of Environmental Control.

Figure 2 – Google Earth Image of Com Ed Monitoring Site



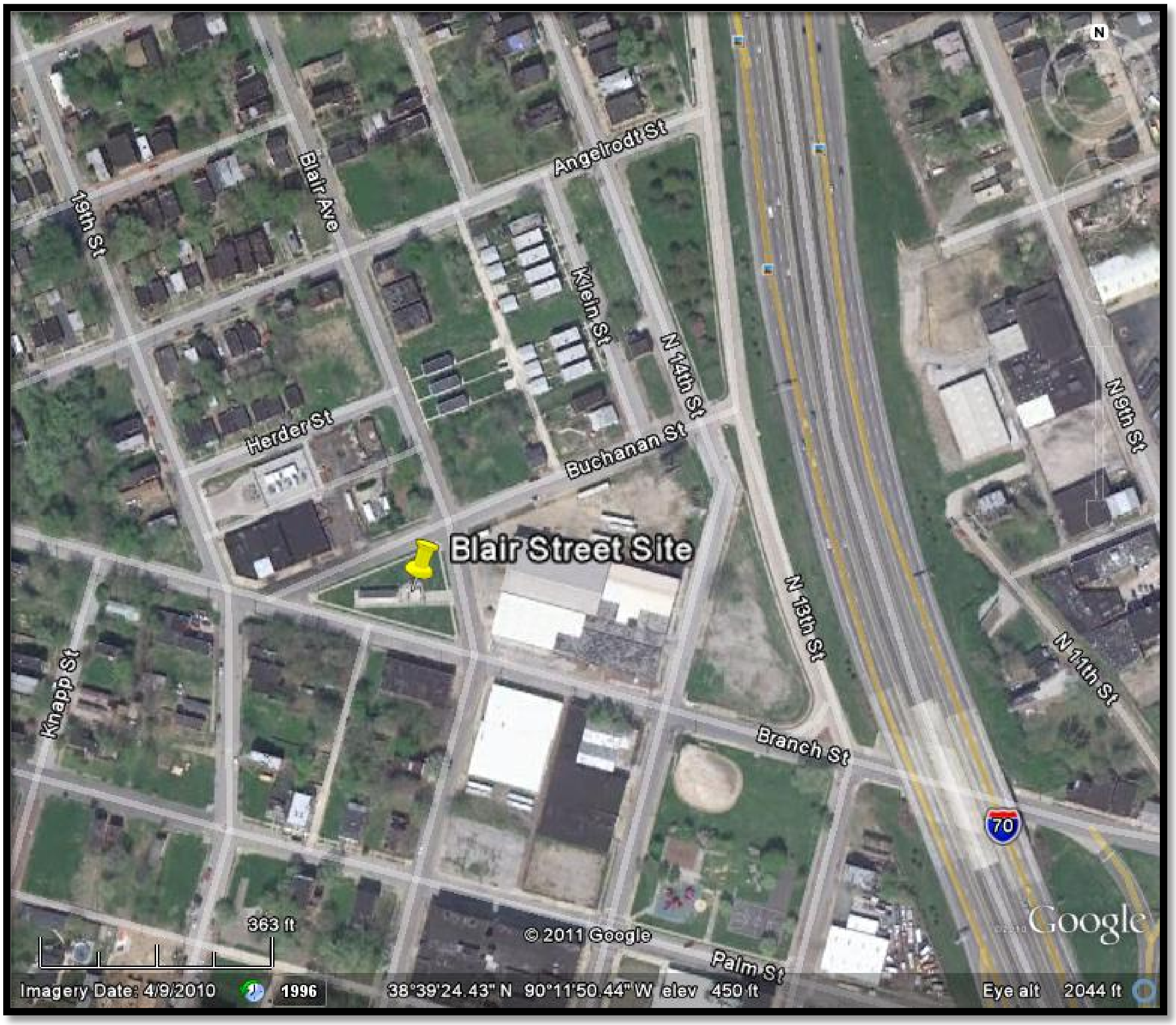
The Washington DC site (McMillan Reservoir) is located at 2500 1st Street NW, Washington DC 20001. The McMillan Reservoir site is classified in AQS (11-001-0043) as commercial land use in an urban and center city location. Day-to-day operations at McMillan Reservoir site will be managed by the District Department of the Environment.

Figure 3 – Google Earth Image of McMillan Reservoir Monitoring Site



The St. Louis, MO site (Blair Street) is located at 3247 Blair Street, St. Louis, MO 63107. The Blair Street site is classified in AQS (29-510-0085) as residential land use in an urban and center city location. Day-to-day operations at the Blair Street site will be managed by the Missouri Department of Natural Resources.

Figure 4 – Google Earth Image of Blair Street Monitoring Site

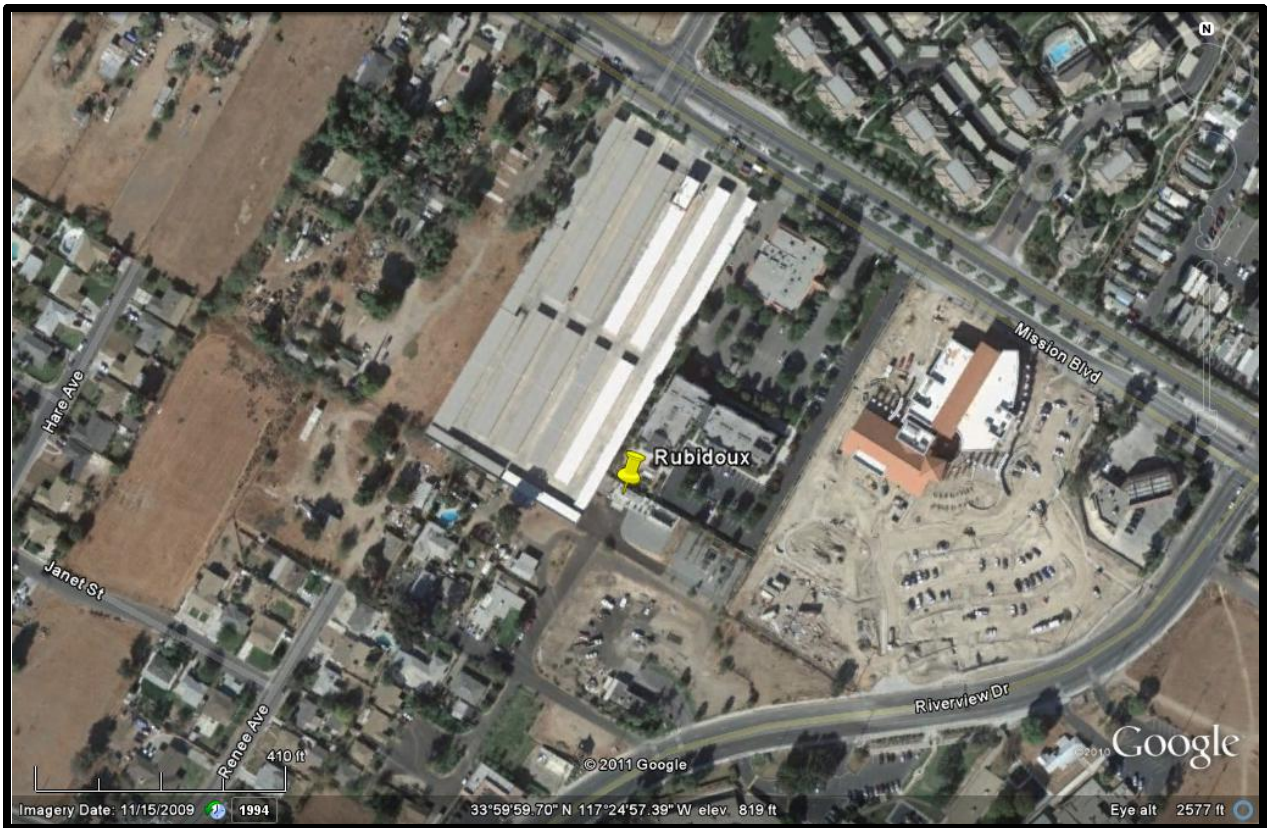


The Houston, TX site (Deer Park) is located at 4514 ½ Durant Street, Deer Park, TX 77536. The Deer Park site is classified in AQS (48-201-1039) as residential land use in a suburban location. Day-to-day operations at the Deer Park site will be managed by the Texas Commission on Environmental Quality.

Figure 5 – Google Earth Image of Deer Park Monitoring Site

The Los Angeles, CA site (Rubidoux) is located at 5888 Mission Blvd., Riverside, CA 92509. The Rubidoux site is classified in AQS (06-065-8001) as residential land use in a suburban location. Day-to-day operations at the Rubidoux site will be managed by the South Coast Air Quality Management District.

Figure 6 – Google Earth Image of Rubidoux Monitoring Site



3.0 Sample Process Design

Table 6 shows the proposed sampling and analysis matrix to be used in the Sunset Evaluation Study, including the number and type of samples expected. Sampling is anticipated to consist of a 1-in-3 day sampling scheme for the URG 3000N, hourly data collection for the Sunset semi-continuous carbon method, and 5-minute collection for the Aethalometer (aggregated to one hour for comparisons). Sampling will be conducted over the course of three years to understand the temporal variability during all the seasons, and to provide data sets large enough to evaluate the comparability of the different sampling methodologies and instrumentation.

Table 6– Sampling and Analysis Matrix

Sampler Type	Filter/Tape Type	Technique	Measurement	Sampling Frequency	Samples Collected (per site per year)
Sunset Semi-Continuous OC/EC	47mm Pall Tissuequartz Quartz Fiber Filter, punched to 17mm	Thermal/Optical Analysis – (TOT[1]) NIOSH 5040 Method	Thermal OC/EC Optical EC	Hourly	8,760
URG 3000N	25mm Pall Tissuequartz Quartz Fiber Filter	Thermal/Optical Analysis (TOR[2]/TOT) – IMPROVE_A Method	Thermal OC/EC Optical EC	Every 3rd Day	121
Magee Scientific Aethalometer	Quartz Fiber Filter Tape with cellulose backing	Continuous Filtration and Optical Transmission at 880nm with 16.6 m^2/g absorption coefficient	Black Carbon	5 minute	105,120

[1] Thermal Optical Transmittance – see Table 7 for the temperature profile during analysis

[2] Thermal Optical Reflectance – see Table 7 for the temperature profile during analysis

Table 7– Temperature Profiles for Analytical Methods

Instrument	Step #	Duration (seconds)	Temperature (°C)	Carrier Gas
Sunset OC/EC TOT	*1*	10	Ambient	Helium
	2	95	600	Helium
	3	90	840	Helium
	4	40	No Heat (cool oven)	Helium
	5	5	550	Helium
	6	10	550	90% Helium/10% Oxygen
	7	25	550	90% Helium/10% Oxygen
	8	45	650	90% Helium/10% Oxygen
	9	110	890	90% Helium/10% Oxygen
	10	120	No Heat	95% Helium/5% Methane Calibration
URG 3000N IMPROVE_A TOR	*1*	150 - 580*	140	Helium
	2	150 - 580*	280	Helium
	3	150 - 580*	480	Helium
	4	150 - 580*	580	Helium
	5	NA	NA	Helium
	6	150 - 580*	580	98% Helium/2% Oxygen
	7	150 - 580*	740	98% Helium/2% Oxygen
	8	150 - 580*	840	98% Helium/2% Oxygen
	9	NA	No Heat	Methane Calibration

*The residence time at each temperature in the IMPROVE_A protocol depends on when the FID signal returns to baseline, to obtain well-defined carbon fraction peaks, with a minimum of 150 seconds and a maximum of 580 seconds.

4.0 Analytical Methods

Note that the work proposed for the URG 3000N is to be carried out according to the EPA-approved CSN QAPP and the approved SOPs that are used in CSN network laboratory and field operations. Existing, ready-to-use SOPs for the analytical method for the TOR/TOT carbon analysis of aerosol filter samples for the URG 3000N are referenced in Appendix H of this QAPP. Analysis of samples by the Sunset and Aethalometer are done in-situ and no subsequent laboratory analysis is performed. SOPs used or adapted for Sunset Carbon Field Analyzer and the Aethalometer and also referenced in Appendices H & J. The Sunset and Aethalometer are semi-continuous instruments that do not require further analysis in a laboratory.

Sample processing for the URG3000N starts with acquisition of the Pall Tissuequartz filters. Personnel in RTI's carbon analysis laboratory will pre-fire the quartz filters and test for acceptance according to the CSN SOP "SOP for Procurement and Acceptance Testing for Teflon, Nylon and Quartz Filters", also included in Appendix H of this QAPP. RTI's Sample Handling and Archive Laboratory (SHAL) will be responsible for (i) assembly/disassembly of components into sampling modules, (ii) packaging and shipment of the sampling media to the site operators, (iii) receipt of samples from the site operators, and (iv) distribution of filters to DRI for analysis. Field data forms will be generated by SHAL personnel, who will also log out and log in all clean filters, and samples (going to the field or laboratories and returning). The SOP for Sample Handling and Archiving Laboratory is included in Appendix H of this QAPP.

In the SHAL, filters are loaded into filter cassettes and then loaded into insulated shipping boxes for shipment to the site operator or pickup by the EPA Site Operator. The exposed filters are returned to the SHAL with ice packs. Field data are entered into the SHAL data base and initial QA validation checks are made; any out-of-tolerance findings are reported to the SHAL manager for further examination and follow up. The quartz filters are sent to the DRI laboratory for analysis of OC/EC in accordance with the DRI SOP, included in Appendix H. Following filter analysis, the remaining portions of the quartz filters from which punches were taken for OC/EC analysis will be stored in DRI's dedicated archive facility in a freezer at -15˚C.

5.0 Quality Control/Quality Assurance

Elements of quality control are given in each of the SOPs listed in Appendices H & J, and are included in the field data sheets/routine operations for operators in Appendices A-G. Table 4 outlines these QC objectives that operators will use. Instrument checks ensure that the sampling instruments are operating within acceptable limits. The table includes corrective action steps for situations where an instrument does not meet its acceptance criteria. Typically if the check shows a failure, troubleshooting will occur that may lead to instrument recalibration. Once the appropriate steps have been taken and the issue resolved, the data must be examined to determine if the error had an effect on data quality. For example, if the time is off by six minutes on the Aethalometer, a simple adjustment of the time and note in the log would be sufficient corrective action, as the incorrect time did not have any effect on the quality of the data collected. However, if the flow rate control check on the URG 3000N is off by 50%, the data collected since the last flow rate control check and the recent failure would need to be examined in detail. This will likely involve communications with the instrument manufacturer to determine if the data would need to flagged or invalidated, and will be conducted on a case by case basis.

Table 5 outlines the maintenance activities that operators must complete at varying frequencies for the different instrumentation. RTI also validates and assesses the quality of its analytical measurements for the URG 3000N filters according to the Data Validation Process for the $PM_{2.5}$ Chemical Speciation Network, referenced in Appendix H. This includes assessment of instrument blanks, field blanks, trip blanks and backup filters. For the duration of the study, field blanks will be collected at an equivalent of 10% of samples, trip blanks at 2% and backup filters at 10%. Instrument blanks will be performed daily by DRI to provide an assessment of filter preparation procedures and analytical system background levels prior to analysis of routine samples. Field blanks provide an estimate of total measurement system contamination. By comparing information from instrument blanks against the field blanks, the amount of contamination due to field activities can be estimated. In addition, one can further evaluate contamination occurring during filter transport and field operations through the use of trip blanks. Field blanks will be loaded in sampling modules and handled by the EPA site operator just as he/she would a module to be exposed, but without drawing a sample through it. Field blanks remain in the sampler for the same duration as the sampled filters. Trip blanks are sent to the field as a normal sample but remain unopened. They are processed as a normal field sample and sent back to the support laboratory and treated as a routine sample from the point of sample receipt and beyond. Corrective actions will be taken if excessive contamination is found on the trip/field blanks. Excessive contamination will be defined as any value that is higher than is typically seen on a trip/field blank from the URG 3000N in the CSN. According to the most recent Data Summary Report for the CSN (see Appendix H), trip and field blank values for Total Carbon (TC) for the URG 3000N typically do not exceed 0.3 $\mu g/m^3$. As the CSN does not have acceptance criteria for trip/field blanks, this value will be used as our target for corrective action. If blank values are seen in excess of this amount, the data will be flagged and an evaluation done to determine if there was an impact on the data and the results of any comparisons. If contamination of the trip/field blanks is proven to have caused an effect, the data may be invalidated. Unfortunately we will not receive the blank data real time, but rather up to 90 days after sampling. In the event that contamination causes large portions of data invalidation after the study has ended, considerations will be made regarding the need to extend sampling.

Quality Control Requirements in the URG 3000N SOP, DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A, and the lab QAPP for the Chemical Speciation of $PM_{2.5}$ Filter Samplers (Appendices H & L) present detailed information on QC requirements and what occurs when quality control findings indicate the need for corrective action. These are also summarized in Table 8 below.

Table 8 – QC Criteria for the OC/EC Analysis by IMPROVE_A/TOR-TOT Methods in RTI's OC/EC Laboratory

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit (MDL)	Annually	MDL ≤ 0.6 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples
Calibration Peak Area	Every Analysis	Within 95%-105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter
Instrument Blank	Daily	Blank ≤ 0.6 µg/cm^2	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples
Full Calibration [sucrose(aq), KHP (aq), CH_4/He and CO_2/He]	Six Months	Slope [force-fit through 0,0], recover, and calibration peak area all within 95% to 105% of average slope, average recovery, and average peak area for each run and for each standard	Determine the cause of the problem and initiate actions that will identify and solve any problem that may have arisen; then repeat the calibration with the standard that appeared to be most different. The individual calibrations for the four standards and their collective results must yield satisfactory results before samples are analyzed
Auto Cal Check	Daily	Peak area for each of the three CH_4/He injections must be within 95% and 105% of the average for the three	Determine the cause of the problem and initiate corrective action, if necessary, to correct the problem; and obtain acceptable Auto Cal results before analyzing samples
Calibration Check (15 µL sucrose standard)	Daily	1) 90%-110% recovery, and 2) Calibration peak area 90%-110% of average for the weekly 3-point calibration	Initiate corrective action, if necessary, to solve the problem before analyzing samples
Duplicate or Replicate Analysis	10% of Samples	1) OC or TC ≥ 10 µg/cm^2 – less than 10% RPD, 2) OC or TC < 10 µg/cm^2 – within 1.0 µg/cm^2, 3) EC ≥ 10 µg/cm^2 – less than 20% RPD, 4) EC < 10 µg/cm^2 – within 2.0 µg/cm^2	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag

*Table taken from the QAPP for the Chemical Speciation of $PM_{2.5}$ Filter Samplers (Appendix L, page 57)

6.0 Data Management

Participating sites are responsible for configuring their Sunset such that it reports to a data logging system, AQS and AirNowTech. In addition to these reporting requirements, data will be manually downloaded from the Sunset instrument onto a memory stick weekly, and transferred to a secure network drive for permanent storage and regular backup. The SD memory card in the URG 3000N will be switched with each sample collected, and will remain with the sample and returned to RTI for data recovery, storage and backup. Prior to returning the sample to RTI, the data will be downloaded from the SD memory card onto the same secure network drive. Similarly, sites running Aethalometers will switch the SD memory card monthly, as a backup to their data logging system, and store the data on the network drive. EPA will retrieve the data from AQS and AirNowTech and evaluate in accordance to Section 2 of this QAPP.

For data logging purposes at the AIRS site, the Environics/DR DAS software Envidas for Windows will be utilized for the Sunset OC/EC instruments as well as the Aethalometer. The Sunset Labs Semi-continuous OC/EC Analyzer to EnvidasFW Data Acquisition System Configuration Guide (Appendix N) was used to configure Envidas to accept data from the Sunset. In addition to the use of Envidas, data will be manually downloaded from the Sunsets, URG 3000N and Aethalometer and transferred to an EPA network drive for permanent storage and regular backup. A management plan for the data collected at AIRS has been detailed in the AIRS Sunset Carbon Evaluation Project QAPP (Appendix I).

Appendix A

OAQPS QUALITY CONTROL MAINTENANCE CHECKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Instrument Serial Number:___________________________ Site:____________________________________

Date/Time of Arrival:_______________________________ Operator:________________________________

☐ Allowed to Finish Sample Run ☐ Interrupted Sampling Cycle (Did Not Analyze)

Carrier Gases	Primary Pressure (PSI)	Action	Secondary Pressure (PSI)	Action	Adjustment Made? (Y/N)
He		Order new cylinder if <1000 PSI Replace cylinder if <500 PSI**		Adjust to ~12 PSI (single instrument) or ~30 PSI (collocated instruments)	
He/O_2					
He/CH_4					

**Must perform a multi-point calibration after changing the He/CH_4 tank (See Appendix B)

Record the following Parameters:

Laser Correction Value:_____________ (should be >0.90)

Back Oven Temperature during Analysis: _____________ (should be ~870°C)

Back Oven Temperature during Sampling: ____________ (should be ~500°C)

	Y/N	Comments
Instrument Gas Flows fairly stable?		
Blank Values < ± 0.3 µg C since last visit?		

Weekly Tasks:

- ☐ Clean the Drop Out Tee
- ☐ Change the Filter, Run Fast-TC clean on Filters
- ☐ Manually set flows to zero and auto zero, if necessary:

Gases	Flows when Manually Set to Zero	Action	Auto zero Performed? (Y/N)
He1 cc/min		Auto zero Flows if any flows are >±0.5 cc/min	
He Purge cc/min			
He/Oxygen cc/min			
Cal Gas cc/min			

- ☐ Download the data
- ☐ Shutdown the Software, Restart the Computer, Reopen the Software (Do Not Auto start the instrument)
- ☐ Verify the PSIG in Idle Mode is <2.75 (may need to replace oven if >3.5) PSIG=__________
- ☐ Change Output Data File, Verify Status is “Checking”. Sample Collection=__________

Comments:

OAQPS QUALITY CONTROL MAINTENANCE CHECKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Bi-Weekly Tasks:
- ☐ Single Point External Standard – complete form in Appendix B
- ☐ Change the file name (if not writing to a new file daily and running on 1 hour sample period)

Monthly Tasks:
- ☐ Change the file name (if not writing to a new file daily and running on 2 hour sample period)
- ☐ Change denuder filter strips and clean the cyclone inlet

Semi-Annual Tasks:
- ☐ Leak Check
- ☐ Multi Point External Calibration – complete form in Appendix B
- ☐ Clean cyclone and inlet tubing
- ☐ Check that flows within ± 2% (He1, HeOx & Cal Gas) and ± 5% (He Purge), recalibrate if necessary – complete form in Appendix C

Comments:

Appendix B

OAQPS EXTERNAL STANDARD SUCROSE CALIBRATION CHECKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Date:________________________________ Site:____________________________________

Operator:_____________________________ Instrument Serial Number____________________

Injection Number	Standard (µg C / µL)	Volume of Sample Injected (µL)	Carbon Injected (µg)	Carbon Measured (µg)	Measured within ±5% of Injected? (Y/N)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

<u>Bi-Weekly Standard Loop Calibration</u> – analyze a 10µl sample from the standard stock solution (~42µg C). Repeat until you receive three injections within 5% of the actual carbon injected.

<u>Semi-Annual Standard Loop Calibration</u> – analyze a 0 µl sample (clean filter), 5 µL sample (~21 µg C), 10µL sample (~42 µg C) and 20µL sample (~84 µg C). Repeat until you receive three injections within 5% for each level of carbon injected.

Appendix C

OAQPS FLOW CALIBRATION WORKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Date:________________________________ Site:________________________________

Operator:______________________________ Instrument Serial Number:__________________

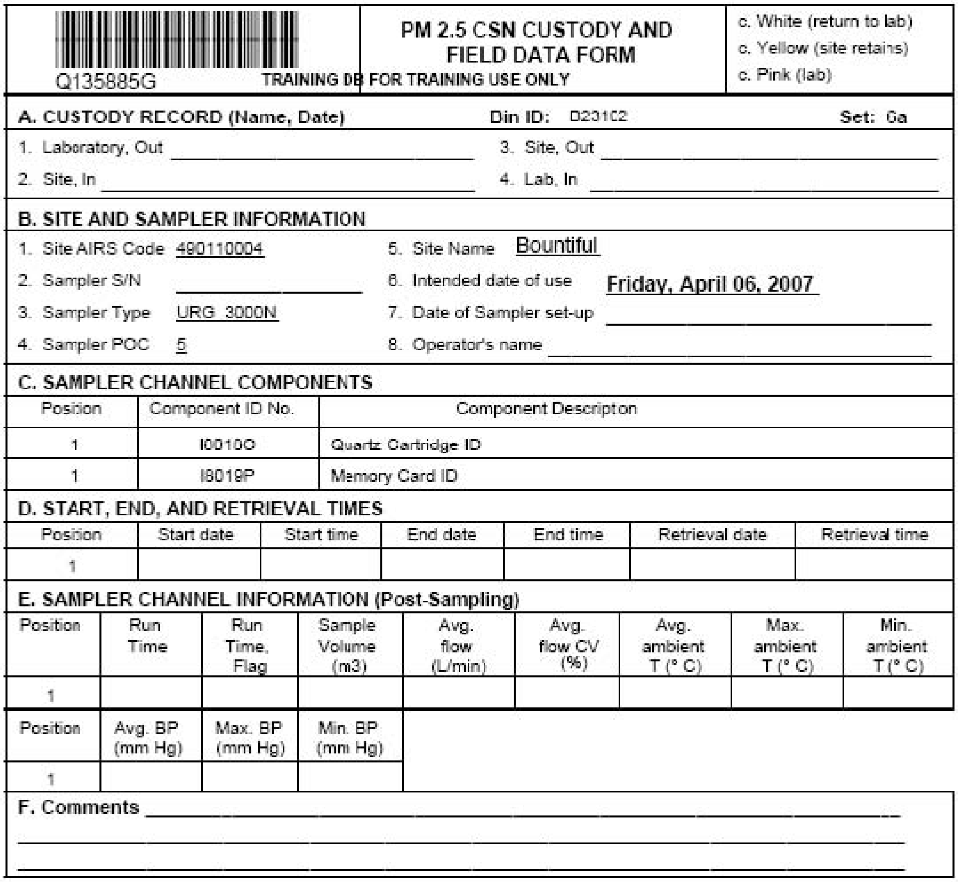
Flow Standard Model:______________________ Flow Standard Serial Number: _______________

Flow Certification Date:___________________

Helium 1			**Helium Purge**		
Flow (cc/min)		Volts	Flow (cc/min)		Volts
Display	Actual		Display	Actual	

Helium / Oxygen			**Calibration Gas**		
Flow (cc/min		Volts	Flow (cc/min)		Volts
Display	Actual		Display	Actual	

Appendix D



Q135885G TRAINING DB FOR TRAINING USE ONLY

PM 2.5 CSN CUSTODY AND FIELD DATA FORM

c. White (return to lab)
c. Yellow (site retains)
c. Pink (lab)

A. CUSTODY RECORD (Name, Date) **Din ID:** D23102 **Set:** 6a

1. Laboratory, Out ____________ 3. Site, Out ____________
2. Site, In ____________ 4. Lab, In ____________

B. SITE AND SAMPLER INFORMATION

1. Site AIRS Code 490110004
2. Sampler S/N ____________
3. Sampler Type URG 3000N
4. Sampler POC 5
5. Site Name Bountiful
6. Intended date of use Friday, April 06, 2007
7. Date of Sampler set-up ____________
8. Operator's name ____________

C. SAMPLER CHANNEL COMPONENTS

Position	Component ID No.	Component Descripton
1	I0010O	Quartz Cartridge ID
1	I8019P	Memory Card ID

D. START, END, AND RETRIEVAL TIMES

Position	Start date	Start time	End date	End time	Retrieval date	Retrieval time
1						

E. SAMPLER CHANNEL INFORMATION (Post-Sampling)

Position	Run Time	Run Time, Flag	Sample Volume (m3)	Avg. flow (L/min)	Avg. flow CV (%)	Avg. ambient T (° C)	Max. ambient T (° C)	Min. ambient T (° C)
1								

Position	Avg. BP (mm Hg)	Max. BP (mm Hg)	Min. BP (mm Hg)
1			

F. Comments ____________

Appendix E

QA/QC Form No. ____________	**$PM_{2.5}$ CSN QA/QC REPORT FORM**	c. 1 (site retains) c. 2 (Agency QAM)

SITE AND SAMPLER INFORMATION

1. Site AQS Code ____________________________
2. Sampler S/N ______________________________
3. Sampler Type _____________________________
4. Sampler POC______________________________
5. Site Name ________________________________
6. Interval: Month_____Quarter_____Special_____
7. Date(s) of QA/QC Checks ___________________
8. Operator's Name ___________________________

DATE AND TIME CHECKS (Transfer Standard Name__________ Transfer Standard ID Number__________)

Sample display date/time	Transfer standard date/time	Date and time agree ± 5 min?	Action taken (a)

LEAK CHECKS (Transfer Standard Name_________________ Transfer Standard Number_________________)

Channel number	Manufacturer's specifications met?	Action taken and recheck results (a)

TEMPERATURE CHECKS (Transfer Standard Name_____________ Transfer Standard Number____________)

Sensor location	Sampler display (°C)	Transfer standard (°C)	Agreement ±2°C	Action taken and recheck results (a)
Ambient				

PRESSURE CHECKS (Transfer Standard Name_______________ Transfer Standard Number_______________)

Sensor location	Sampler display (mm Hg)	Transfer standard (mm Hg)	Agreement ±10 mm Hg	Action taken and recheck results (a)
Ambient				

FLOW RATE CHECKS (Transfer Standard Name______________ Transfer Standard Number______________)

Channel Number	Sampler display (L/min)	Transfer standard display (L/min)	Design flow rate (L/min)	Agreement within ±10 percent? (b)	Action taken and recheck results (a)
1					
2					
3					
4					
5					

COMMENTS

(Revised 09.23.99)

Appendix F

EPA MONTLY QUALITY CONTROL/MAINTENANCE CHECKLIST
Magee Scientific Aethalometer

Location: Month/Year:

Date	Weekly Checks				Monthly Checks
	Flow Display	Correct Time/Date	Standard Flow (LPM)		Inlet Cleaned
	LPM	Yes or No	Pre-Cal	Post-Cal	Yes or No

Station Number: Operator:

Analyzer Property Number: Agency:

Operator Instructions:

1) Daily Checks: Review daily data. Verify Aethalometer status and there are no error messages.
2) Weekly Checks: Assure sampler flow on display read to within 0.2 LPM of previous week. Verify time and date is within five (5) minutes of data logger.
3) Monthly Checks: Check flow with standard. Recalibrate as necessary. Clean inlet cyclone.

Date	Comments or Maintenance Performed

Label and replace SD state memory drive.

4) Semi-Annual Checks: Perform Calibration and Optical Test Strip procedures. Perform Self Test.
Date of last calibration: Date of last Self Test:
5) Annual Checks: Clean or replace inlet probe line. Date last Cleaned:
Determine residence time: seconds (not to exceed 20 seconds).

Reviewed by: Date:

Appendix G

EPA INSTRUMENT CALIBRATION REPORT
Magee Scientific Aethalometer

Instrument Information:

Site Name:			**State**	
Site Number:			**City**	
Property Decal #			**Calibration Date**	
Agency:			**Last Calibration**	

Flow Meter:

Flow Standard Model	
Flow Standard SN	
Flow Certification Date	

Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)

If % difference is > 5% proceed to Flow Meter Calibration

Flow Meter Calibration:

Previous Scale Factor	New Scale Factor

Repeat Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)

Operator:	
Comments:	

Appendix H - References

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Appendix I

AIRS Sunset Carbon Evaluation Project Quality Assurance Project Plan (QAPP), Version 1, April 2011.

AIRS Sunset Carbon Evaluation Project

Quality Assurance Project Plan (QAPP)

QA Level IV

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Air Quality Assessment Division
Ambient Air Monitoring Group

Sunset Team
Elizabeth Oswald – Study Lead
Joann Rice – Aethalometer Technical Support
David Shelow – Sunset Technical Support
Solomon Ricks – URG 3000N Technical Support

April 8, 2011

AIRS Sunset Carbon QA Project Plan
QAPP Approval Signatures
Category IV QAPP

Lewis Weinstock	4/11/11
Lewis Weinstock, Group Lead	Date
	4/8/11
Elizabeth Oswald, EPA Project Lead	Date
Michael Papp	4/11/11
Mike Papp, EPA QA Lead	Date
Joann R	4/8/11
Joann Rice, Aethalometer Technical Support	Date
	4/11/11
David Shelow, Sunset Technical Support	Date
Solomon Ricks	4/11/2011
Solomon Ricks, URG 3000N Technical Support	Date

1.0 Introduction

This is a level IV Quality Assurance Project Plan (QAPP) that covers an Environmental Data Operation (EDO) conducted by the Ambient Air Monitoring Group (AAMG) to collect field data at EPA's Ambient Air Innovation and Research Site (AIRS) in Research Triangle Park (RTP), North Carolina. Several experiments will be conducted to perform an instrument evaluation of the Sunset Semi-Continuous Organic and Elemental Carbon (OC/EC) monitor and a data comparison with the URG 3000N and Magee Scientific Aethalometer. The QAPP is a formal document describing the necessary Quality Assurance (QA), Quality Control (QC) and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. The Office of Air Quality Planning and Standards (OAQPS) utilizes a four-tiered project category approach to its QA Program. Category I involves the most stringent QA approach, whereas Category IV is the least stringent. This project falls into Category IV, which is defined as "*Projects involving EDOs to study basic phenomena or issues, including proof of concepts, screening for particular analytical species, etc. Such projects generally do not require extensive detailed QA/QC activities and documentation.*" Such projects include those producing results that are used to evaluate and select options for interim decisions or to perform feasibility studies or preliminary assessments of unexplored areas for possible future work. Level IV projects include monitoring, modeling, and/or analyses involving one time studies or local scale monitoring; monitoring, modeling, emission inventories, and assessments; field testing of performance test methods and source monitoring procedures; evaluating formal requests to allow the use of alternative methods; and investigating the feasibility of new or modified performance test methods or source monitoring procedures.

Note that the $PM_{2.5}$ filters collected from the URG 3000N will be analyzed (chemically and physically) by existing, EPA-approved, methods given in the QA Project Plan and accompanying Standard Operating Procedures (SOPs) in use under the EPA/OAQPS Chemical Speciation Network (CSN) contract EP-D-09-010. The procedures and analytical methods used by the CSN are expected to meet the analytical needs for the $PM_{2.5}$ filters. The Sunset Instrument and Aethalometer are continuous/semi-continuous instruments that do not require further laboratory analysis.

1.1 Project/Task Description

One of the major areas of interest in air monitoring is the investigation of continuous monitoring technologies that could potentially lead to a reduction in filter based technologies. In the CSN alone, over 180 sites are collecting 24-hr filter based samples that are analyzed for Mass, Trace Elements, Major Ions, and Organic Carbon/Elemental Carbon (OC/EC). OC/EC samples are collected on to quartz filters every third or sixth day and shipped to Research Triangle Institute (RTI) for analysis. The cost of sample preparation, shipping and analysis for the carbon network is approximately $2M per year. In an effort to move towards continuous, higher time resolution sampling and reduce the need for expensive, time consuming, filter based sampling, OAQPS is committed to the evaluation of new, continuous monitoring technologies. For this reason, the AAMG purchased eight Sunset Semi-Continuous OC/EC instruments for future deployment to monitoring agencies.

The data gathered from the AIRS Sunset Evaluation Project will be used to develop an EPA SOP for the instrument. The study will solely take place at the AIRS monitoring site on EPA's campus in RTP, NC. These study data are **not** being collected for compliance purposes. Two Sunset field instruments will be operated for the purposes of:

- Gaining proficiency in the proper operation and maintenance of the instrument
- Developing an SOP for the use of the instrument
- Evaluating collocated instrument precision and verifying detection limits
- Comparability of the Sunset thermal OC/EC with the URG 3000N thermal OC/EC
- Comparability of the Sunset optical EC with the Aethalometer optical black carbon (BC)

Table 1 provides the major milestones and deliverables for the study. The final deliverable is expected to be completed in August 2012.

Table 1 – Major Milestones and Deliverables

Task Description	**Person(s) Responsible**	**Deliverable Date**
Purchase of miscellaneous items to support operation	Shelow, Rice, Oswald	Completed January 2011
Instrument unpack and setup	Shelow, Rice, Ricks, Oswald	Completed January 2011
Calibration of Sunset, URG 3000N & Aethalometer	Oswald, Rice, Ricks	Completed February 2011
Field Operation (see Table 3)	Oswald, Ricks, Rice	April 2011 – July 2011
Draft Sunset SOP	Oswald	Ongoing
Final SOP	Oswald	August 2011
Data Summary Report	Oswald	August 2012

1.2 Study Objectives

The primary study objectives are to gain an understanding of how the Sunset instrument works (routine operation and maintenance); determine how to optimize operation through various experiments; develop a SOP for the instrument; establish precision and detection limits; and determine how well the Sunset compares with the URG 3000N and the Aethalometer.

As a secondary objective, the information from the study will be used, to the extent possible, to inform and gain insight regarding the questions below. These questions may not be definitively answered. The data will be assessed and the confidence in which we can draw conclusions regarding these questions will be made at the conclusion of the study.

- What are the space considerations for operating the Sunset analyzer in a shelter? Do any special considerations need to be made for control of shelter temperature and relative humidity? What interferences exist that may be problematic for implementation?

- What important parameters should be tracked or documented for QC purposes (e.g. Laser Correction Value, Oven Temperature, Pressures, etc.)? How should the data be validated? What is the Sunset instrument data capture rate?
- What is the ideal sample collection period for a rural sampling location similar to AIRS? How often should sucrose standard injections be performed? What is the typical value of nightly blanks? What type of denuder (parallel plate or carbon monolith) removes organic vapors more efficiently and is more practical to use?
- What are the capital costs, including additional equipment, for operating each analyzer? What level of effort and training are necessary for routine operation?

1.3 Standard Operating Procedures (SOPs)

A primary goal of the AIRS Sunset Carbon Evaluation Project is to develop an SOP for the Sunset instrument. For the Sunset Carbon Semi-Continuous Field Instrument, a vendor provided operators manual and SOP will initially be used to operate the field sampling device. At the conclusion of the field study, an SOP will be developed by EPA in accordance with EPA QA/G-6; "Guidance for Preparing Standard Operating Procedures (SOPs)" available at: www.epa.gov/quality/qs-docs/g6-final.pdf. For operation of the Magee Scientific Aethalometer, an existing SOP developed by the Office of Research and Development will be used. The SOP for the operation of the URG 3000N is covered under the $PM_{2.5}$ Chemical Speciation Network (CSN) program. The SOP for the analysis of the filters by Desert Research Institute (DRI) is also covered under the CSN program.

The field sampling and analysis method SOPs and operating manuals to initially be used for this project are referenced in Appendix H.

2.0 Quality Objectives and Criteria for Measurement Data

Formal Data Quality Objectives (DQOs) are not required for Category IV QAPPs; however, project objectives/goals have been defined in section 1.2 and Measurement Quality Objectives (MQOs) are defined below. MQOs identify the quality control samples and acceptance criteria for samples that will allow one to control and assess the quality of the data. See Table 5 for a detailed list of Quality Control Objectives. The focus of this project is the assessment of the Sunset OC/EC instrument. The data from this study will be used to determine estimates of certain measurement quality attributes or indicators for the Sunset instrument.

- **Precision** - a measure of agreement among repeated measurements of the same property under identical, or substantially similar, conditions. This is the random component of error. Precision is estimated by various statistical techniques typically using some derivation of the standard deviation. We will assess collocated precision for the Sunset instruments running on both a 1 hour sampling period and a 2 hour sampling period. Precision will be calculated in the following ways:

  Coefficient of Variation

  CV = coefficient of variation $\quad CV = 100 * \left(\frac{\sigma}{\mu}\right)$

σ = standard deviation $\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2}$

μ = mean $\mu = \frac{1}{N}\sum_{i=1}^{N} x_i$

Mean Relative Percent Difference

MRPD = mean relative percent difference $\mathrm{MRPD} = \frac{1}{N}\sum_{i=1}^{N} abs\left[\frac{x_i - y_i}{x_i + y_i/_2}\right] * 100$

- **Comparability** - a measure of the confidence with which one data set or method can be compared to another, considering the units of measurement and applicability to standard statistical techniques. Comparability of datasets is critical to evaluating their measurement uncertainty and usefulness. The OC and EC data from the Sunset, URG 3000N and Aethalometer will be compared, as they are making similar carbon measurements, in the following ways:

  Linear Least Squares Regression

  A linear least square regression will be done to provide slope, intercept, R (coefficient of linear correlation – measures the strength of association between x and y) and R^2 (coefficient of determination – measures the quality of the regression line as a means of predicting y from x) values when making the comparison between two different instruments.

  Comparison of the Means including Variability

  The different instruments will also be compared by looking at their mean values including variance (precision). If the mean value for one instrument falls within the range of the mean value ± the variance (precision) of another instrument, the two instruments can be deemed comparable. We will not be running collocated precision experiments for the Aethalometer and URG 3000N as part of this study, thus we will use the precision estimates provided in Table 2 for these two instruments. Collocated precision will be calculated for the Sunset (as described above) as part of the experiments taking place at AIRS.

  Ratio of the Means

  As a quick way to compare the different instruments, the ratio of the mean Sunset OC/URG OC, Sunset EC/URG EC, Sunset Optical EC/Aethalometer BC will be calculated.

- **Detection Limits** - the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated level of probability (a measure of the smallest signal an instrument can produce). The detection limit of the Sunset instrument will be assessed by injecting low concentration sucrose standards and taking the standard deviation of seven replicates. It will also be estimated using collocated data (Hyslop and White, 2008). These estimates will be compared to the values provided by the vendor. Vendor-provided estimates of instrument detection limits will be used for the URG3000N and Aethalometer (see Table 2).

- **Completeness** - the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct, normal conditions. The targeted completeness for each experiment in this study is 80%.

- **Bias** - the systematic or persistent distortion of a measurement process which causes error in one direction. Bias is typically determined by estimating the positive and negative deviation from the true value as a percentage of the true value. However, there are no Federal Reference Methods or reference materials for carbon measurements to assess bias. Nevertheless, known amounts of Sucrose, ≥99.5% (GC), from Sigma Aldrich (Product #S9378) will be injected into the Sunset instruments bi-weekly to assess bias relative to the current calibration curve. The flows will also be measured with a National Institute of Standards and Technology (NIST) traceable flow meters (tetraCal and Bios), that are recalibrated annually, to assure that the Sunsets, URG 3000N and Aethalometer are performing within specifications. The temperature and pressure sensors on the URG 3000N will also be checked with the same NIST traceable meter (tetraCal).

The analyzer operating conditions and performance are provided in Table 2 below. We do not currently have precision estimates for the Sunset OC/EC Instrument, so as mentioned previously, this will be a main goal of the AIRS experiments. The precision estimates for the Sunset will be used to in our assessment of comparability of the Sunset to the other instruments.

Table 2 –Analyzer Operating Conditions and Performance

Make/Model	Flow Rate	Sample Cycle	Measurement Range	Detection Limits	Precision Estimates
Sunset OC/EC Model 4	8LPM	1 hour	OC: 0.4-200 µg C/m^3 EC: 0.2-40 µg C/m^3	OC: 0.4 µg C/m^3 EC: 0.2 µg C/m^3	[B]MQO for TC: CV ≤ 15%
		2 hour	OC: 0.2-100 µg C/m^3 EC: 0.1-20 µg C/m^3	OC: 0.2 µg C/m^3 EC: 0.1 µg C/m^3	[B]MQO for TC: CV ≤ 15%
Magee Scientific Aethalometer	5LPM	5 min	None Provided	BC: 0.05 µg C/m^3	[C]CV ~ 15% (5 min) [C]CV ~ 3.5% (24 hour)
URG 3000N	22LPM	24±1 hour	[A]0.05-750 µg C/cm^2	OC: 0.064 µg C/m^3 EC: 0.064 µg C/m^3	[D]OC (CV) ~ 17.7% [D]DEC (CV) ~ 28.8%

[A] Analytical measurement range for DRI Model 2001 carbon analyzer for a typical punch size of 0.5 cm^2 (DRI SOP)
[B] Measurement Quality Objective (MQO) for Total Carbon (TC) from the Strategic Plan for the Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trends Sites (Appendix H)
[C] CV from the Environmental Technology Verification Report for the Aethalometer (Appendix H)
[D] CV provided by RTI and calculated from 2011 CSN Data Summary Report (Appendix H)

3.0 Sample Process Design

The purpose of this section is to describe all relevant components of the experimental design; define key parameters to be estimated; indicate the number and type of samples expected; and describe where, when and how samples will be taken. The key or critical parameters to be collected are thermal OC/EC, optical EC, and optical BC. The following equipment will be installed and operated at the AIRS Monitoring Site:

- Two (2) Semi-Continuous OC/EC Instruments (Sunset Model 4) – thermal OC/EC and optical EC;
- One (1) Sequential Particulate Speciation Sampler (URG 3000N) – thermal OC/EC; and
- One (1) Aethalometer (Magee Scientific AE-21) – optical BC

The EPA AIRS site has adequate power, space and the infrastructure necessary to support the project. The filter-based samplers (URG 3000N) will run every Tuesday, Thursday and Saturday from midnight- to- midnight on local standard time for the study period (17 weeks). See Table 3 for the 17 week monitoring schedule. See Table 4 below for the total number of samples collected from each instrument during the experiments planned at AIRS.

Table 3 – Timeline of Experiments at AIRS

Sunset #1 **Sunset #2** **URG 3000N** **Parallel Plate Denuder (PPD)** **Carbon Monolith Denuder (CMD)**

	Monday	*Tuesday*	*Wednesday*	*Thursday*	*Friday*	*Saturday*	*Sunday*
Week 1 *(Experiment 1)*	2 hr / 2 hr PPD	2 hr / 2 hr filter #1 PPD	2 hr / 2 hr PPD	2 hr / 2 hr filter #2 PPD	2 hr / 2 hr PPD	2 hr / 2 hr filter #3 PPD	2 hr / 2 hr PPD
Week 2 *(Experiment 2)*	Teflon Filter Test	Swap Denuders	Teflon Filter Test	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD
Week 3 *(Experiment 2)*	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD
Week 4 *(Experiment 2)*	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	2 hr / 2 hr PPD/CMD	Swap Denuders	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD
Week 5 *(Experiment 2)*	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD
Week 6 *(Experiment 2)*	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	2 hr / 2 hr CMD/ PPD	Teflon Filter Test	Swap Denuders	Teflon Filter Test
Week & *(Experiment 1)*	2 hr / 2 hr PPD	2 hr / 2 hr filter #4 PPD	2 hr / 2 hr PPD	2 hr / 2 hr filter #5 PPD	2 hr / 2 hr PPD	2 hr / 2 hr filter #6 PPD	2 hr / 2 hr PPD
Week 8 *(Experiment 3)*	1 hr / 1 hr PPD	1 hr / 1 hr filter #7 PPD	1 hr / 1 hr PPD	1 hr / 1 hr filter #8 PPD	1 hr / 1 hr PPD	1 hr / 1 hr filter #9 PPD	1 hr / 1 hr PPD
Week 9 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #10 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #11 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #12 PPD	2 hr / 1 hr PPD
Week 10 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #13 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #14 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #15 PPD	2 hr / 1 hr PPD
Week 11 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #16 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #17 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #18 PPD	2 hr / 1 hr PPD
Week 12 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #19 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #20 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #21 PPD	2 hr / 1 hr PPD
Week 13 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #22 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #23 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #24 PPD	2 hr / 1 hr PPD
Week 14 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #25 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #26 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #27 PPD	2 hr / 1 hr PPD
Week 15 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #28 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #29 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #30 PPD	2 hr / 1 hr PPD
Week 16 *(Experiment 4)*	2 hr / 1 hr PPD	2 hr / 1 hr filter #31 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #32 PPD	2 hr / 1 hr PPD	2 hr / 1 hr filter #33 PPD	2 hr / 1 hr PPD
Week 17 *(Experiment 3)*	1 hr / 1 hr PPD	1 hr / 1 hr filter #34 PPD	1 hr / 1 hr PPD	1 hr / 1 hr filter #35 PPD	1 hr / 1 hr PPD	1 hr / 1 hr filter #36 PPD	1 hr / 1 hr PPD

Several experiments will take place during the 17 week study period at the AIRS Monitoring Site. Below is an explanation of each experiment:

Experiment #1 - Collocated Precision and Sensitivity (2hr)
Both Sunset instruments will be run with a 2 hour sampling frequency using the default RTquartz temperature profile for two weeks (Week 1 and Week 7). This will provide 168 data points from each Sunset, six 24-hour integrated filter samples from the URG 3000N, and 4,032 five minute observations from the Aethalometer. The collocated data collected will also be used to estimate sensitivity of the Sunset (detection limits) using an empirical approach.

Experiment #2 – Denuder Comparison and Exploration of OC Artifact
Both Sunset instruments will be run with a 2 hour sampling frequency using the default RTquartz temperature profile for four weeks (vendor recommended period of use). One instrument will have a parallel plate denuder installed in line with the inlet and the other will have a carbon monolith denuder. This will provide 336 data points from each Sunset for comparison to determine if the data is significantly different. At the beginning and end of the experiment, a Teflon filter will be placed upstream of the organic denuders. The Teflon filter should remove the particles, and the denuder should remove the organic vapors. The measured value of the organic carbon in the instrument during this test will provide a value for the OC artifact that is not being efficiently removed by each denuder. The Teflon filter will be left on the denuders for 24-hours. The following day, the denuders will be swapped between the two Sunsets to determine if any measured differences are due to the denuders themselves or the instrument. The Teflon filter test will again be conducted for 24-hours. Following this test, the Teflon filters will be removed and the Sunsets will collect data for two weeks. After two weeks of sampling, the denuders will again be swapped between the two Sunsets to determine if any measured differences are due to the denuders themselves or the instrument. After two more weeks of sampling, the 24-hour Teflon filter test will be performed, the denuders swapped, and performed again. By performing this test at the beginning and end of the experiment, we will be able to see how efficiently each denuder removes organic vapors with age.

Experiment #3 – Collocated Precision and Sensitivity (1hr)
Both Sunset instruments will be run with a 1 hour sampling frequency using the default RTquartz temperature profile for two weeks (Week 8 and Week 17). This will provide 336 data points from each Sunset, six 24-hour integrated filter samples from the URG 3000N, and 4,032 five minute observations from the Aethalometer. The collocated data will also be used to estimate sensitivity of the Sunset (detection limits) using an empirical approach.

Experiment #4 – Comparison of Sunset with URG 3000N and Aethalometer
One Sunset will be run with a 2 hour sampling frequency and the other with a 1 hour sampling frequency for a total of 8 weeks. This will provide 672 data points from the 2 hour Sunset and 1,344 sampling points from the 1 hour Sunset, as well as twenty-four 24-hour integrated filter samples from the URG 3000N and 16,128 five minute observations from the Aethalometer. When combined with the data collected in Experiments #1 and #3, a total of thirty 24-hour integrated filters will have been collected to compare with the Sunset on both a 1 hour sampling frequency and 2 hour sampling frequency, as well as 20,160 five minute observations from the Aethalometer.

See Table 4 below for the total number of samples collected from each instrument during the experiments planned at AIRS.

Table 4 – Samples Collected during Experiments

	Sunset #1	**Sunset #2**	**Aethalometer**	**URG 3000N**
Experiment #1 –Collocated Precision (2hr)				
Denuder	Parallel Plate	Parallel Plate	Parallel Plate	n/a
Sampling Period	2 hours	2 hours	2 hours	-
Total Samples Collected	**168**	**168**	**168**	-
Experiment #2 – Denuder Comparison & Exploration of OC Artifact				
Denuder	Carbon Monolith	Carbon Monolith	n/a	n/a
Sampling Period	2 hours	2 hours	5 min	24 hours
Total Samples Collected	**336**	**336**	**4032**	**6**
Experiment #3 –Collocated Precision (1hr)				
Denuder	Parallel Plate	Parallel Plate	n/a	n/a
Sampling Period	1 hours	1 hours	5 min	24 hours
Total Samples Collected	**336**	**336**	**4032**	**6**
Experiment #4 –Sunset Comparison with URG 3000N & Aethalometer (incorporates data from Experiments #1&3)				
Denuder	Parallel Plate	Parallel Plate	n/a	n/a
Sampling Period	2 hours	1 hours	5 min	24 hours
Total Samples Collected	**840**	**1680**	**20160**	**30**

4.0 Analytical Methods

Note that the work proposed for the URG 3000N is to be carried out according to the EPA-approved Chemical Speciation Network (CSN) QA Project Plan and the approved SOPs that are used in CSN network laboratory and field operations. Existing, ready-to-use SOPs for the analytical method for the Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples for the URG 3000N are referenced in Appendix H of this QAPP. Analysis of samples by the Sunset and Aethalometer are done in-situ and no subsequent laboratory analysis is performed. SOPs used or adapted for Sunset Carbon Field Analyzer and the Aethalometer and also referenced in Appendix H. The Sunset and Aethalometer are continuous/semi-continuous instruments that do not require further analysis in a laboratory.

Sample processing for the URG3000N starts with acquisition of the appropriate quartz filters. The quartz filters are cleaned, submitted for acceptance testing and shipped to the Sample Handling and Archive Laboratory (SHAL) at RTI. Personnel in RTI's SHAL will be responsible for assembly/disassembly of components into sampling modules, packaging of sampling media for pickup from the EPA Site Operator, receipt of samples from the EPA Site Operator, and distribution of filters to STI for analysis. Field Data Forms will be generated by SHAL personnel, who will also log out and log in all clean filters, and samples (going to the field or laboratories and returning). The SOP for SHAL is included in Appendix H of this QAPP.

In the SHAL, filters are loaded into filter cassettes and then loaded into insulated shipping boxes for the EPA Site Operator to pickup. The exposed filters are returned to the SHAL at ice pack temperature. Field data are entered into the SHAL data base and initial QA validation checks are made; any out-of-tolerance findings are reported to the SHAL manager for further examination and follow up. The quartz filters are sent to the laboratory for analysis of OC/EC in accordance with the DRI SOP, included in Appendix H. Following filter analysis, the remaining portions of the quartz filters from which punches were taken for OC/EC analysis will be stored in RTI's dedicated archive facility in a freezer at -15°C.

5.0 Quality Control/Quality Assurance

Elements of quality control are given in each of the SOPs listed in Appendix H, and are included in the field data sheets/routine operations for operators in Appendices A through G. Table 5 below outlines these QC objectives that operators will use at AIRS. Instrument checks ensure that the sampling instruments are operating within acceptable limits. The table includes corrective action steps for situations where an instrument does not meet its acceptance criteria. Typically if the check shows a failure, troubleshooting will occur that may lead to instrument recalibration. Once the appropriate steps have been taken and the issue resolved, the data must be examined to determine if the error had an effect on data quality. For example, if the time is off by six minutes on the Aethalometer, a simple adjustment of the time and note in the log would be sufficient corrective action, as the incorrect time did not have any effect on the quality of the data collected. However, if the flow rate control check on the URG 3000N is off by 50%, the data collected since the last flow rate control check and the recent failure would need to be examined in detail. This will likely involve communications with the instrument manufacturer to determine if the data would need to flagged or invalidated, and will be conducted on a case by case basis.

Table 5 – Quality Control Objectives for AIRS Instrumentation

Instrument	Requirement	Frequency	Acceptance Criteria	Corrective Action
Sunset	Midnight Blanks	Daily (as possible)	<±0.3 µg C (TC)	^{1}Check for leaks, ^{2}Check system pressure, ^{3}Check oxygen trap, ^{4}Check gas lines to be sure no Teflon is used
	Laser Correction Value	Weekly	>0.90	^{1}Check if filter is still in vertical position, ^{2}Check filter for holes/tears, ^{3}Change filter and record any findings in log
	Flows manually set to 0	Weekly	±0.5 cc/min	Perform autozero, note in log
	Precision Calculation	Weekly	CV ≤ 30%	Contact Sunset for troubleshooting assistance
	Single-point External Standard Verification	Bi-Weekly	±5%	^{1}Carefully prepare and re-run two standards, ^{2}Check gas flows, ^{3}Check for leaks, ^{4}Check system temperatures, ^{5}Remake stock solution and rerun samples, ^{6}Perform multipoint calibration and update calibration parameter file
	Multi-point External Standard Verification	Semi-Annually & after changing cal gas tank	±5%	
	Flow check	Semi-Annually & after 1 month of sampling	±2% (He1, HeOx & Cal Gas), ±5% (He Purge)	Perform a flow sensor calibration
URG 3000N	Date and Time checks	Monthly & Daylight Savings Time Changes	±5 min	Correct Date/Time, note in the log
	Leak Check	Monthly	Vacuum drop <225 mm Hg in 35 seconds	^{1}Reseat cassette and reattempt, ^{2}Replace the cassette and reattempt, ^{3}Inspect o-rings on cyclone for tears or damage, ^{4}Inspect temperature probe plug o-rings for tears or damage, ^{5}Inspect o-rings in inlet tee for tears or other damage, ^{6}Contact URG for further assistance.
	Temp. Control Check	Monthly	±2°C	Perform a temperature calibration, note in log
	Pressure Control Check	Monthly	±10 mm Hg	Perform a pressure calibration, note in log
	Flow Rate Control Check	Monthly	±10%	Perform a flow calibration, note in log
	Temp. Control Audit*	Before & After Study	±2°C	Perform a temperature calibration, note in log
	Pressure Control Audit*	Before & After Study	±10 mm Hg	Perform a pressure calibration, note in log
	Flow Rate Control Audit*	Before & After Study	±10%	Perform a flow calibration, note in log
Magee Scientific Aethalometer	Date and Time checks	Weekly	±5 min	Correct Date/Time, note in the log
	Verify Flow on Display	Weekly	5± 0.2 LPM	Verify setting was not accidentally changed
	External Flow check	Monthly	±10%	Contact Magee – may need to perform a flow calibration, note new scale factor in log

* Standard independent of that used for monthly check

Table 6 below outlines the maintenance activities that operators must complete at varying frequencies for the different instrumentation at AIRS.

Table 6– Maintenance Activities for AIRS Instrumentation

Instrument	Frequency	Requirement(s)
Sunset	Weekly	• Verify Carrier Gas Pressures- Order new if primary <1000 PSI, replace if primary <500 PSI, verify secondary ~20 PSI for collocated and ~12 PSI for single • Check that Instrument Gas Flows are relatively stable • Verify Back oven Temperature (~870°C during analysis and ~500°C during sampling) • Change Filter, Shutdown Software, Restart Computer & Download Data • Check Trap below "Drop Out Tee" • Check PSIG in Idle Mode
	Biweekly	• Change the file name (if not writing to a new file daily and on 1 hour sample period) – *restart computer after renaming*
	Monthly	• Change the file name (if not writing to a new file daily and on 2 hour sample period) – *restart computer after renaming* • Change denuder filter strips • Clean inlet cyclone
	Semi-Annually	• Clean inlet tubing
URG 3000N	Every Visit	• Check o-rings on each filter cassette for wear, damage & proper seat • Clean off any moisture around the outside of the sampler and controller modules
	Monthly	• Clean the interior of the sample and controller modules with KimWipe tissues or paper towel • Clean sampler inlet surfaces
	Quarterly	• Check all Tygon® tubing & vacuum lines; replace if necessary • Inspect electrical line connections • Clean sampler inlet tube (using slightly moistened paper towel and wooden dowel) – allow to dry • Rotate quartz filter cassettes on the "AUDIT" cartridge
Magee Scientific Aethalometer	Weekly	• Check filter tape supply • Re-tension tape roll take-up spool if necessary • Inspect borders of visible spots on the used filter tape
	Monthly	• Clean inlet cyclone • Replace SD Memory Card
	Semi-Annually	• Perform calibration • Perform self test • Perform optical test
	Annually	• Clean or replace inlet probe line • Determine residence time

RTI must also assess the quality of its analytical measurements for the URG 3000N filters. This will include assessment of instrument blanks, field blanks, trip blanks and backup filters. For the duration of the study, field blanks will be collected at an equivalent of 10% of samples, trip blanks at 2% and backup filters at 10%. Instrument blanks will be performed daily by DRI to provide an assessment of filter preparation procedures and analytical system background levels prior to analysis of routine samples. Field blanks provide an estimate of total measurement system contamination. By comparing information from instrument blanks against the field blanks, the amount of contamination due to field activities can be estimated. In addition, one can further evaluate contamination occurring during filter transport and field operations through the use of trip blanks. Field blanks will be loaded in sampling modules and handled by the EPA site operator just as he/she would a module to be exposed, but without drawing a sample through it. Field blanks remain in the sampler for the same duration as the sampled filters. Trip blanks are sent to the field as a normal sample but remain unopened. They are processed as a normal field sample and sent back to the support laboratory and treated as a routine sample from the point of sample receipt and beyond. Corrective actions may be taken if excessive contamination is found on the trip/field blanks. Excessive contamination will be defined as any value that is higher than is typically seen on a trip/field blank from the URG 3000N in the CSN. According to the most recent Data Summary Report for the CSN (see Appendix H), field blank values for Total Carbon (TC) typically do not exceed 0.3 $\mu g/m^3$. As the CSN does not have acceptance criteria for trip/field blanks, this value will be used as our cutoff. If blank values are seen in excess of this amount, the data will be flagged and an evaluation done to determine if there was an impact on the data and the results of any comparisons. If contamination of the trip/field blanks is proven to have caused an effect, the data may be invalidated. Unfortunately we will not receive the blank data real time, but rather up to 90 days after sampling. In the event that contamination causes large portions of data invalidation after the study has ended, considerations will be made regarding the need to repeat certain experiments.

Quality Control Requirements in the QAPP for the Chemical Speciation of $PM_{2.5}$ Filter Samplers (Appendix H) presents detailed information on QC requirements and what occurs when quality control findings indicate the need for corrective action.

6.0 Data Management

For data logging purposes, the Environics/DR DAS software Envidas for Windows will be utilized for the Sunset OC/EC instruments as well as the Aethalometer. In addition to the use of Envidas, data will be manually downloaded from the Sunset instruments onto a memory stick weekly at the time of the filter change. The data will be stored on an EPA network drive for permanent storage and regular backup. The SD memory card in the Aethalometer will be switched monthly as a backup to the Envidas data and also stored on the EPA network drive. The SD memory card in the URG 3000N will be switched with each sample collected, and will remain with the samples and returned to RTI for data recovery, storage and backup.

Table 7 below provides a summary of the data analysis planned following data collection.

Table 7 – Data Analysis Plan

Data Analysis	Explanation
Precision	Sunset #1 thermal OC/EC vs. Sunset #2 thermal OC/EC (2hr)
	Sunset #1 optical EC vs. Sunset #2 optical EC (2hr)
	Sunset #1 thermal OC/EC vs. Sunset #2 thermal OC/EC (1hr)
	Sunset #1 optical EC vs. Sunset #2 optical EC (1hr)
Estimation of Detection Limits	Detection Limit based on 1 hour collocated data
	Detection Limit based on 2 hour collocated data
	Detection Limit based on sucrose injections
Comparison of URG with Sunset	URG thermal OC/EC (24hr) vs. Sunset thermal OC/EC (12-2hr)
	URG thermal OC/EC (24hr) vs. Sunset thermal OC/EC (24-1hr)
Comparison of Aethalometer with Sunset	Aethalometer BC vs. Sunset Thermal EC (2hr)
	Aethalometer BC vs. Sunset Optical EC (2 hr)
	Aethalometer BC vs. Sunset Thermal EC (1 hr)
	Aethalometer BC vs. Sunset Optical EC (1hr)
Comparison of Sunset Optical and Thermal EC	Optical EC vs. Thermal EC (2hr)
	Optical EC vs. Thermal EC (1hr)
Comparison of Denuders	Sunset #1 Thermal OC/EC vs. Sunset #2 Thermal OC/EC (2hr)
	Evaluation of OC artifact

Appendix A

OAQPS QUALITY CONTROL MAINTENANCE CHECKSHEET
FOR THE SUNSET OC/EC FIELD INSTRUMENT

Date:____________________________ Site:_______________________________

Operator:___________________________ Instrument Serial Number_________________

Carrier Gases	Primary Pressure (PSI)	Action	Secondary Pressure (PSI)	Action	Adjustment Made? (Y/N)
He		Order new cylinder if <1000 PSI Replace cylinder if <500 PSI**		Adjust to ~12 PSI (single instrument) or ~20 PSI (collocated instruments)	
He/O_2					
He/CH_4					

**Must perform a multi-point calibration after changing the He/CH_4 tank (See Appendix B)

Record the following Parameters:

Laser Correction Value:____________ (should be >0.90)
Back Oven Temperature during Analysis: ____________ (should be ~870°C)
Back Oven Temperature during Sampling: ____________ (should be ~500°C)

	Y/N	Comments
Instrument Gas Flows fairly stable?		
Blank Values < ± 0.3 µg C since last visit?		

Weekly Tasks:

- ☐ Clean the Drop Out Tee
- ☐ Change the Filter, Shutdown the Software, Restart the Computer
- ☐ Verify the PSIG in Idle Mode is <2.75 (may need to replace oven if >3.5) PSIG=__________
- ☐ Manually set flows to zero and auto zero, if necessary:

Gases	Flows when Manually Set to Zero	Action	Auto zero Performed? (Y/N)
He1 cc/min		Auto zero Flows if any flows are >±0.5 cc/min	
He Purge cc/min			
He/Oxygen cc/min			
Cal Gas cc/min			

Bi-Weekly Tasks:

- ☐ Single Point External Standard – complete form in Appendix B
- ☐ Change the file name (if not writing to a new file daily and running on 1 hour sample period)

Monthly Tasks:

- ☐ Change the file name (if not writing to a new file daily and running on 2 hour sample period)
- ☐ Change denuder filter strips and clean the cyclone inlet

Semi-Annual Tasks:

- ☐ Leak Check
- ☐ Multi Point External Calibration – complete form in Appendix B
- ☐ Clean cyclone and inlet tubing
- ☐ Check that flows within ± 2% (He1, HeOx & Cal Gas) and ± 5% (He Purge), recalibrate if necessary – complete form in Appendix C

Appendix B

OAQPS EXTERNAL STANDARD SUCROSE CALIBRATION CHECKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Date:__________________________ Site:__________________________

Operator:________________________ Instrument Serial Number________________

Injection Number	Standard (μg C / μL)	Volume of Sample Injected (μL)	Carbon Injected (μg)	Carbon Measured (μg)	Measured within ±5% of Injected? (Y/N)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

Bi-Weekly Standard Loop Calibration – analyze a 10μl sample from the standard stock solution (~42μg C). Repeat until you receive three injections within 5% of the actual carbon injected.

Semi-Annual Standard Loop Calibration – analyze a 0 μl sample (clean filter), 5 μL sample (~21 μg C), 10μL sample (~42 μg C) and 20μL sample (~84 μg C). Repeat until you receive three injections within 5% for each level of carbon injected.

Appendix C

OAQPS FLOW CALIBRATION WORKSHEET FOR THE SUNSET OC/EC FIELD INSTRUMENT

Date:__________ Site:__________

Operator:__________ Instrument Serial Number:__________

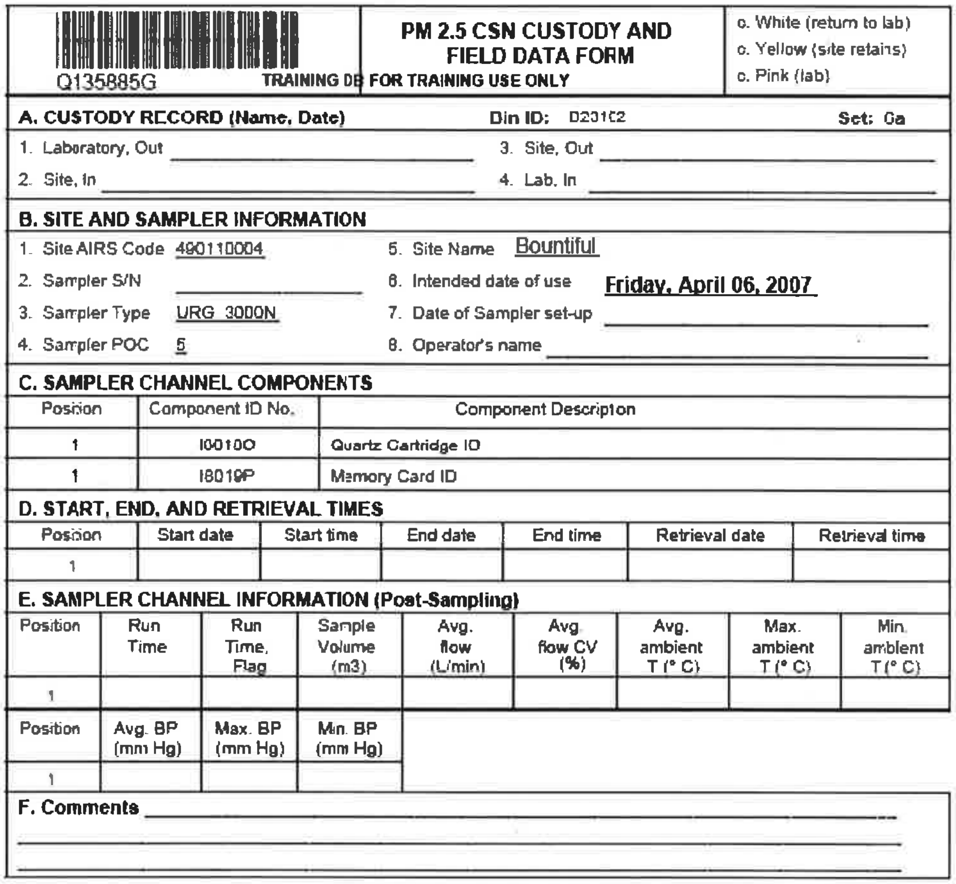
Flow Standard Model:__________ Flow Standard Serial Number: __________

Flow Certification Date:__________

Helium 1			**Helium Purge**		
Flow (cc/min)		Volts	Flow (cc/min)		Volts
Display	Actual		Display	Actual	

Helium / Oxygen			**Calibration Gas**		
Flow (cc/min		Volts	Flow (cc/min)		Volts
Display	Actual		Display	Actual	

Appendix D



Q135885G

TRAINING DB FOR TRAINING USE ONLY

PM 2.5 CSN CUSTODY AND FIELD DATA FORM

c. White (return to lab)
c. Yellow (site retains)
c. Pink (lab)

A. CUSTODY RECORD (Name, Date) **Din ID:** D20102 **Set:** 6a

1. Laboratory, Out ____________ 3. Site, Out ____________
2. Site, In ____________ 4. Lab, In ____________

B. SITE AND SAMPLER INFORMATION

1. Site AIRS Code 490110004
2. Sampler S/N ____________
3. Sampler Type URG 3000N
4. Sampler POC 5
5. Site Name Bountiful
6. Intended date of use **Friday, April 06, 2007**
7. Date of Sampler set-up ____________
8. Operator's name ____________

C. SAMPLER CHANNEL COMPONENTS

Position	Component ID No.	Component Description
1	I00100	Quartz Cartridge ID
1	I8019P	Memory Card ID

D. START, END, AND RETRIEVAL TIMES

Position	Start date	Start time	End date	End time	Retrieval date	Retrieval time
1						

E. SAMPLER CHANNEL INFORMATION (Post-Sampling)

Position	Run Time	Run Time, Flag	Sample Volume (m3)	Avg. flow (L/min)	Avg flow CV (%)	Avg. ambient T (° C)	Max. ambient T (° C)	Min. ambient T (° C)
1								

Position	Avg. BP (mm Hg)	Max. BP (mm Hg)	Min. BP (mm Hg)
1			

F. Comments ____________

Appendix E

QA/QC Form No. ________	**$PM_{2.5}$ CSN QA/QC REPORT FORM**	c. 1 (site retains) c. 2 (Agency QAM)

SITE AND SAMPLER INFORMATION

1. Site AQS Code ______________________
2. Sampler S/N ______________________
3. Sampler Type ______________________
4. Sampler POC ______________________
5. Site Name ______________________
6. Interval: Month_____Quarter_____Special_____
7. Date(s) of QA/QC Checks ______________
8. Operator's Name ______________________

DATE AND TIME CHECKS (Transfer Standard Name__________ Transfer Standard ID Number__________)

Sample display date/time	Transfer standard date/time	Date and time agree ± 5 min?	Action taken (a)

LEAK CHECKS (Transfer Standard Name________________ Transfer Standard Number________________)

Channel number	Manufacturer's specifications met?	Action taken and recheck results (a)

TEMPERATURE CHECKS (Transfer Standard Name_____________ Transfer Standard Number_____________)

Sensor location	Sampler display (°C)	Transfer standard (°C)	Agreement ±2°C	Action taken and recheck results (a)
Ambient				

PRESSURE CHECKS (Transfer Standard Name_______________ Transfer Standard Number_______________)

Sensor location	Sampler display (mm Hg)	Transfer standard (mm Hg)	Agreement ±10 mm Hg	Action taken and recheck results (a)
Ambient				

FLOW RATE CHECKS (Transfer Standard Name______________ Transfer Standard Number______________)

Channel Number	Sampler display (L/min)	Transfer standard display (L/min)	Design flow rate (L/min)	Agreement within ±10 percent? (b)	Action taken and recheck results (a)
1					
2					
3					
4					
5					

COMMENTS

(Revised 09.23.99)

Appendix F

EPA MONTLY QUALITY CONTROL/MAINTENANCE CHECKLIST
Magee Scientific Aethalometer

Location: Month/Year:

Date	Weekly Checks				Monthly Checks
	Flow Display	Correct Time/Date	Standard Flow (LPM)		Inlet Cleaned
	LPM	Yes or No	Pre-Cal	Post-Cal	Yes or No

Station Number: Operator:

Analyzer Property Number: Agency:

Operator Instructions:

1) Daily Checks: Review daily data. Verify Aethalometer status and there are no error messages.
2) Weekly Checks: Assure sampler flow on display read to within 0.2 LPM of previous week. Verify time and date is within five (5) minutes of data logger.
3) Monthly Checks: Check flow with standard. Recalibrate as necessary. Clean inlet cyclone.

Date	Comments or Maintenance Performed

Label and replace SD state memory drive.

4) Semi-Annual Checks: Perform Calibration and Optical Test Strip procedures. Perform Self Test.
Date of last calibration: Date of last Self Test:
5) Annual Checks: Clean or replace inlet probe line. Date last Cleaned:
Determine residence time: seconds (not to exceed 20 seconds).

Reviewed by: Date:

Appendix G

EPA INSTRUMENT CALIBRATION REPORT
Magee Scientific Aethalometer

Instrument Information:

Site Name:			**State**	
Site Number:			**City**	
Property Decal #			**Calibration Date**	
Agency:			**Last Calibration**	

Flow Meter:

Flow Standard Model	
Flow Standard SN	
Flow Certification Date	

Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)

If % difference is > 5% proceed to Flow Meter Calibration

Flow Meter Calibration:

Previous Scale Factor	New Scale Factor

Repeat Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)

Operator:	
Comments:	

Appendix H

References

Annual Data Summary Report for the Chemical Speciation of PM2.5 Filter Samples Project, RTI/0212053/02ADS, February 28, 2011.

The Aethalometer™, 2005.07, Berkeley, CA, 2005.

Environmental Technology Verification Report for the Magee Scientific Aethalometer™ Particulate Carbon Monitor, Battelle, August 2001.

EPA NERL Standard Operating Procedure Magee Scientific Aethalometer Models AE-22 & AE-31, Version 1.4, February 2011.

Hyslop, Nicole P. and Warren H. White, "An Empirical Approach to Estimating Detection Limits Using Collocated Data," *Environmental Science & Technology,* 2008, *42,* 5235-5240.

Quality Assurance Project Plan for the Chemical Speciation of $PM_{2.5}$ Filter Samples, Revision 6, Research Triangle Park, NC, February 2009.

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Standard Operating Procedure (SOP) for the Analysis of Organic and Elemental Carbon (OC/EC) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer, Portland, Oregon, January 2005.

Standard Operating Procedure (SOP) for the URG-3000N Sequential Particulate Speciation System (Interim Version 1.0), Revision 1, Research Triangle Park, NC, April 2007.

Strategic Plan for the Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trend Sites, US EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC, April 1999.

Sunset Laboratory Inc. Semi-Continuous OCEC Instrument Manual, Version 6.4.

Appendix J

EPA NERL Standard Operating Procedure Magee Scientific Aethalometer Models AE-22 & AE-31, Version 1.4, February 2011.

EPA United States Environmental Protection Agency

NATIONAL EXPOSURE RESEARCH LABORATORY

HUMAN EXPOSURE & ATMOSPHERIC SCIENCES DIVISION

Standard Operating Procedure

Magee Scientific Aethalometer®

Models AE-22 & AE-31

Version 1.4

February 11, 2011

FORWARD

This SOP covers the Magee Scientific Rack Mount Models AE-22 dual and AE-31 spectrum Aethalometers that EPA NERL uses to quantify high time resolution ambient $PM_{2.5}$ "Black" or Elemental Carbon. The Model AE22 measures the light absorption of carbon particles at two wavelengths: 880 nm (IR), quantitative for the mass of black carbon; and 370 nm (UV), that some researchers believe indicates the presence of aromatic organic compounds such as are found in wood smoke, biomass-burning smoke, and tobacco smoke. The real-time measurements can be made with time resolution from one second to one hour. Performing the 2 wavelength measurement may be important in determining the source(s) of airborne black carbon (BC) particles (e.g., diesel exhaust *versus* wood smoke combustion). The Model AE31 measures light absorption by particles at seven wavelengths, from 370 nm (UV) to 950 nm (IR). Real-time measurements of particle concentrations can be made with a time resolution of two minutes to one hour. Interpretation of the differences in optical response across the wavelength spectrum may reveal information regarding aerosol size distribution, physical properties, and assist in identifying the primary components.

The Magee Scientific Model AE-22 dual and Model AE-31 spectrum Aethalometers are used in monitoring applications involving human exposure to localized, community-based sources of air pollution as well as general particulate matter characterization and source apportionment studies. The Model AE-22 and AE-31 are virtually identical in most installation, operational, and maintenance operations. Operational settings that are unique are clearly detailed in the following sections by model number. Some of the following text is based upon the California Environmental Protection Agency Air Resources Board AQSB SOP 407.

Questions or comments on this SOP should be directed to:

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919-541-4841

CONVENTIONS

The following symbol conventions are used throughout this manual:

NOTE ☛	NOTE messages denote a procedure, practice, or condition that is important and should be highlighted.
CAUTION ✋	CAUTION messages call attention to a procedure that, if incorrectly done, could result in damage to an instrument or loss of data.
DANGER	DANGER messages call attention to a personal hazard or to a procedure that, if incorrectly done, could result in injury or death.

CONTENTS

1.0 GENERAL INFORMATION

2.0 INSTALLATION PROCEDURE

3.0 CALIBRATION INFORMATION

4.0 ROUTINE SERVICE CHECKS

FIGURES

APPENDICES

1

GENERAL INFORMATION

1.1 Introduction:

The purpose of this Standard Operating Procedure (SOP) is to document the procedures used by U.S. EPA Office of Research and Development National Exposure Research Laboratory (NERL) to operate the Magee Scientific Model AE-22 and AE-31 Aethalometers. The goal of this SOP is to (i) formalize Aethalometer installation, configuration and operation procedures in order to ensure comparability among Aethalometer data, and (ii) to describe supplemental information and modifications to the Magee Scientific Operation Manual version 2005.07. The Aethalometer Operation Manual is a good source of information pertinent to the operation, maintenance and understanding of this instrument, and therefore staff should thoroughly review of the Aethalometer Operation Manual prior to using the instrument.

1.2 Principle of Operation:

The Aethalometer is an instrument that provides real-time black carbon aerosol (BC) concentrations in ambient air. These aerosols (“soot”) are emitted from all types of combustion sources, most notably from diesel exhaust.

The Aethalometer is a self-contained instrument that provides a means to measure the rate of change of optical transmission through a spot on a filter tape. The aerosol is continuously collected and deposited on the filter as an accumulation of optically-absorbing material in the sampled air stream. The instrument measures the transmitted light intensities through the ‘sensing’ portion of the filter tape, on which the aerosol spot is being collected, and a ‘reference’ portion of the filter tape, as a check on the stability of the optical source. A mass flow meter monitors the sample air flow rate. The data from these three measurements is used in the calculations to determine the EC concentration in ambient air.

During the sampling process, the tape does not move. The roll of tape contains can accommodate approximately 1500 spots. When the ‘Filter Change At’ value is set equal to zero, then the tape is automatically advanced when optical attenuation of the filter spot is reached. Maximum Attenuation value is specified in the Change Settings menu.

The display on the front panel shows the calculated BC concentration, and provides a keypad for interaction with the instrument’s embedded computer. Connectors on the rear panel provide for power input and fuse, an analog output whose voltage may be scaled to represent the measured BC concentration, and RS-232 digital communications with an external computer.

The aerosol inlet is plumbed through a connector on the rear panel and a pump is used to provide flow at the inlet: Some models have an internally-mounted variable-speed pump. The sampling flow rate is stabilized by software control of the pump speed, based on the mass flow meter reading. Other models require an external pump connected to the quick release on the rear panel. The aerosol collecting filter tape is held in a spring-loaded optical head behind the front panel.

The Aethalometer calculates one new aerosol BC concentration reading every time base period. The user sets the time base for the desired data rate, usually 5 minutes, although BC data to one reading per second are possible. The data is written to a solid state Compact Flash memory card, transmitted by the COM port, and produced as an analog voltage.

1.3 Interferences/Limitations:

Temperature - Because the Aethalometer contains sensitive electronics and a processor and may have an internal pump, **NERL recommends that the instrument be operated in a temperature and humidity controlled, weather tight environment**. Large or rapid changes in ambient temperature may contribute second-order errors to the calculation of aerosol BC concentration. Keep the instrument clear from the direct air flow of a vent, heater or air-conditioner. Aethalometer data quality can be jeopardized if the air-conditioning thermostat has substantial hysteresis and/or the equipment is exposed to forced air whose temperature undergoes large fluctuations.

Inlet Plumbing - The sample inlet flow may be highly charged, in which case explicitly-electrically-conducting tubing should be used. Aerosol losses due to electrostatic precipitation in the inlet tubing are normally small. The Aethalometer Operation Manual, section 5.8, Installation Requirements, recommends that Teflon tubing should **not** be used for the sample inlet. **NERL recommends a grounded, ½" inch stainless steel inlet tubing not longer than fifteen (15) feet in length to support the BGI model SCC 1.829 $PM_{2.5}$ cyclone. Inlet can also include a length of conductive plastic tubing to make penetration through a shelter or to facilitate a tight radius.**

Contaminants - It is important to protect the Aethalometer inlet from insects. The quartz fiber filter will clog and rapidly change its optical properties if insects are pulled into the system. **NERL staff, therefore, recommends enclosing the cyclone inlet in a mesh bag or mesh screen with a weave dense enough to exclude insects.**

1.4 Safety Precautions:

Only properly trained personnel should perform Aethalometer testing, installation, operation, maintenance and calibration procedures. As with all monitoring equipment, precautions should be taken when working around electricity, power tools and above ground elevations. Always operate the instrument with a ground connection (earthing).

Under no circumstances remove or open the internal ground connection. If the

Instrument is turned on, the electrical connections are charged and therefore do not attempt to touch internal components when the instrument is turned on. Internal components should only be touched or removed when the monitor has been turned off and unplugged. The power supply is operated at high voltage. Do not attempt to touch the power supply when the instrument is turned on. Do not touch the interior components of the instrument when it is turned on. Never operate the instrument if the cover or any other parts the instruments are removed. If you observe that the instrument has insufficient grounding or that the grounding connection is damaged, remove the instrument from operation for repair.

2

INSTALLATION PROCEDURE

2.1 List of Tools/Supplies:

A set of open end SAE 7/16”, 1/2”, 9/16” wrenches or a crescent wrench. Any tools required to install inlet tubing from Aethalometer inlet to the source inlet such as drill and bits, fasteners, etc.

A standard external flow meter capable of reading air flow rates in the range of 2 to 10 liters minute^{-1} (LPM), with a low resistance to flow, traceable to a primary standard such as NIST.

2.2 Physical Inspection:

A complete Aethalometer installation requires the following items:

1) The Aethalometer instrument which includes a power cord, sample inlet tubing, and a selection of fittings for sample inlet connection. EPA recommends 1/4” Swagelock® stainless steel fittings.
2) A roll of Filter tape, installed in instrument.
3) The instrument instruction manual.
4) Factory documentation: Final inspection record, CE certificate, Calibration test document.
5) The original program diskette for backup or solid state memory drive.
6) An optical test strip.
7) A Compact Flash memory card.

2.3 Initial Setup:

1) Connect the Aethalometer to an AC power outlet, turn power switch on, and ensure that the instrument powers up.
2) Insert Compact Flash solid state memory card.
3) Remove the clear plastic filter protection strip from the optical analysis head by holding **TAPE ADVANCE** and pulling gently.

NOTE ☞ Do not tear tape

2.4 Hardware Set-Up:

Sample inlet flow through the Aethalometer is produced either by an internal or external pump. When an internal pump is used the flow rate is controlled by an electronic motor speed control. The external pump models flow rate is controlled by a valve connected to the pump. Since the mass flow meter monitors the actual mass flow, the average measured mass air flow is used to calculate the sample volume.

Internal diaphragm pump – Variable-Speed DC Motor

The Aethalometer is most commonly supplied with a dual-diaphragm pump operated by a variable-speed brushless DC motor. The motor speed (and hence the flow rate) is controlled automatically by the Aethalometer microprocessor using feedback from the mass flow meter to achieve a desired flow rate.

External Pump

The purpose of using an external pump is to provide higher sample inlet airflow through the Aethalometer. For these cases, the Aethalometer may be used with the supplied quick-disconnect suction fitting on the rear panel, and a valve to attach to the pump to adjust the flow. Minimum pump requirements are that it can provide the necessary flow at a gauge vacuum of up to –0.5 atmospheres.

A GAST Manufacturing Inc. pump, model DOA-V722-AA or equivalent is suitable. These can be obtained either from GAST or from distributors such as W. W. Grainger (their catalog no. 2Z866) and McMaster-Carr (Catalog no. 4176K11).

Connect the sample inlet port to the inlet line. If the instrument is configured for ‘External Pump’, plug in the pump, check that it is operating correctly, and connect it to the ‘Vacuum Pump’ suction connector on the rear panel.

Turn the instrument on to verify that it is drawing air through the Aethalometer such that suction can be felt at the end of the sample inlet tubing.

When the power to the Aethalometer is turned on, the display screen will illuminate. For the first 30 seconds the computer is performing its program loading and initialization procedure, and the screen will only show a flashing cursor block. The screen will then display the opening dialog. The instrument can begin operation automatically from this point, and will do so after 60 seconds if none of the keypad keys are pressed.

Sample Inlet Tubing Connectors

The sample inlet port on the rear panel is a standard ¼” female pipe thread socket. It accepts any fitting that the user may wish to employ for connection to the air sampling stream. A selection of fittings is provided with each new Aethalometer, including a gray plastic ‘instant’ push-to-fit connector for the 3/8” (6 mm.) OD tubing that is supplied.

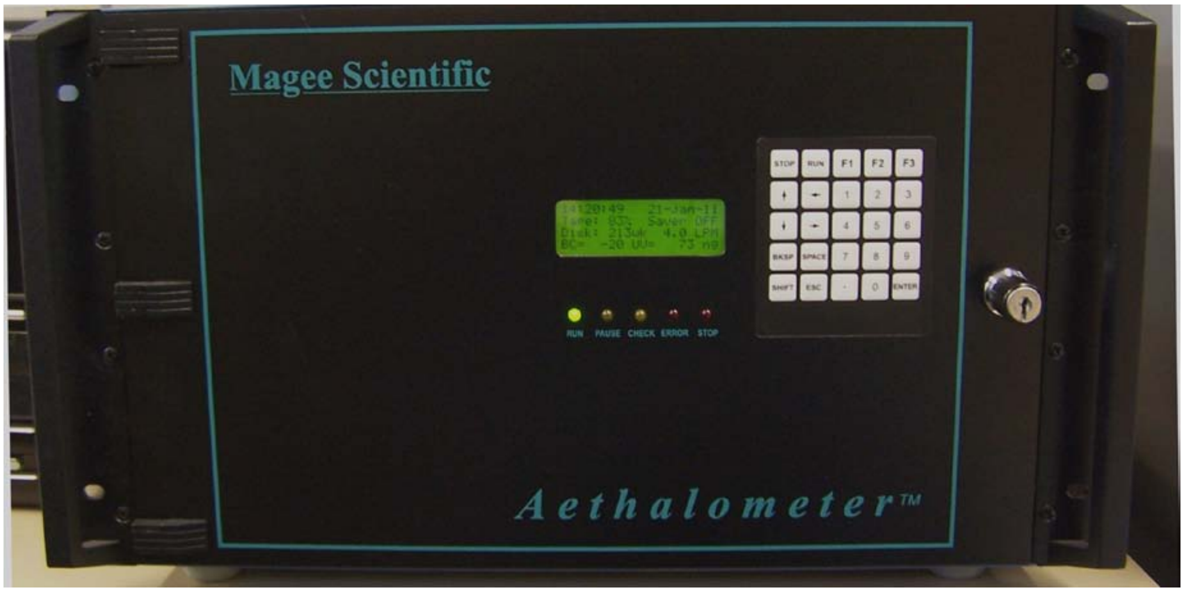
NOTE ☞

If using this fitting, it is **very important** that the tubing must be pushed firmly all the way into the fitting, in order to make a leak-tight seal on the o-ring that is inside the connector.

To remove the tubing from the connector, press firmly on the release collar ring closest to the tubing, while simultaneously pulling the tubing out of the fitting. See Section 1.3 Interferences/Limitations, Inlet Plumbing

Size Selective Inlet
Follow the manufacturer's (BGI) procedures for installation and cleaning of the Model CSS 1.829 $PM_{2.5}$ size selective inlet (Appendix D). Aethalometer flow rate should be set to 5.0 LPM for correct $PM_{2.5}$ MMAD size cut.

Figure 1
Aethalometer Front Panel



2.5 Software Set-Up:

Main Menu Overview: The opening screen displays an opening "Aethalometer" logo; the software version number; a countdown from 60 seconds for the automatic start; and the prompt to "Press Any Key for Main Menu".

The Main Menu offers the following selections:

- Operate
- Change Settings
- Signals + Flow
- Self Test
- Calibrate Flow Meter
- Software Upgrade
- Optical Test
- Install New Tape

2.5.1 Operate: This option of the Main Menu allows for automatic operation or for manual input while preparing the instrument to sample. The first screen display asks "**Go To**

Auto Mode?" The default response **Y** is displayed. If **ENTER** is pressed, the instrument immediately proceeds with fully-automatic operation, and no further operator interaction is required.

If **N** is selected with the down-arrow key, and **ENTER** is pressed, the program provides the following interactions: The program asks the user if new titles should be read (e.g. for a new study name or sampling period). These titles will appear in the 'MF' message files. To enter new titles, use any plain-ascii text editor to write two separate lines title1 and title2 in a text file TITLES.TXT, and insert into the floppy disk drive or the solid-state memory drive, at the prompt. These titles will be saved for future sampling periods. The program prompts the user whether the solid-state Compact Flash memory drive, should be replaced, even if it is not full yet. Note that the option "**Overwrite Old Data"**, if set to **YES** in the Change Settings menu, will simply overwrite the oldest data when the disk or the solid-state memory card drive becomes full.

The screen will show a Flow rate display. This allows the operator to verify the air flow rate desired. The air flow rate is checked after a 30-second countdown that allows the flow meter to stabilize. The flow rate display provides an opportunity for the flow rate to be adjusted. If the flow rate is acceptable, press any key.
Titles confirmation, "Title 1" ; "Title 2" .. "Retain Old Titles" / "Read New Titles". This allows new titles to be uploaded.

Measurements will start automatically after the following two screens display:
(1) "Advancing Tape – Wait"
(2) "Waiting for Start Time"
The screen displays a countdown to start of the next integral time base period

2.5.2 Change Settings: This menu allows the system settings to be changed according to the user's needs. The following parameters may be altered:

Time & Date: This menu allows the user to change the current time and date. If the date is changed, the time must be re-set also. Use the left-arrow and right-arrow keys to position the cursor over the item to be changed. Use the up-arrow and down-arrow keys to change the value. Note: The new time value is not written until the change menu is completely exited and saved. It is advisable to set the time to the next minute with zero seconds, exit the change menu to the point of "Write System Settings?", and press ENTER at exactly the actual minute roll-over. **NERL operates equipment on Eastern Standard Time (EST) year round**.

Flow Rate: Usable range 1 – 6 LPM. This allows the user to set the sample air flow rate in standard liters minute^{-1} (SLPM). On units with the internal pump, the computer and electronics automatically control the variable-speed pump to maintain the desired flow rate based on the signal from the air mass flow meter. **NERL operates Aethalometers at 5 LPM to meet BGI SCC 1.829 size selective cyclone inlet requirements**.

Time base: Valid values: 1 sec - 60 min. This defines the time period over which the aerosol is collected and analyzed. At the end of each time base, the data is written to disk and the display is updated. **NERL uses a 5 min time base**.

Tape Saver: Selections: '**OFF', 'X3', 'X10'** This parameter controls the flow bypass valve to prolong the lifetime of each filter tape spot, and thus to reduce the consumption of tape in locations of high BC concentration. **NERL recommends setting the tape saver to "OFF"**.

Analog Output Port: Selections: **SIGNAL OUTPUT / ALARM**. This function allows the analog voltage output connector either to provide a data output, for connection to an analog data logger or to operate as an alarm switch. If **SIGNAL OUTPUT** is selected:
Output Scale Factor: Valid values:
1 - 100,000 (ng BC m^{-3}) / V, when the BC Display Unit is set to ng m^{-3};
1 - 1000 (µg BC m^{-3}) / V, when the BC Display Unit is set to µg m^{-3}.
This parameter defines the scaling factor of the analog voltage on the output connector that represents the measured black carbon concentration in "Signal Output" mode. This output voltage is swung to the value of -5 V to indicate "No Valid Data" during periods of instrument warm-up, operator intervention and menu selection, and also during the tape advance process. The analog output voltage is scaled with its factor from 0 to +5 V to represent data when it is valid.

If **ALARM** is selected: Alarm On/Off allows the alarm function to be enabled or disabled. Valid concentration values are 0.01 - 100,000 µg m^{-3}. **NERL recommends setting the analog output port to "OFF"**.

Analog Out Channel: This is used only on multiple-wavelength models (AE2- and AE3-), and selects which wavelength's data will be used to control the output of the analog port.

Warm Up Wait: Selections: YES / NO
If this parameter is set to "YES", the instrument displays optical sensing and flow voltages for 30 minutes at the start or restart of the program, before proceeding with automatic operation. Note: If the electrical power is interrupted even momentarily, 30 minutes of data loss will be introduced at every power-up automatic restart. **NERL recommends setting the Warm up Wait to "NO"**.

Communication Parameters: COM mode, COM settings.
This menu controls the activity of RS-232 port on the rear panel of the instrument.
'OFF' disables the COM port activity.
The COM Settings sub-menu sets the communications parameters:
BAUD (9600, 4800, 2400, 1200); DATA bits (8 or 7); STOP bits (1 or 2); PARITY (None, Even, Odd).
Note! If DATA BITS is set to **8** then PARITY **must** be set to **None**.
NERL recommends setting the following comm. Parameters "9600, 8, 1, N".

Overwrite Old Data: Selections: YES / NO. **NERL recommends setting the overwrite variable to "NO"**.
If this parameter is set to "YES", then the instrument automatically overwrites the oldest files on the memory card when the disk becomes full.

Filter Change At: Valid values: 0-30 hours. **NERL recommends setting the filter**

change variable to "0". Set value to **0** to allow automatic filter tape advancing. This parameter affects the triggering of filter tape advances at fixed time intervals, if the 'Filter Change At' value is greater than zero. If the Filter Change At value **is set equal to zero**, then the tape is automatically advanced when optical saturation of the filter spot is reached. If the Filter Change At value is **greater than zero**, then the tape is advanced only when the determined time period expires.

Security code: This allows access to the following protected functions:
Exit from Operate to the Main System Menu after pressing the STOP key.
Upload a software upgrade.
Change certain 'protected' setup parameters.
In all cases the user must enter the correct security code within 10 seconds. If this time-out expires, the program reverts to the previous menu item.
The security code is initially set to **111** when the instrument is shipped from the factory.

Date Format: This parameter controls the conversion of the date to a 6-digit number for the purposes of constructing file names for the 'BC' and 'MF' files written to disk. The filename date is constructed as MMDDYY.

BC Display Unit: Selections: Nanograms / Micrograms
This selects the concentration unit for the screen display. 'Nanograms' displays no decimal fractions (i.e. XXXX ng m^{-3}) and is recommended for use in remote or unpolluted locations; 'Micrograms' displays 2 decimal fractions (i.e. XX.XX µg m^{-3}) and is recommended for use in urban or polluted locations.

Data Format: Selections: Expanded / Compressed
This option controls the format in which data is written to disk and sent to the COM port. In 'Expanded' format, the data record consists of numeric fields, each separated by commas. The file 'DATACOLS.CSV' is written to the floppy disk to identify the data columns for the various instrument options. Many of the columns represent internal signal parameters that are only required for performance verification: the measurement data of value to the user are represented by 'Date', 'Time' and Concentration'.

In 'Compressed' format, the data record consists of a reduced number of columns. The first entries are 'Date', 'Time' and 'Concentration', while the following column(s) are string(s) of alpha characters whose coding represents all the internal signals. For routine operation, this codeword may be discarded: it will appear as the final column(s) if the data is imported to a spreadsheet in '.CSV' format. If required, the codeword may be decompressed for instrument diagnosis using the 'COMDECOM' program available from Magee Scientific. **NERL recommends setting the Data Format to "Expanded".**

UV Channel ON/OFF:
Selections: ON / OFF. **NERL recommends setting the UV Channel "ON"**.

Hardware Configuration: This allows the user to correctly specify the various hardware options, so that the software will function correctly. The sub-menu items are as follows:
Instrument Type (Optics)
Selections are:

‘AE1x – Standard’ (e.g. AE16 single wavelength, BC only) ;
‘AE2x - UV+LED’ (e.g. AE21 combination BC + UV absorption) ;
‘AE3x - 7 x LED’ (e.g. AE31 multiple-wavelength “spectral” measurement).

Spot Size: There are two settings “Extended Range” for larger oval spots (1.67 cm^2) on newer units and “Standard Range” for smaller circular spots (0.50 cm^2) on older units.

NOTE ☞

Spot size setting must match the physical spot type that you observe on the tape or the concentrations will be erroneous!

Sigma for Lamps: This setting permits change to the mass absorption coefficient or proportionality constant “Sigma” that is used to convert optical attenuation to a BC mass. This may be used to tailor the optical response, or to switch between “Magee BC” and “Harvard BC” calibrations. **NERL recommends the following settings: value 1 = 16.6 m^2 gram^{-1} and value 2 = 39.5 m^2 gram^{-1}.**

Spots per Advance: This setting allows the user to control the spacing of the spots collected on the filter tape. If “1” is selected, the spots will be close together and essentially touching, minimizing the use of filter tape. It is possible that the spots may actually overlap by a very small amount: this does **not** affect the accuracy of the measurement, due to the nature of the algorithm. However, there may be situations in which the spots are to be collected afterwards for analysis or archiving. If touching of spots would be unacceptable for these requirements, select the value of “2” for this parameter. In this case, the tape advance mechanism will perform two complete cycles for each tape spot advance. **NERL recommends setting the spot advance value to 1.**

Maximum Attenuation: This allows the user to specify the maximum value of optical attenuation that defines the point at which an automatic tape advance is triggered. **NERL recommends a Maximum Attenuation of 125 on Model AE-22 when UV channel is on and on Model AE-33. If the UV channel is off on the Model AE-22, then NERL recommends a Maximum Attenuation of 75.**

Return to Main: This concludes the *Change Settings* menu, and asks if the user wishes to save the changes by writing the parameters to an internal file.

2.5.3 Signals & Flow Display: This selection allows the user to check the optical signals and the flow meter response. It is useful for checking the optics or verifying a desired flow rate. The lamp(s) may be turned ON and OFF by toggling the UP/DOWN keys. The lamp condition is shown on the right-hand side of the top line of the display screen as follows: AE2- and AE3- series instruments allow for testing of the additional lamps:
“Lamp=0” : lamp(s) OFF
“Lamp=1” : 880-nm lamp turned ON : “wavelength 1” BC measurement
“Lamp=2” : 370-nm UV lamp turned ON : “wavelength 2” UV measurement in AE-2 series instruments
“Lamp=3” to “Lamp=7” : other wavelength lamps turned ON for testing AE-3 series instruments.

2.5.4 Self Test: This selection activates a sequence of tests of the instrument hardware. The series of tests are performed automatically and any error messages are shown on the screen.
Lamp test: The lamp(s) are turned on and off, and measurements are made of the optical signals in the sensing and reference detectors. For multiple-source instruments, this procedure is repeated. Comparison of the signals allows for the following fault analyses:
LAMP is burned out (OFF all the time)
LAMP is ON all the time (electronics fault)
TAPE torn or ended (signals too large)
LAMP TEST PASSED.

Pump & bypass test: This test measures the air flow: the user is prompted to connect the pump (in case the instrument is configured for ‘External Pump’). The air flow is calculated using the flow meter zero voltage and the flow scale factor that were set by the Calibrate Flow meter routine. If the flow rate is smaller than 1 LPM, an error message is displayed. The flow rate is compared for both positions of the bypass valve, to make sure that it is not blocked in either position.

Analog output test: The analog output connector on the rear panel is presented with a sequence of voltages to allow an external data logger or alarm relay to be tested. The sequence is: V = 0 ; +1 VDC; +2 VDC; +5 VDC.

COM port test: This routine allows the user to test the transmission of RS232 code from the COM port on the rear of the instrument, in order (for example) to test communications with a data logger or other receiver. This routine first allows the user to change COM parameters (baud rate, etc.) if desired. The screen then prompts “ENTER to send data”. Press ENTER to transmit one data line using the COM parameters. This may be repeated as often as desired. Press ESC to escape.

Screen test: This routine tests the display screen as follows:
All LED’s are turned ON.
All LED’s are FLASHED.
All LED’s are turned OFF.
The screen is filled with characters.
The screen backlight is turned OFF.
The screen backlight is turned ON.

Tape advance test: The tape feeder is activated: the user is prompted to watch the mechanism to verify correct operation. A countdown timer indicates the approximate duration of the test.

2.5.5 Calibrate Flow Meter:
The program first allows the user to switch between ‘Standard’ and ‘Volumetric’ flow units. NERL recommends the selection of Standard Units to report the air flow rate as SLPM, i.e. volume occupied by a given mass of air at a temperature of 20°C and a pressure of 1013 mb. (If ‘Volumetric’ flow units are selected, it is necessary for the barometric pressure and ambient air temperature be entered by

the user – they are not measured by the instrument). If not measured the Aethalometer cannot control volumetric flow.

Flow Meter Re-Calibration:

NERL recommends the performance of this flow meter calibration if the monthly flow verification test deviates by more than 5% of the NIST traceable reference meter value. This is 'protected' and requires the Security Code as a password. This procedure calibrates the flow meter response by measuring the flow meter zero voltage and determining the flow scale factor. These two factors are used during measurements to calculate the actual air flow through the flow meter.

You will need a NIST certified standard external flow meter or calibrator capable of reading air flow rates in the range of 2 to 10 SLPM, with a low resistance to flow (e.g., BIOS DRYCAL). Connect this calibrator firmly to the Sample Inlet Port with no possibility of an air leak. Allow the instrument to warm up for at least 30 minutes with power and air flow 'on', before performing the re-calibration.

Aethalometers with an **internal** pump are controlled by a microprocessor and electronics, and this allows the program to set 'zero' and 'span' flows. All that is required of the operator is to connect a standard external flow calibrator, and observe its reading.

The routine first automatically reduces the pump speed slowly to zero, while measuring the signal from the internal flow meter. When this has reached a steady low value as determined by no more change in voltage output, the value of the reading is used as the flow meter zero voltage. The pump is then re-started and run up to its previous speed. When the flow meter signal is steady, the screen displays the flow rate in LPM derived from the new zero and the previous scale factor. By pressing the keypad UP- and DOWN-arrow keys will change the flow scale factor. Press these keys until the displayed value agrees with the measurement from the external calibrator. Press ENTER when the displayed value is correct.

On Aethalometers with an **external** pump, close the external valve to bring the flow rate to zero. Compare the displayed value of flow with the actual value as measured by the external standard. Open the valve to set the flow. Compare the displayed value of flow with the actual value as measured by the external standard. By pressing the keypad UP- and DOWN-arrow keys will change the flow scale factor. Press these keys until the displayed value agrees with the measurement from the external calibrator. Press ENTER when the displayed value is correct.

Upon return to the main system menu the user is asked to confirm writing the newly measured response factors to the setup file. The previous flow calibration values are not replaced until this confirmation is made. In case of any doubt, repeat the procedure.

2.5.6 Software Upload

This is a 'protected' function and requires the Security Code as a password. The Software Upgrade selection provides a convenient means to load new software from the SD memory card.

2.5.7 Optical Test Procedure

This is a ‘protected’ function and requires the Security Code as a password. This procedure performs a routine QC/QA check on the correct operation of the photodetectors, whose signals are the fundamental basis of the measurement. It uses the Optical Test Strip provided with the instrument. **Do Not Lose This Strip! Keep the Test Strip Clean, Flat and Smooth!** Contact Magee Scientific if a replacement is required, but be informed that the test is only relevant when repeatedly performed with the same test strip.

The Optical Test Strip consists of laminated material whose optical density at one end is greater than that at the other. The test procedure automatically determines the optical densities measured by the photodetectors, and writes the results to disk as a user-friendly ASCII text file. The significance of the test is to verify that the photodetectors output remain constant over time (e.g., from one test to the next). The actual numerical values of the calculated parameters are intrinsically meaningless: it is their constancy when measuring the same test strip that assures consistent performance of the instrument. The Optical Test Procedure guides the user through the various actions that are necessary, with prompts on the display screen.

The Optical Test Strip has a serial number printed at one end that should match the serial number of the instrument. Enter this number when prompted. Check that there is a Compact Flash memory card in the drive.

Open the door, and remove the two thumb screws that secure the rectangular metal cover over the sampling chamber in the center of the instrument. This provides access to the area where the filter tape passes through the analysis system.

Cut the filter tape on the left side of the chamber with scissors. Press ENTER when prompted. The remaining tape will be pulled out onto the right-hand spool.

When prompted, insert the test strip from the left-hand side. Its printed serial number should be facing upwards on the right-hand side. Push it in from the left until the tip of the arrow printed on it is just visible in alignment with the edge of the base block. Press ENTER when ready.

The first phase of the test will proceed automatically: the lamp will turn ON and OFF to determine the optical transmission signals for the ‘front’ portion of the test strip.

At the end of the first set of measurements, the transmission values will be displayed. It is not necessary to write them down, as they are saved to disk. Press ENTER to proceed. The mechanism will go through three tape-advance cycles in order to pull the test strip forward, taking approximately 5 minutes. The second phase of the test will cycle the lamps again and measure the optical transmission signals for the ‘rear’ portion of the test strip. The program will then calculate the quantities ‘S Density’, ‘R Density’, and ‘Balance’. The signals, results and other information will be written to a file on the disk under file name ‘OTxxxxxx.TXT’ where ‘OT’ represents Optical Test, and ‘xxxxxx’ is the date.

This text file provides the definitive report on the optical transmission signals and the balance between the Sensing and Reference signals. This text file should be printed out and saved. The display screen will then prompt the user to re-insert the filter tape from the left-hand side. After pulling it through, re-attach it to the tape on the right-hand take-up spool. Replace the rectangular metal cover with its two thumb screws.

2.5.8 Install New Roll of Tape:

This is a “protected” function and requires the Security Code as a password. The display screen shows an estimate of the percentage of the tape roll that remains: when this falls below 10%, the “Check” lamp on the display panel will be lit.

The menu item “Install New Tape” contains an option to display an abbreviated set of sequential instructions with prompts. This not only guides the user through the necessary steps, but also re-sets the tape percentage counter to 100%. For this reason, the software procedure must be used when installing a fresh roll of tape, even if the user is very familiar with the procedure.

The first screen asks “**List Instructions*?.***” If **NO** is selected, the instrument assumes that the operator is familiar with the tape installation procedure, and will not require guidance. The software skips the detailed instructions, re-sets the tape counter to 100%, and returns to the Main Menu.

If **YES** is selected, the display screen guides the user through all the operations required for changing the tape. After each phrase, the user must press any key to proceed to the next:

(a) Remove spool screws
(b) Remove cover screws
(c) Pull out guide rod
(d) Cut old tape
(e) Remove supply roll
(f) Remove take-up roll
(g) Install new roll
(h) Lift up chamber 2 mm
(i) Push tape through
(j) Lift up chamber 2 mm
(k) Pull 10 cm tape
(l) Install take-up hub
(m) Clip tape to hub (under old tape role)
(n) Push in guide rod
(o) Replace cover
(p) Replace spools
(q) Tighten spool screws

The screen then asks: ‘Is the tape properly replaced?’ Entering ***YES*** will re-set the tape counter to 100% and concludes the process.

Figure 2

Front View Interior

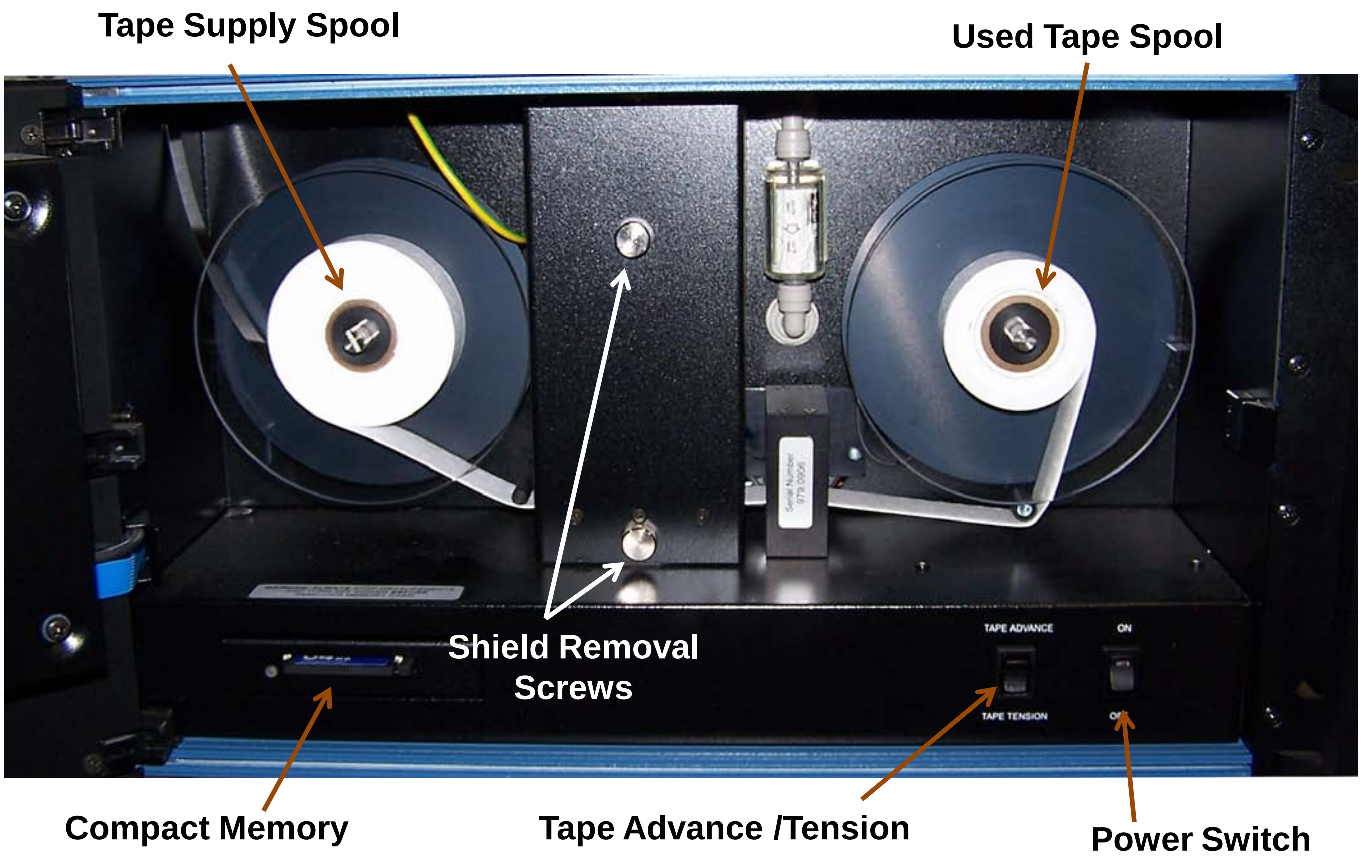
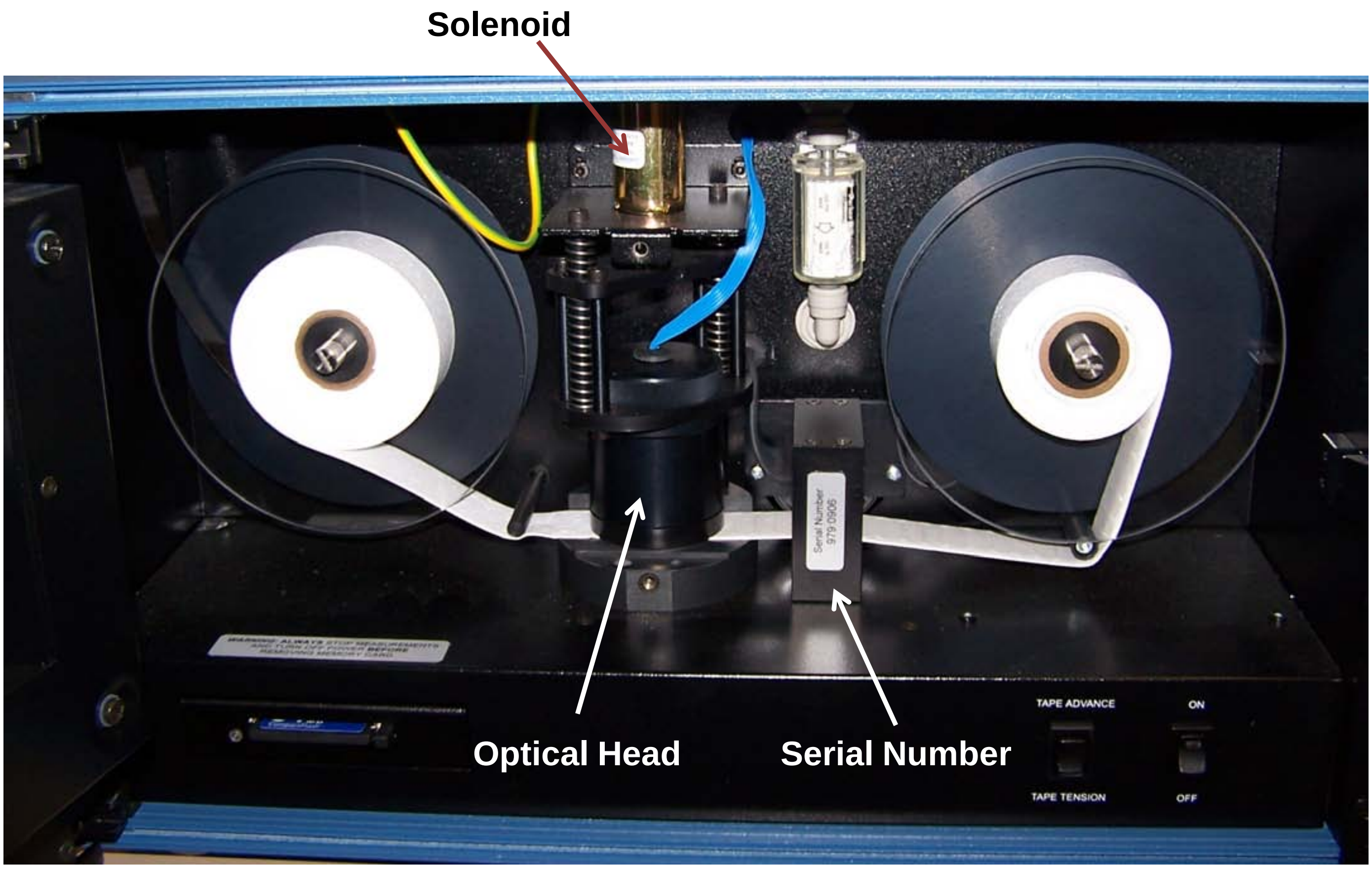


Figure 3

Front View Interior W/O Light Shield



2.6 Data Logger Connection:

Analog Output Port – Selections: **SIGNAL OUTPUT / ALARM**. This function allows the analog voltage output connector either to provide a data output, for connection to an analog datalogger or chart recorder, or to operate as an alarm switch.

Select **SIGNAL OUTPUT**:

Output scale factor:
1-100,000 (ng BC /m3) / V, when the BC display unit is set to ng/m3;
1-1000 (µg BC /m3) / V, when the BC display unit is set to µg/m3.
This parameter defines the scaling factor of the analog voltage on the output connector that represents the measured black carbon concentration in "Signal Output" mode. This output voltage decreases to the value of –5 V to indicate "No Valid Data" during periods of instrument warm-up, operator intervention and menu selection, and also during the tape advance process. The analog output voltage is scaled with its factor from 0 to +5 V to represent data when it is valid. Note that when BC concentrations are extremely low, instrumental noise can lead to computed values of BC that are slightly negative. These noise values will be presented as slightly negative analog output

voltages, but still represent valid data.

The analog voltage output range is –5 to +5 volts DC. It has 3 modes of operation. The operator can choose between "Signal Output" and "Alarm" in the software setup. The –5 volt "Data Not Valid" flag is always active.

WARNING

In the Aethalometer Manual 2005.07, Section 15.2.1 Analog Output Port Principle states that when the analog output port is connected to a D/A converter operated by the embedded computer; "**It is intended as an indicative signal voltage output only**. **It is not intended to be the primary definitive data output of record"**. "Primary definitive data is the digital data either on diskette or transmitted by the COM port". See Appendix C, Example of a Typical Data File.

3

CALIBRATION INFORMATION

3.1 Calibration Introduction:

The purpose of this section is to outline the Magee Scientific Aethalometer calibration procedures used by NERL.

The Magee Scientific Aethalometer Operation Manual is an important resource of information, and the AQSB recommends a thorough review of the manual before calibrating the instrument. Under normal operating conditions, the Aethalometer should not need to be calibrated. The internal mass flow meter has been calibrated at the factory and re-calibration should only be performed if the flow meter response is more than +/-10% of set flow. NOTE: If size selective inlet is used, refer to manufacturers flow tolerances. A calibration report is required when installed and when verified/calibrated.

3.2 Calibration Overview:

This procedure calibrates the mass flow meter response by measuring the flow meter zero voltage and determining the flow scale factor. These two factors are used during measurements to calculate the actual airflow through the flow meter. An external flow-measuring device, which is traceable to a National Institute of Standards and Technology (NIST) primary standard, is used to calculate the actual airflow of the instrument. The instrument response is then adjusted until the internal flow meter is reading the actual flow rate.

3.3 Calibration Transfer Standards and Equipment:

Standard external flow meter capable of reading air flow rates in the range of 2 to 10 LPM, with a low resistance to flow, traceable to a primary standard such as NIST (e.g., BIOS DRYCAL).

3.4 Calibration Procedures:

If the instrument incorporates an internal pump, it will be necessary to remove six screws securing the rear cover plate; open the rear cover; and disconnect either the suction connection or the electrical plug to the internal pump. If the instrument incorporates an external pump, disconnect the airflow. Wait for the flow meter to settle to a zero level. After a short time, the flow meter zero voltage is measured. Reconnect or restart the airflow, and set a flow rate that is verified by a standard external flow meter.

The flow meter voltage is measured again, and an estimated airflow is calculated using the flow meter zero voltage and the previous flow scale factor. The displayed value of air flow must then be changed by the keypad arrow keys in increments of 0.1 LPM until it equals the actual flow measured by the external standard. In this way the flow scale factor is updated. The default value of the flow scale factor is set to 2.0 LPM/V.

3.5 Optical Test Strip:

Use of the Optical Test Strip is a simple means of verifying the radiometric performance of the photodetectors as part of a routine QA/QC program.

3.6 Optical Test Strip Procedure:

Refer to section 2.5.7 of this document for optical test procedure.
Six signals are measured during the Optical Test Strip procedure. These signals are denoted SEN0, REF0, SEN1, REF1, SEN2, REF2.

The following quantities are calculated using natural logarithms:

Sensing Beam Test Value = 100 * ln((SEN1-SENo)/(SEN2-SEN0))

Reference Beam Test Value = 100 * ln((REF1-REF0)/(REF2-REF0))

Optical Test Ratio = (Sensing Beam Test Value)/(Ref. Beam Test Value)

These test values should be positive numbers in the region of 30 to 50, depending on the individual Optical Test Strip itself: The Optical Test Ratio should be close to unity.

It is important to ensure that the numbers do not change appreciably over time. Changes from measurement procedure to the next should be less than 10 % of the test values, less than +/- 0.1 in the Test Ratio. If these specifications cannot be met, contact Magee Scientific for further instructions. The Aethalometer operation manual should be consulted for specific procedures regarding the Optical Test Strip.

4

ROUTINE SERVICE CHECKS

4.1 General Information:

Perform the following service checks according to the procedures documented in this section. Routine service checks may be performed more frequently, but should be performed at least at the prescribed intervals. All field data sheets should be filled out accordingly and stored in the site binder. These sheets would be used to validate data.

4.2 Daily Checks:

Review data to ensure instrument is operating properly.

4.3 Weekly Checks:

Check the system date and time on the Aethalometer. The time should be within one (1) minutes of the external data logger.

Check the sample flow on the Aethalometer display and record value on the check sheet. Ensure sampler flow as displayed is within 0.2 LPM of previous week.

Check the filter tape supply and re-tension the tape roll take-up spool if needed.

4.4 Monthly Checks:

Perform flow verification with an independent flow meter and recalibrate as necessary.

Clean inlet cyclone.

Label and replace Compact Flash solid state memory drive.

4.5 Semi-Annual Checks:

Perform Calibration, Optical Test Strip procedures and Self Test.

4.6 Annual Checks:

Clean or replace sample inlet probe line.

Remove and clean optical sampling and analysis cylinder as outlined in the instrument operation manual.

APPENDIX A

NERL MONTHLY QUALITY CONTROL MAINTENANCE CHECK SHEET

Magee Scientific Aethalometer

Location: Month/Year:

Date	Weekly Checks				Monthly Checks
	Flow Display	Correct Time/Date	Standard Flow (LPM)		Inlet Cleaned
	LPM	Yes or No	Pre-Cal	Post-Cal	Yes or No

Station Number: Operator:

Analyzer Property Number: Agency:

Operator Instructions:

1) Daily Checks: Review daily data. Verify Aethalometer status and there are no error messages.

2) Weekly Checks: Assure sampler flow on display reads to within 0.2 LPM of previous week. Verify time and date is within five (5) minutes of data logger.

3) Monthly Checks: Check flow with standard. Recalibrate as necessary. Clean inlet cyclone.

Date	Comments or Maintenance Performed

Label and replace SD state memory drive.

4) Semi-Annual Checks: Perform Calibration and Optical Test Strip procedures. Perform Self Test.
Date of last calibration: Date of last Self Test:

5) Annual Checks: Clean or replace inlet probe line. Date last cleaned:
Determine residence time: seconds (not to exceed 20 seconds).

Reviewed by: Date:

APPENDIX B

NERL Instrument Calibration Report - Aethalometer

Magee Scientific Aethalometer

Instrument Information:

Site Name:	I96 - 100 meter DW		**State**	Michigan
Site Number:	I96-001		**City**	Detroit
Property Decal #	A99765		**Calibration Date**	01/04/2011
Agency:	EPA		**Last Calibration**	09/05/2010

Flow Meter:

Flow Standard Model	BIOS - Definer 220
Flow Standard SN	116920
Flow Certification Date	10/29/2010

Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)
5.00	4.88	2.46

If % difference is > 5% proceed to Flow Meter Calibration

Flow Meter Calibration:

Previous Scale Factor	New Scale Factor

Repeat Flow Verification:

Aethalometer Flow Display	Flow Meter Average	Standard Flow (% diff)
5.00	5.01	0.20

Operator:	Matthew Landis
Comments:	

APPENDIX C

Aethalometer Data Files

The Model AE-22 Dual Channel Aethalometer will generate a daily comma delimited data file with the following 18 data columns: Instrument ID; Date; Time; BC Concentration (ng m^{-3}); UV Total (ng m^{-3}); Flow Rate (LPM); BC Sensing Zero Signal; BC Sensing Beam Signal; BC Reference Zero Signal; BC Reference Beam Signal; Bypass Fraction; BC Optical Attenuation; UV Sensing Zero Signal; UV Sensing Beam Signal; UV Reference Beam Zero Signal; UV Reference Beam Signal; Bypass Fraction; UV Optical Attenuation.

The Model AE-31 Spectrum Aethalometer will generate a daily comma delimited data file with the following 52 data columns: Date; Time; UV (370 nm) Result; Blue (470 nm) Result; Green (520 nm) Result; Yellow (590 nm) Result; Red (660 nm) Result; IR1 (880 nm) Result; IR2 (950 nm) Result; Flow (LPM); UV Sensing Zero Signal; UV Sensing Beam Signal; UV Reference Zero Signal; UV Reference Beam Signal; Bypass Fraction; UV Optical Attenuation; Blue Sensing Zero Signal; Blue Sensing Beam Signal; Blue Reference Zero Signal, Blue Reference Beam Signal; Bypass Fraction; Blue Optical Attenuation; Green Sensing Zero Signal; Green Sensing Beam Signal; Green Reference Zero Signal; Green Reference Beam Signal; Bypass Fraction; Green Optical Attenuation; Yellow Sensing Zero Signal; Yellow Sensing Beam Signal; Yellow Reference Zero Signal; Yellow Reference Beam Signal; Bypass Fraction; Yellow Optical Attenuation; Red Sensing Zero Signal; Red Sensing Beam Signal; Red Reference Zero Signal; Red Reference Beam Signal; Bypass Fraction; Red Optical Attenuation; IR1 Sensing Zero Signal; IR1 Sensing Beam Signal; IR1 Reference Zero Signal; IR1 Reference Beam Signal; Bypass Fraction; IR1 Optical Attenuation; IR2 Sensing Zero Signal; IR2 Sensing Beam Signal; IR2 Reference Zero Signal; IR2 Reference Beam Signal; Bypass Fraction; IR2 Optical Attenuation..

NOTE ☞

The time corresponds to the starting time of the measurement cycle.

NOTE ☞

The “Bypass Fraction” columns are repeated to allow for easy visual identification of the separation between the seven sets of data columns in the Spectrum Aethalometer output files.

APPENDIX D

BGI Inlet Cyclone Information

INSTRUCTIONS: Ambient Cyclones for Environmental Samplers

SCC 1.829 – 5 LPM for $PM_{2.5}$
SCC 2.654 – 10 LPM for $PM_{2.5}$
SCC 0.732 – 2 LPM for PM_1
SCC 1.197 – 5 LPM for PM_1
See below for secondary performance data.

Introduction:

The cyclones SCC 1.829 and SCC 2.654 are intended to be used with any photometer or environmental air sampler which has a ½ **inch** O.D. (12.7 mm) vertical inlet tube and requires **PM 2.5** performance at either 5 or 10 LPM in the ambient, industrial or indoor environment. The cyclones SCC 0.732 and SCC 1.197 are intended to be used with any photometer or environmental air sampler which has a **3/8 inch** O.D. (9.5 mm) vertical inlet tube and requires **PM 1** performance at either 2 or 5 LPM in the ambient, industrial or indoor environment.

At the stipulated flow rate, the units, which are based on the Sharp Cut Cyclone model[1,2] conform to EPA ideals for size selective sampling at this cut point. They are fitted with omnidirectional inlets designed to the TSP standard which requires an intake velocity equal to the sedimentation velocity of a 100 µm AED particle. The use of this type of fundamental design is intended to minimize the aspiration of large particles and aerosol water droplets. The assembled unit is generically depicted in Figure 1 and detailed part numbered views are shown in Figures 2 and 3.

Calibration:

When using the unit on a sampler, for the first time, it will be necessary to audit the flow rate calibration, of the photometers flow management system. The reason for this procedure is to make any necessary adjustments for the increased resistance of the cyclone, upon the system.

SCC 1.829	1.3 cm. of H_2O
SCC 2.654	1.4 cm. of H_2O
SCC 0.732	10 cm. of H_2O
SCC 1.197	10 cm. of H_2O

To perform this check it is necessary to remove the omnidirectional inlet in order to attach a hose, leading to the calibration device. Remove the cap securing screw (10002) and the cap (2279, 2280, 2426 or 2901). Loosen the three set (10004) screws and pull the cap support (2281, 2290 or 2425) from the inlet tube. The cyclone may now be installed on the sampler with a hose leading to the calibration device. Calibrate according to the sampler manufacturer's instructions. BGI calibrators that may be used for this purpose are the TetraCal (formally triCal) and the deltaCal with the DC-11 adapter. Once the flow verification/adjustment is complete, remove the cyclone from the sampler and reassemble the inlet shroud.

Operation:

The Complete cyclone is installed on the sampler and switched on. When using in the ambient environment, some thought must be given to operation in the presence of precipitation and fog. The inlet shroud will minimize but, not eliminate the ingress of particulate water. Therefore, if the photometer or air sampler will, in any way, be damaged by the effect of water being drawn in, it should not be operated during inclement weather.

In the event that the cyclone is inadvertently operated at the wrong flow rate or a different cut point is desired, equations are provided on our web site at (http://www.bgiusa.com/cyc/cyclone_calculator.xls) which will permit calculation of the cut point. Important points are given below:

	Q – LPM	D_{50} – µm
SCC 1.829	1.5	10
	3.3	4.0
	5.0	2.5
	11	1.0
SCC 2.654	3.0	10
	6.6	4.0
	10	2.5
	21	1.0
SCC 0.732	2.0	1.0
	0.91	2.5
	0.6	4.0
SCC 1.197	5.0	1.0
	2.27	2.5
	1.51	4.0

The cyclones will exhibit different pressure drops at different flow rates and the effect on the systems pumping capacity must be taken into account. Our web site presents the Q vs. • P curves for each cyclone (http://www.bgiusa.com/cyc/cyclone_calculator.xls)

Cleaning:

The cleaning interval for the cyclone is entirely dependent upon the environment in which it is deployed. In ambient environments it should be inspected and cleaned on a weekly basis until sufficient experience is gained, such that longer intervals can be utilized. A month between cleanings is entirely possible. In harsh industrial environments, daily attention may be required,

Remove the grit pot by unscrewing it. Dispose of its contents and clean and dry it. Remove the three screws from the top of the cyclone and remove the top. The parts can now be cleaned, thoroughly. The method of first choice is immersion in an ultrasonic cleaner with water and mild soap. Usually hand wiping with a water dampened lint free cloth will suffice. PROTRACTED SOAKING IN SOAP/CAUSTIC SOLUTIONS WILL DAMAGE THE ALUMINUM COMPONENTS!

WARNING: Because of the almost infinite variety of dusts which, may be sampled with this device, it is not possible to give specific recommendations for cleaning substances. Also, it must be noted to be careful not to re-aerosolize hazardous materials when using compressed air for cleaning. Utilize good hygiene practices at all times.

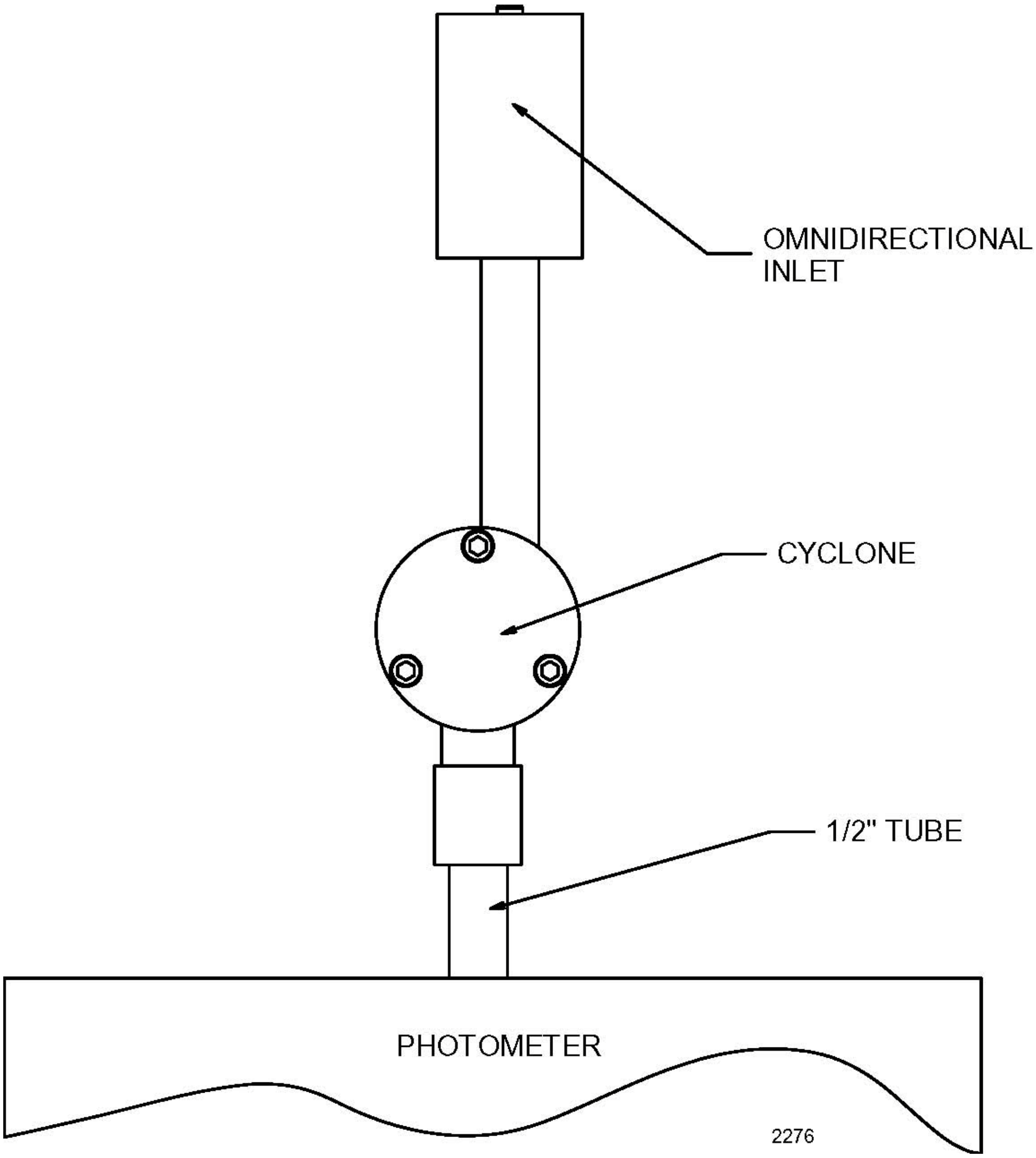


Figure 1 – View of Assembled Cyclone

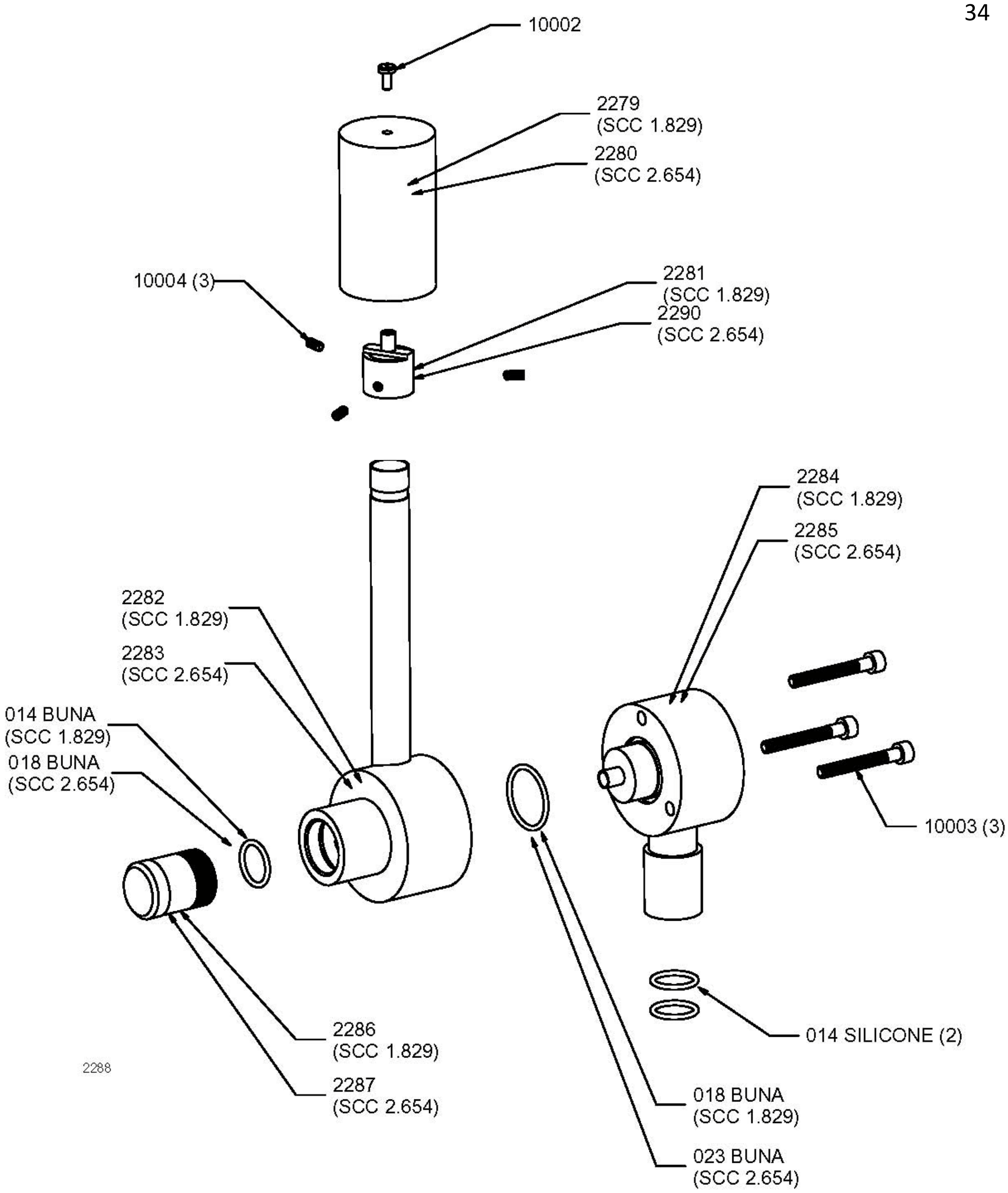


Figure 2 – Exploded View of SCC 1.829 and SCC 2.654 Cyclones

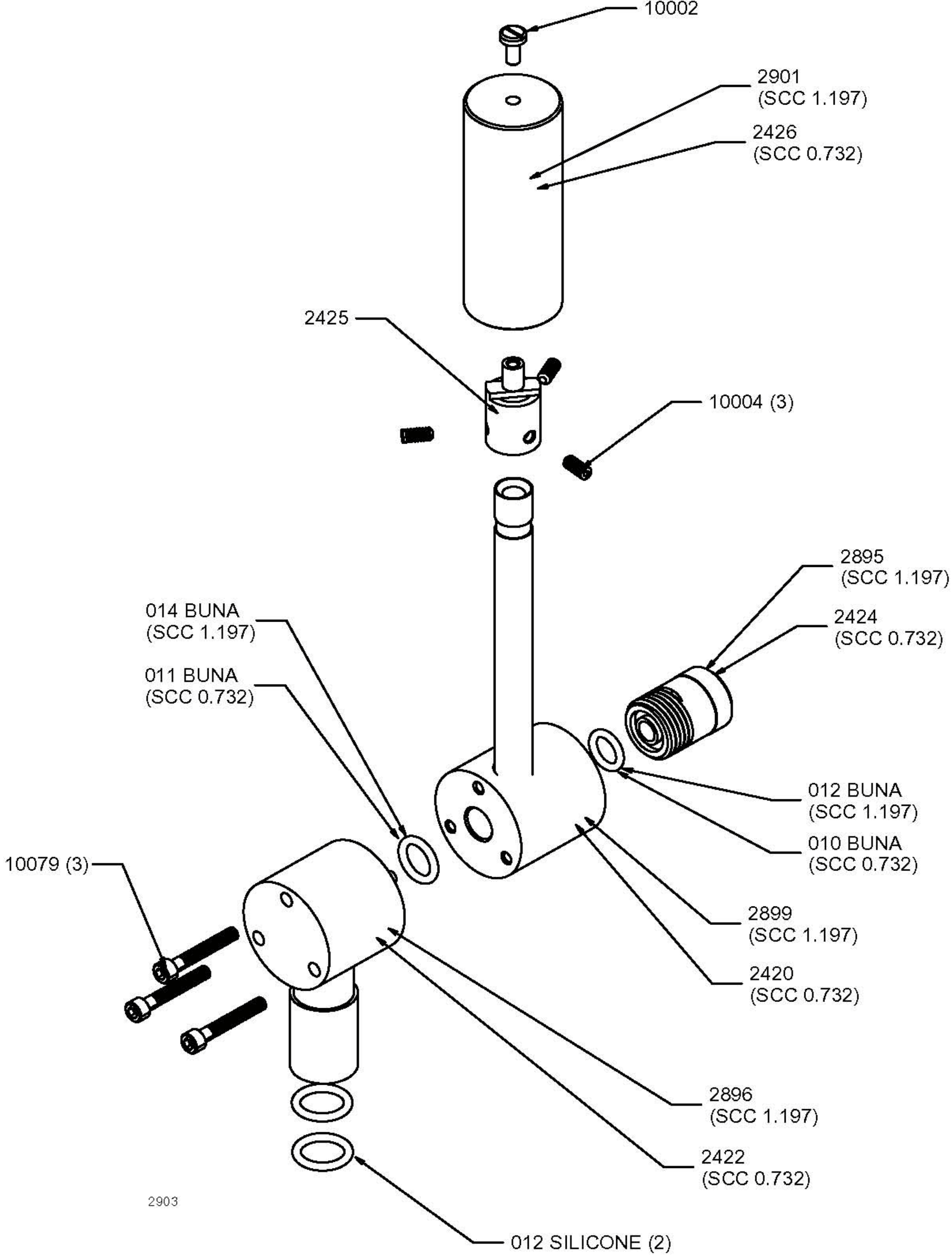


Figure 3 – Exploded View of SCC 0.732 and SCC 1.197 Cyclones

Parts List:

Part No. Qty 10002 1 10003 3 10004 3 014 Buna 1 014 Silicone 2 018 Buna 1 2279 1 2281 1 2284 1 2286 1 2291 1 2292 1 2282 1

10002 1 10003 3 10004 3 014 Silicone 2 018 Buna 1 023 Buna 1 2280 1 2285 1 2287 1 2290 1 2291 1 2293 1 2283 1

Description Cyclone #4-40 x ¼ Phillips Pan Head w/Seal SCC 1.829 #8-32 x 1 ¼ SS Allen Cap Screw SCC 1.829 #4-40 x 1/8 SS Set Screw SCC 1.829 #014 Buna O Ring SCC 1.829 #014 Silicone O Ring SCC 1.829 #018 Buna O Ring SCC 1.829 Inlet Cover SCC 1.829 Inlet Body SCC 1.829 Cyclone Top SCC 1.829 Dust Cup SCC 1.829 Exit Tube SCC 1.829 Inlet Tube SCC 1.829 Cyclone Body SCC 1.829

#4-40 x ¼ Phillips Pan Head w/Seal SCC 2.654 #8-32 x 1 ¼ SS Allen Cap Screw SCC 2.654 #4-40 x 1/8 SS Set Screw SCC 2.654 #014 Silicone O Ring SCC 2.654 #018 Buna O Ring SCC 2.654 #023 Buna O Ring SCC 2.654 Inlet Cover SCC 2.654 Cyclone Top SCC 2.654 Dust Cup SCC 2.654 Inlet Body SCC 2.654 Exit Tube SCC 2.654 Inlet Tube SCC 2.654 Cyclone Body SCC 2.654

Part No.	Qty	Description	Cyclone
10002	1	#4-40 x ¼ Phillips Pan Head w/Seal	SCC 1.197
10079	3	#4-40 x 1 1/8 SS Allen Cap Screw	SCC 1.197
10004	3	#4-40 x 1/8 SS Set Screw	SCC 1.197
012 Buna	1	#012 Buna O Ring	SCC 1.197
012 Silicone	2	#014 Silicone O Ring	SCC 1.197
014 Buna	1	#014 Buna O Ring	SCC 1.197
2901	1	Inlet Cover	SCC 1.197
2425	1	Inlet Body	SCC 1.197
2896	1	Cyclone Top	SCC 1.197
2895	1	Dust Cup	SCC 1.197
2898	1	Exit Tube	SCC 1.197
2900	1	Inlet Tube	SCC 1.197
2899	1	Cyclone Body	SCC 1.197
10002	1	#4-40 x ¼ Phillips Pan Head w/Seal	SCC 2.654
10079	3	#8-32 x 1 1/8 SS Allen Cap Screw	SCC 2.654
10004	3	#4-40 x 1/8 SS Set Screw	SCC 2.654
012 Silicone	2	#012 Silicone O Ring	SCC 2.654
011 Buna	1	#011 Buna O Ring	SCC 2.654
010 Buna	1	#011 Buna O Ring	SCC 2.654
2426	1	Inlet Cover	SCC 2.654
2422	1	Cyclone Top	SCC 2.654
2424	1	Dust Cup	SCC 2.654
2425	1	Inlet Body	SCC 2.654
2423	1	Exit Tube	SCC 2.654
2421	1	Inlet Tube	SCC 2.654
2420	1	Cyclone Body	SCC 2.654

References:

1. Kenny L.C. *et al* (2000) Development of a Sharp Cut cyclone for Ambient Aerosol Monitoring Applications, *J. Aerosol Science and Technology*, Vol.32: 338-358
2. Kenny L.C. *et al* (2000) A Direct Approach to the Design of Cyclones for Aerosol-Monitoring Applications, *J. Aerosol Science*, Vol. 31: 1407-1420.

Revision history:

Version 2.0 Added SCC 0.732 and SCC 1.197 Cyclones Sept. 2005 Version 2.1 Added pressure drops for SCC0.732 & 1.197 Dec. 2005 May,2007 Added “tetraCal”, Ch’d version to date revision.

Appendix K

Hyslop, Nicole P. and Warren H. White, “An Empirical Approach to Estimating Detection Limits Using Collocated Data,” *Environmental Science & Technology*, 2008, *42*, 5235-5240.

Environ. Sci. Technol. **2008,** *42,* 5235–5240

An Empirical Approach to Estimating Detection Limits Using Collocated Data

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Measurements of trace species generally become less certain as concentrations decrease. Data analysts need guidance on the ranges in which particular measurements are meaningful. This guidance is normally stated in the form of detection limits. The International Union for Pure and Applied Chemistry (IUPAC) has defined several parameters to characterize measurement detection limits (Currie, L. A. *Pure Appl. Chem.* 1995, *67*, 1699). The published guidelines envision an ability to prepare reference materials with concentrations close to the detection limits using the same methods as for normal samples. For multianalyte methods such as X-ray fluorescence (XRF), multiple reference materials may be required for each analyte to characterize the effects of interferences. The creation and characterization of such complex reference materials at the detection limits of modern XRF systems represents a considerable technical challenge. This paper describes an observational approach to estimating the detection limits defined by IUPAC. Our empirical approach takes advantage of collocated (duplicate) measurements that are routinely collected by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and Speciation Trends Network (STN). The analysis is successfully demonstrated by deriving detection limits at the measurement system level for six elements measured on $PM_{2.5}$ samples by XRF in both networks. The two networks' detection limits are found to be similar in terms of loading (areal density, ng cm^{-2}) on the filters as measured by the XRF instruments despite many differences in sample collection, handling, and analysis. IMPROVE detection limits are an order of magnitude lower than STN's in terms of atmospheric concentrations (ng m^{-3}), because IMPROVE uses smaller filters and higher flow rates which lead to more concentrated sample deposits.

Introduction

Detection capabilities are fundamental performance characteristics of a measurement process. They must be characterized in order to identify marginal data and to design a measurement process that meets specified goals. This paper takes advantage of existing quality assurance data to develop an empirical approach to estimate detection limits.

Properly defined detection limits address two subtly different questions (*1*). The first question often arises after the measurement is made: At what threshold of reported concentrations can we be confident that the analyte is truly present? The second question arises when evaluating a measurement program: At what minimum actual concentration can we be confident that the analyte will be measured? These questions are familiar in forensic and clinical settings where two types of errors are distinguished: false positives, often called type I errors, and false negatives or type II errors. Our confidence in detection limits is expressed in terms of the rates at which we expect to make these errors. Measurement distributions are required to characterize these error rates.

Figure 1 illustrates both types of detection errors with actual measurement distributions from the IMPROVE program. The histograms on the left in both graphs depict the distribution of measured loadings from 374 network field blanks. The histograms on the right depict the distribution of replicate XRF analyses of two lightly loaded sample filters. False positives arise from the variation of blank Si; a few blanks have loadings that are well above the mean loading of the real sample. False negatives arise from the variation measured on V sample loading, which went undetected (zero loadings) in several XRF analyses even though the mean reported loading (1.7 ng cm^{-2}) was seven times the reported minimum detection limit (MDL).

Detection limits are inherently resource-intensive to characterize because they are based on knowledge about the behavior at the outside edges of the distributions. Large amounts of data are required to characterize the edges of a distribution relative to characterizing the central tendencies of the distribution. For example, the United States Environmental Protection Agency's (USEPA) guidance for wastewater analyses requires a confidence level of 99% in the detection limit (*2*). If 100 randomly selected blanks are analyzed to establish this level, the probability is 0.99^{100} (>36%) that none of the measurements will be in the top percentile of the overall blank population. Therefore, unless the exact form of the distribution is known *a priori*, hundreds of analyses are required to characterize the 99% confidence level.

The concept of detection has been complicated over the years by inconsistent and incomplete definitions (*3–5*). Several rigorous approaches have been proposed for estimating meaningful detection limits (*2, 3, 6–10*), all relying on the availability of standard reference materials of specified compositions at arbitrarily low concentrations. These are difficult to implement for routine multielement analyses of environmental samples, where testing would have to cover a wide range of potential interferences and matrix effects. XRF analyses instead customarily report a lower limit of detection based on some multiple of the statistical uncertainty in the background counting rate (*11*). This addresses the hypothetical question of the least concentration that can be measured under ideal conditions in the absence of any interfering species. Both STN and IMPROVE report variants of this limit with their data, the STN value being identified as the "method detection limit" (*12*) and the IMPROVE value as the "minimum detectable limit" (*13*). Following the networks' practices, the common acronym MDL will be used in this paper for both parameters.

IUPAC Detection Limit Definitions. In 1995, the International Union of Pure and Applied Chemistry (IUPAC) published recommendations for "Nomenclature in evaluation of analytical methods including detection and quantification capabilities" (*1*). The publication includes definitions of detection limits to avoid type I and type II errors.

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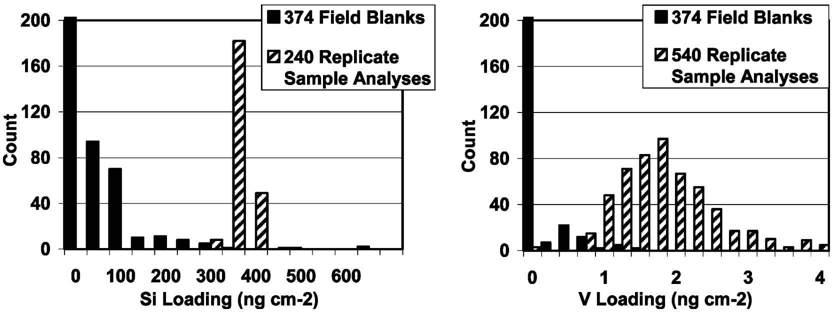

FIGURE 1. Measurement histograms of 374 field blank filter analyses and multiple analyses of a single lightly loaded sample filter for Si (left) and a different lightly loaded sample filter for V (right).

It will facilitate the discussion of the IUPAC recommendations to first introduce some terminology and notation. The value sought by a measurement will be identified with L, the mean outcome expected from many repetitions of the measurement. This convention allows for our usual ignorance of a measurand's "true" value. An individual measurement will be denoted by $\hat{L}$. The probability that A is true given that B is true will be written Pr(A|B).

To avoid type I errors a *critical limit* L_c is set such that measurements above that limit indicate the analyte is present with a high level of confidence. For a given probability α of type I error, L_c is the minimum value satisfying the inequality

$$\Pr(\hat{L} > L_c | L = 0) \leq \alpha \tag{1}$$

An error rate of $\alpha = 5\%$ is commonly considered tolerable and will be adopted here. Measurements above L_c provide confidence that the analyte is present above background, but the converse is not true; measurements below L_c do not quantify confidence that there is no analyte present. Practical examples of type I error are mistaking sample contamination or analytical noise for positive concentrations. Figure 2 shows an idealized example of blank filter variations (i.e., measured $\hat{L}$ when $L = 0$) and the location of L_c relative to that distribution. The type I error rate is represented by the area labeled "α"; in this area, the blank measurements are greater than L_c and indicate that the analyte is present (false positive). The blank distribution in Figure 2 is illustrated by a dashed line to the left of the mean because the blank mean is often zero and values below zero may not be reported; this fact must be considered if the blank distribution is modeled by a normal distribution.

To avoid type II errors, a *limit of detection* L_D is set such that atmospheric concentrations of the analyte at or above that threshold will be detected with a high level of confidence. L_D is dependent on L_c because the analyte must be measured above L_c to be considered present. For a given probability β of type II error, L_D is the minimum value satisfying the inequality

$$\Pr(\hat{L} < L_c | L = L_D) \leq \beta \tag{2}$$

A rate of $\beta = 5\%$ for type II error will be accepted in subsequent analyses. L_D can be substantially higher than L_c when other components of a sample interfere with the measurement of the target analyte. Figure 2 illustrates an ideal measurement distribution with a mean concentration of exactly L_D. The type II error rate is represented by the area labeled "β"; in this area, the measured concentrations are less than L_c and are interpreted as indicating that the analyte is not present (false negative). Note that the α and β areas are adjacent because the depicted sample mean is exactly L_D.

Materials and Methods

Data from IMPROVE and STN are used in this analysis. Both networks use a variety of analytical techniques to measure elements, ions, and carbonaceous species in airborne particulate matter with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$). This paper focuses on determining the detection limits for six elements measured by XRF analysis: Ti, Mn, Cu, As, Se, and Pb. The following subsections briefly summarize the operations and XRF measurements in these two air quality monitoring networks.

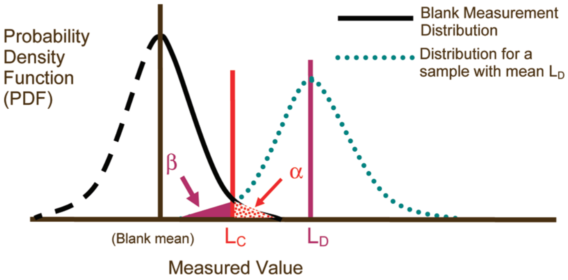

FIGURE 2. Illustration of the detection limit definitions using idealized measurement distributions of blank filters and a sample with a mean value of L_D where L_c is the critical value, α is the type I error rate, L_D is the limit of detection, and β is the type II error rate (*1*).

Sampling Techniques. IMPROVE is designed to characterize current visibility and aerosol conditions in scenic areas (primarily national parks and forests). The IMPROVE network collects $PM_{2.5}$ samples on filter media over 24-h periods every three days at approximately 170 sites across the United States (US). IMPROVE sites are primarily located in rural or remote locations. The samplers used in IMPROVE were designed by the University of California in Davis (UCD). The samplers use a flow rate of 22.8 lpm and collect XRF samples on 25 mm diameter Pall Corporation Teflo^{TM} PTFE membranes with a sample deposit area of 3.53 cm^2. More information about the network can be found on the project Web site, http://vista.cira.colostate.edu/improve/.

STN is designed to support the National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ and provides data on the chemical composition of $PM_{2.5}$. STN collects $PM_{2.5}$ samples over 24-h periods every three or six days at 54 sites across the US. STN sites are primarily located in urban and suburban areas. Three different types of samplers are certified for use in STN: MetOne SASS, Andersen RAAS, and URG MASS. The vast majority of the sites use SASS samplers. This analysis only uses samples collected with SASS samplers to limit the number of variables. The SASS samplers use a flow rate of 6.7 lpm and collect XRF samples on 47 mm diameter Whatman PTFE Teflon membranes with a sample deposit area of 11.3 cm^2. More information about STN can be obtained at http://www.epa.gov/ttn/amtic/specgen.html.

XRF Measurements. Energy-dispersive XRF analysis (EDXRF) is used to analyze both the IMPROVE and STN samples. EDXRF is a nonselective analytical technique, meaning that it does not focus on each element individually. Instead, a range of X-rays is directed at the sample filter, and all elements present in the sample with absorption bands in that range are excited and measured simultaneously. The advantage of EDXRF systems is that they provide rapid multielement results. XRF analysis is based on the principle that atoms emit X-ray photons of characteristic energies when excited by an external energy source. A silicon−lithium detector is used to count the photons and determine their energies (*11*).

The XRF instruments and peak identification software used to analyze the IMPROVE samples were designed and constructed by UCD. Twenty-four elements between Na and Pb are reported from the XRF analyses. Two separate XRF systems, one with a copper anode (Cu-XRF) for the lower atomic number elements (Na through Fe) and another with a molybdenum anode (Mo-XRF) for the higher atomic number elements (Ni through Pb), are employed to measure the elements. A major change to the UCD Cu-XRF instrument was made in the middle of the data set used for this analysis, replacing a He purge of the analysis chamber with a vacuum environment (*14*). This change provides a cleaner spectral background and improves sensitivities for the lightest elements (*15*). The energy spectra from both systems are reduced to elemental loadings by a custom software program (*16*) that integrates peak counts and applies the relevant calibration factors. If no local peak is discernible in an element's assigned energy range, a nondetect (zero loading) is reported.

STN reports concentrations of 48 elements, including the 24 elements reported by IMPROVE. Research Triangle Institute (*17*) performs the majority of the XRF analyses for STN using two ThemoNoran QuanX instruments, and Chester Laboratories analyzes a fraction of the filters using two Kevex instruments (models Delta 770 and 771). All these instruments analyze the samples in a vacuum environment. Instead of using different anodes, these instruments use a single rhodium (Rh) anode X-ray tube along with several filters to obtain different source X-ray energies to preferentially excite subgroups of elements.

Blank Filters. IMPROVE collects field blanks at random sites at a rate of approximately 1% of the routine samples. IMPROVE field blanks are loaded into cassettes, transported to the site, loaded into the sampler, left in the sampler for a week along with the sample filters, and transported back to the laboratory just like routine samples. The only difference is that ambient air is never pulled through the field blank filters. All XRF data from blank filters collected during 2004 through June 2006 were included in this analysis. This amounted to a total of 454 blank filters analyzed by the Cu-XRF instruments and 568 blank filters analyzed by the Mo-XRF instrument. IMPROVE does not publicly report blank filter data. The blank data used in this analysis were obtained directly from UCD.

STN reports data from field and trip blanks, respectively collected at rates of 10% and 3% of the routine samples (*18*). The STN field blanks are loaded into the sampler and then immediately removed and returned to their containers; they are not left in the sampler with the sample filters as the IMPROVE field blanks are. Trip and field blank data for 2004 through 2006 were used in this analysis and were downloaded from http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm on January 25, 2007.

Collocated Sampling. IMPROVE began installing collocated samplers in October 2003, and the installations continued through December 2004 (*19*). There are seven duplicate samplers spread throughout the network. Data through May 2006 were used in this analysis. Most of the IMPROVE collocated data used in this analysis were downloaded from the VIEWS Web site (http://vista.cira.colostate.edu/views/) on 29 June 2007. The Phoenix collocated data are not available from VIEWS and were obtained directly from UCD.

STN started operating collocated samplers in 2000 (*20*). SASS samplers are used at five of the six collocated sites. Data from 2003 through 2006 were used in this analysis. The STN collocated data were extracted from AQS (http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm/) in May 2007.

Analysis and Discussion

The XRF instruments measure sample loadings (or densities) in units of elemental mass per filter collection area (ng cm^{-2}). The analyses that follow present the XRF measurements directly in these terms. A final summary graph then reinterprets the results in terms of concentrations in air, accounting for the differing sample volumes and filter sizes employed by IMPROVE and STN.

Of the 24 elements measured by both IMPROVE and STN, six are included in this analysis: Ti, Mn, Cu, As, Se, and Pb. These six elements were chosen with both objective and subjective criteria. Most importantly, the element had to be measured at a wide enough range of concentrations to span its L_D at the collocated sites in both networks. Fourteen of the twenty four elements met this criterion; the remaining ten elements were either always above or below their L_D. Of the fourteen elements with adequate ranges, a few showed unusual behaviors. The lightest atomic weight elements were affected by the change from a He purge to vacuum in the IMPROVE Cu-XRF and were excluded for that reason. Of the remaining elements, six were selected to provide representative examples.

Critical Limit, L_c, Estimates. L_c, as defined by IUPAC, is the minimum significant measured value. L_c is dependent on the sample collection and preparation techniques, the sample media, the sensitivity of the instrument, and analytical interferences. The combined effect of these factors, excluding analytical interferences, can be estimated by analyzing blank filters. To avoid making assumptions about the distribution, L_c is set equal to the 95th percentile blank measurement, providing a type I error rate of $\alpha = 5\%$.

L_c's are estimated for the entire period in each network from XRF analyses of the field blanks for IMPROVE and of the trip and field blanks for STN. The STN trip and field blanks were combined because RTI reports that the distributions have shown little difference (*18*). Figure 3 shows the Ti, Mn, Cu, As, Se, and Pb loadings for the IMPROVE and STN blanks collected and analyzed from 2004 through 2006. The *y*-axis shows the percentile corresponding to the blank filter loading on the *x*-axis. Most elements are not detected (i.e., loading is reported as zero) on the majority of blank filters; the percent of nondetects for an element is indicated by the percent at which the curve begins. For example, Ti was not detected on 52% of the STN blank filters and was not detected on 58% of the IMPROVE blank filters. In all six graphs, the STN blank measurements begin at lower loadings than the IMPROVE measurements. This pattern persisted for all 24 of the XRF elements reported by both networks and is likely related to differences in the spectral processing software.

Table 1 summarizes the L_c estimates. The agreement between the L_c's in the two networks is interesting given that the filters are from different manufacturers and are treated differently in the two networks. Despite the fact that the IMPROVE blanks are exposed to the ambient environment for longer periods of time, they do not show consistently higher loadings than the STN blanks. These L_c's will be used to estimate L_D's.

Limit of Detection, L_D, Estimates. L_D is the minimum concentration at which the analyte is reliably detected and measured as significant. This requires $1-\beta$ probability that the measured value will be above L_c. Interfering elements can

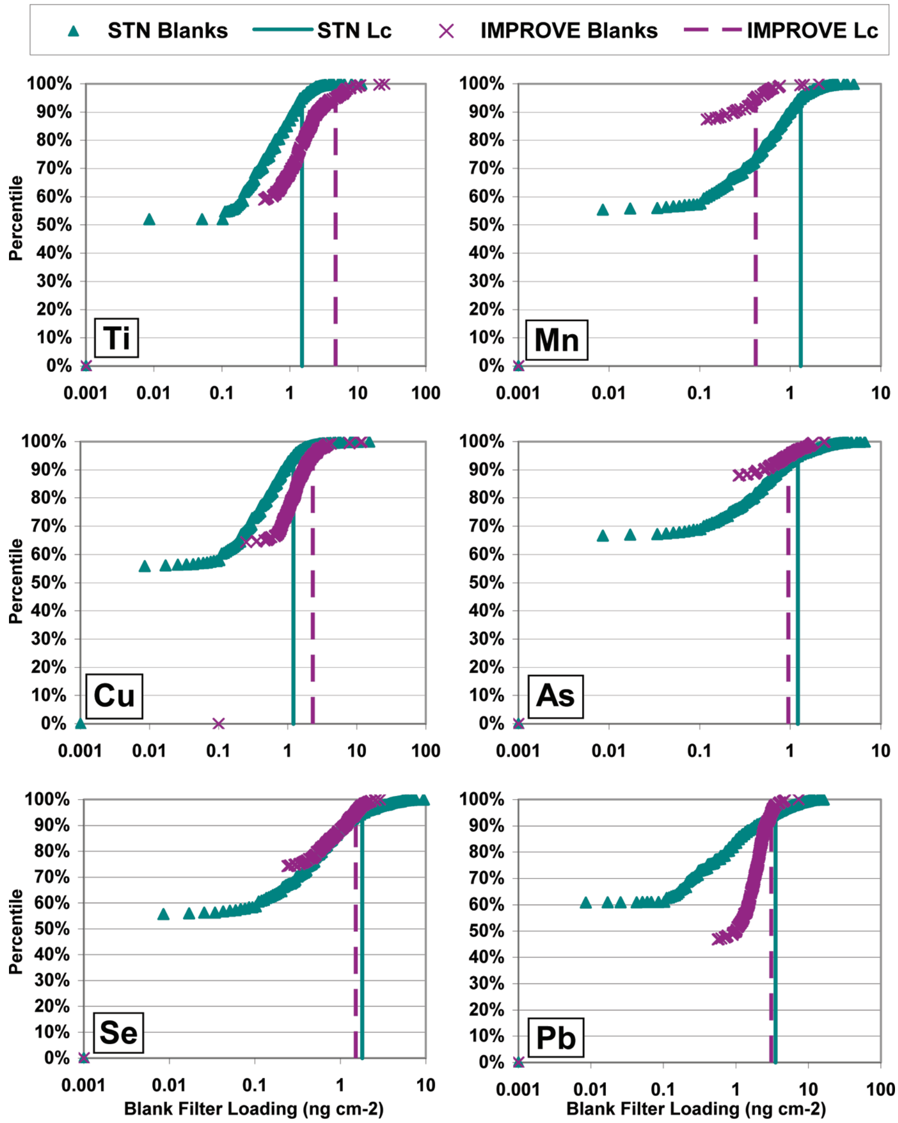

FIGURE 3. STN and IMPROVE blank filter distributions for (a) Ti, (b) Mn, (c) Cu, (d) As, (e) Se, and (f) Pb.

TABLE 1. Summary of STN and IMPROVE L_c estimates, L_D estimates, and MDLs Reported by the Respective Network

element	network	L_c 95th percentile (90−99th percentiles) (ng cm^{-2})	L_D 95% detection probability (92−97% probability) (ng cm^{-2})	reported MDL mean ± standard deviation (ng cm^{-2})
Ti	STN	1.5 (1.1−2.4)	6.0 (5.2−11)	3.7 ± 2.3
	IMPROVE	4.7 (2.6−9.5)	8.0 (7.2−100)	0.32 ± 0.05
Mn	STN	1.3 (1.0−2.2)	3.8 (3.0−4.7)	1.9 ± 0.6
	IMPROVE	0.41 (0.24−0.75)	3.0 (1.6−10)	0.29 ± 0.06
Cu	STN	1.2 (0.9−2.5)	3.4 (2.8−5.1)	1.8 ± 0.3
	IMPROVE	2.3 (1.7−3.7)	3.6 (3.4−3.9)	0.6 ± 0.2
As	STN	1.2 (0.7−2.6)	3.7 (3.4−7)	1.9 ± 1.0
	IMPROVE	0.95 (0.51−1.7)	2.6 (2.3−2.8)	0.5 ± 0.3
Se	STN	1.8 (1.1−4.4)	3.5 (2.9−5.0)	2.2 ± 0.6
	IMPROVE	1.5 (1.1−2.1)	2.1 (2.0−2.5)	0.4 ± 0.2
Pb	STN	3.5 (1.8−8.1)	6.5 (6.3−7.0)	4.3 ± 2.3
	IMPROVE	3.1 (2.6−4.2)	5.1 (4.8−6.0)	0.7 ± 0.2

obstruct detection at levels well above a target element's L_c. Collocated data offer additional information near L_D, because an element that is measured below L_c on one filter may be measured above L_c on the collocated filter. L_D can then be estimated by looking at the percent of time that the element is measured above L_c on both filters as a function of the mean concentration measured on both filters. This approach to estimating L_D incorporates uncertainties associated with sample collection and preparation techniques, sample media, sensitivity of the instrument, and analytical interferences.

The collocated data come from independent measurements by equivalent methods of the same air parcel. The expected value L and the measurement distribution $\Pr(\hat{L}|L)$ can thus be assumed to be the same for both measurements. The probability that both measurements independently yield values above L_c is then the square of the probability that a

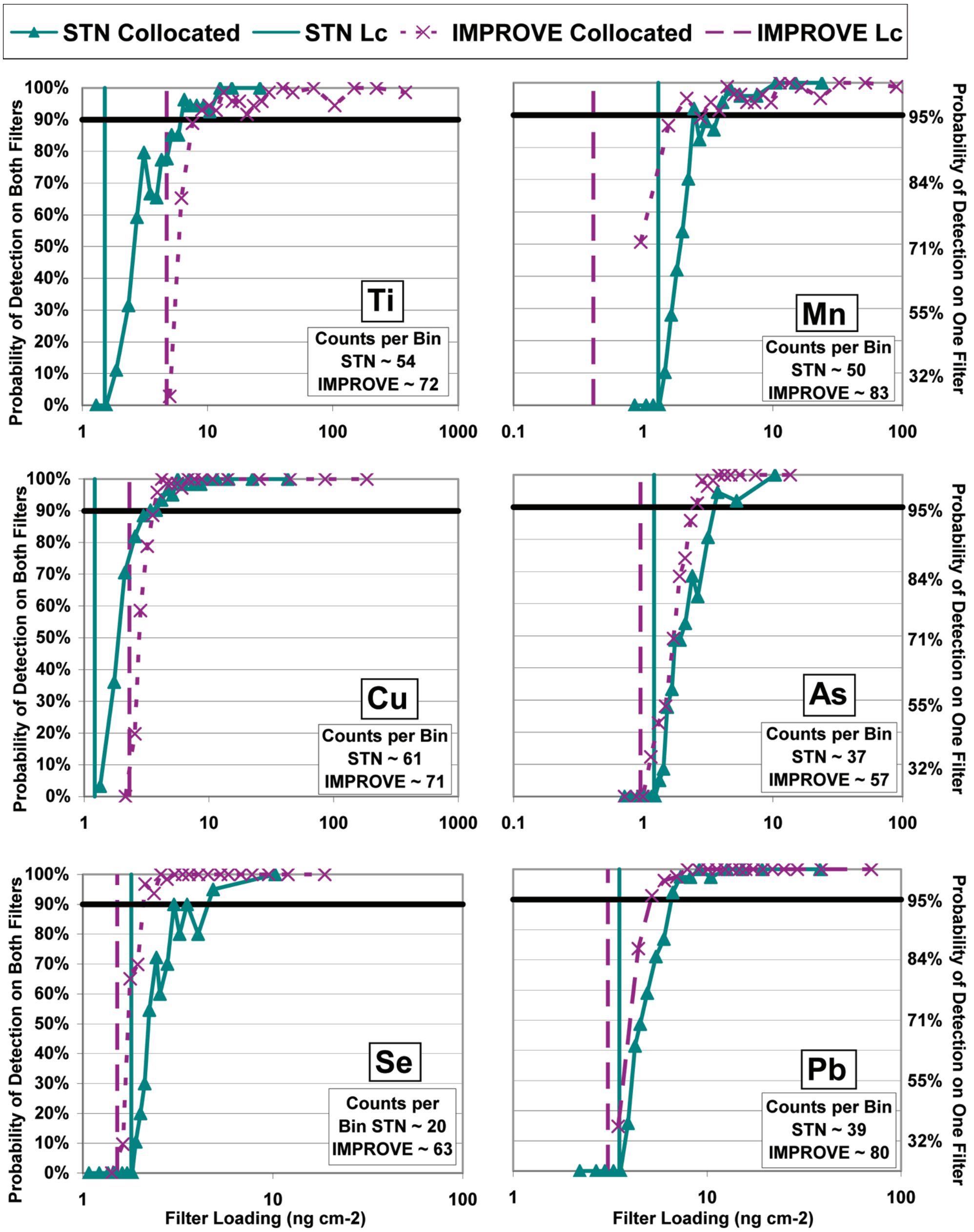

FIGURE 4. Probability of detecting the element at a loading greater than L_c in collocated filter pairs as a function of the mean reported filter loading. The L_D is set equal to the loading with a 90% probability of detecting the element above L_c on both filters which translates into a 95% probability of detecting the element above L_c on one filter.

single measurement does, $\Pr(\hat{L}_1 \geq L_c, \hat{L}_2 \geq L_c|L) = \Pr(\hat{L} \geq L_c|L)^2$. L_D can therefore be estimated as the minimum value satisfying the inequality, $\Pr(\hat{L}_1 \geq L_c, \hat{L}_2 \geq L_c|L = L_D) \geq (1 - \beta)^2$. This is the loading, estimated by the average of the reported loadings, at which both measurements report the analyte at or above L_c in at least $(1 - \beta)^2$ of the sample pairs. For $\beta = 5\%$, $(1 - \beta)^2 \cong 90\%$ is a convenient approximation.

Figure 4 shows the probability of detecting the element above L_c as a function of the mean element loading for Ti, Mn, Cu, As, Se, and Pb. The left axes show the probability of detecting the element above L_c on both filters, and the right axes show the probability of detecting the element above L_c on one filter, which is the square root of the left axis. The mean loading on the collocated filter pair is used for the x-axis. The data are grouped into equal bins according to the mean loading percentiles; each of the 20 points on the graph represents one of these bins. The counts of filter pairs included in each bin are listed in the text box in the bottom right corner of the graphs. The vertical lines indicate the L_c estimates.

The STN and IMPROVE curves shown in Figure 4 are generally similar. In some cases the curves are slightly shifted between the two networks as a result of different L_c values. The smoothness of the curve tends to improve with more data. Despite the fact that STN had more collocated data available for this analysis, IMPROVE has more collocated data above the L_c values ("counts per bin") for all the elements shown in Figure 4; this is related to the sample volume and will be addressed in more detail in the next section.

Table 1 lists L_D's estimated from the graphs in Figure 4 for a 5% type II error rate. The range in parentheses indicates the 85% to 95% probabilities of detecting the element at a loading greater than L_c on both filters, which correspond to 92% to 97% probabilities of detecting the element on one filter and 8% to 3% type II error rates.

Discusssion

Collocated data offer an opportunity to empirically estimate the limit of detection, L_D. This approach integrates the

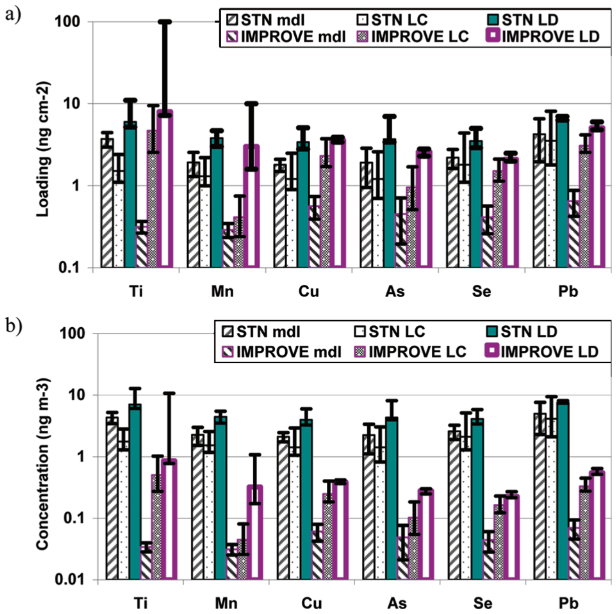

FIGURE 5. Summary of STN and IMPROVE detection limits (a) in terms of analytical measurement units (ng cm^{-2}) and (b) in terms of airborne concentrations (ng m^{-3}): reported MDL values, L_c estimates based on 95th percentile blank, and L_D estimates based on collocated data.

uncertainties from several aspects of the measurement process and thus provides the most realistic estimates of L_D. This approach can only be used for species that are measured over a range of concentrations spanning both L_c and L_D at the collocated sites.

The L_c and L_D estimates can be compared to the MDLs reported by each network. Table 1 and Figure 5a summarize the detection limits in both networks in terms of analytical measurement units, including the reported MDLs. The L_D estimates for STN and IMPROVE are very similar, suggesting that the two networks' analytical techniques are of comparable sensitivity. The idealized MDLs reported by IMPROVE are consistently lower than the empirical L_c and L_D estimates, often by an order of magnitude. The more realistic MDLs reported by STN consistently fall between the L_c and L_D estimates.

The detection limits for airborne concentrations are influenced by sample volume and sample deposit area in addition to the analytical factors considered up to this point. Our discussion has been in terms of analytical measurement units, but the data are reported and utilized in terms of airborne concentration units. Therefore, Figure 5b summarizes the detection limits in terms of airborne concentrations based on the flowrate and sample deposit areas used in the respective networks. IMPROVE uses higher flow rates and smaller deposit areas, which result in more concentrated samples by a factor of 10.9 (ratio of IMPROVE filter area per volume to STN filter area per volume). Consequently, the IMPROVE detection limits are all better than the STN detection limits in terms of ambient concentration. The lower flow rate and larger sample deposit area in STN are necessary given that most of the samplers are located in urban areas which typically experience higher $PM_{2.5}$ concentrations than IMPROVE sites. At high ambient concentrations, the IMPROVE filters are prone to clogging problems and the IMPROVE sampling configuration is thus less suitable for the STN network.

As more collocated data are obtained, the quality of these L_D estimates will improve. Also, additional collocated data from the new vacuum Cu-XRF system will allow L_D's to be estimated for the lower atomic weight elements.

Acknowledgments

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Appendix L

Quality Assurance Project Plan for the Chemical Speciation of $PM_{2.5}$ Filter Samples, Revision 6, Research Triangle Park, NC, February 2009.

RTI/0212053/01QA February 20, 2009

Quality Assurance Project Plan
Chemical Speciation of $PM_{2.5}$ Filter Samples

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

EPA Contract No. EP-D-09-010

Prepared by:

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[*] *RTI International is a trade name of Research Triangle Institute.*

A.1 QA Project Plan Identification and Approval

Quality Assurance Project Plan

Chemical Speciation of PM Filter Samples

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

Approvals:

EPA/OAQPS Project Officer Margaret Dougherty	Date
EPA/OAQPS Quality Assurance Officer Dennis Crumpler	Date
Research Triangle Institute Program Manager R. K. M. Jayanty	Date
Research Triangle Institute Quality Assurance Manager James B. Flanagan	Date

A.2 Table of Contents

List of Tables

List of Figures

A.3 Distribution

Upon finalization, controlled copies of this Quality Assurance Project Plan (QAPP) will be distributed in hard copy to the individuals listed in **Table A.3.1.** The latest version of each Standard Operating Procedure (SOP) will also be available at the laboratory where it is used. The Quality Assurance (QA) Manager will oversee control and update of the QAPP and SOPs.

Table A.3.1. QAPP Distribution List

Copy Number	Recipient Name	Position	Organization
1	M. Dougherty	Project Officer	U.S. EPA/OAQPS
2	D. Shelow	Technical Project Manager	U.S. EPA/OAQPS
3	D. Crumpler	Quality Assurance Officer	U.S. EPA/OAQPS
4	P. Schraufnagel	Delivery Order Project Officer	U.S. EPA
5	M. Copeland	Delivery Order Project Officer	U.S. EPA
6	G. Noah	Delivery Order Project Officer	U.S. EPA
7	E. Boswell	EPA Quality Assurance Laboratory Director	U.S. EPA/ Montgomery
8	R.K.M. Jayanty	Program Manager	RTI/EISD
9	D.M. Haas	Administrative Coordinator	RTI/EISD
10	J.B. Flanagan	Quality Assurance Manager	RTI/EISD
11	J.A. O'Rourke*	SHAL Technical Area Supervisor	RTI/EISD
13	L.C. Greene*	Gravimetric Mass Technical Area Supervisor	RTI/EISD
14	E.D. Hardison*	Ions Analysis Technical Area Supervisor	RTI/EISD
15	E.E. Rickman*	Data Management Technical Area Supervisor	RTI/EISD
16	W.C. Eaton*	Denuder Refurbishment Technical Area Supervisor	RTI/EISD
18	A.C. McWilliams*	Elemental Analysis Technical Area Supervisor	RTI/EISD
19	M.R. Peterson*	Carbon Analysis Technical Area Supervisor	RTI/EISD
20	F.X. Weber*	ICP-MS Technical Area Supervisor	RTI/EISD
21	R. Tropp*	DRI Quality Assurance Manager	DRI
22	P. Duda*	CHESTER LabNet Quality Assurance Manager	CHESTER LabNet

* Individuals responsible for maintaining current SOPs at laboratory stations where procedures are performed.

A.4 Project/Task Organization

This QAPP describes quality planning for contract number EP-D-09-010 with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Work on this contract in support of the PM Chemical Speciation Network (CSN) program is performed by staff from RTI International's Environmental and Industrial Sciences Division (EISD), which is a component of the Science and Engineering Group (SEG). CHESTER LabNet, a subcontractor to RTI, and RTI will perform x-ray fluorescence (XRF) analysis. Desert Research Institute (DRI), another subcontractor to RTI, will perform organic/elemental carbon (OC/EC) analysis using the same method that is used in the Interagency Monitoring of Protected Visual

Environments (IMPROVE) program: and semivolatile organic compounds (SVOC), and optical density (OD) analysis on selected filters. Sound management requires a clear understanding of the roles, functions, and assignments of each position within the project structure. **Table A.4.1** shows the responsibilities and lines of communication for each of the positions on this program.

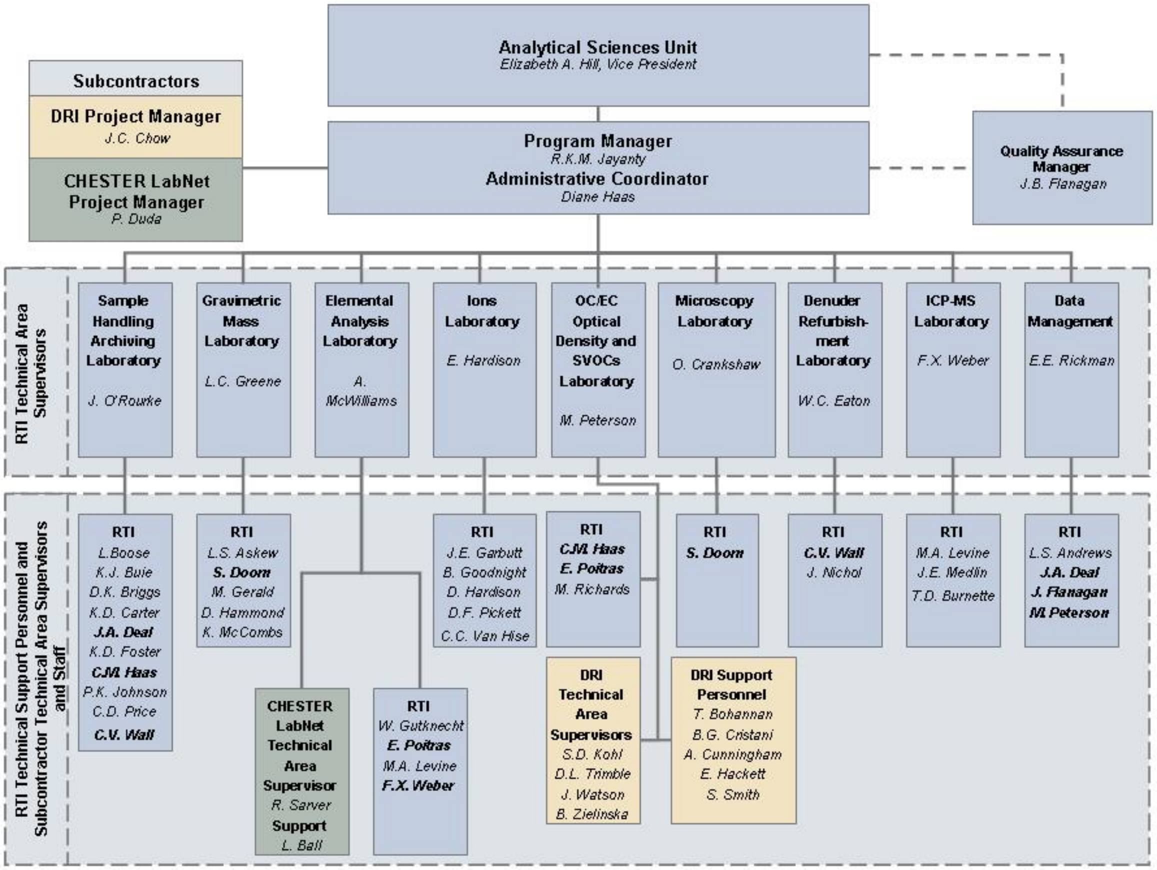

Figure A.4.1. Schematic of RTI's team members and organization for the chemical speciation of $PM_{2.5}$ filter samples.

A.4.1 Key Personnel

A.4.1.1 Program Manager and Administrative Program Coordinator

The CSN program is led by Dr. R. K. M. Jayanty, who provides overall supervision to ensure that the technical program is being performed in accordance with the EPA statement of work and according to this QAPP. As Project Manager for many projects, Dr. Jayanty has considerable supervisory experience.

- The RTI Program Manager's responsibilities include:

1. Maintaining cooperative working relationships with the EPA Project Manager, Delivery Order Project Officer (DOPO), and QA Manager in the following ways:
   - Conference calls to be held biweekly initially, or as frequently as needed
   - Meetings with EPA staff in RTP on an as-needed basis
   - Written communications and e-mails to document planning and decisions
2. Facilitating interaction among team personnel
3. Ensuring that proper techniques and procedures are followed
4. Ensuring that reporting requirements are satisfied
5. Maintaining cost and schedule control
6. Adjusting schedules to meet the needs of the client
7. Reviewing and approving deliverables submitted to the client.

Ms. Diane M. Haas is the Administrative Program Coordinator for the CSN program and is responsible for financial and other project coordination activities within RTI.

Table A.4.1. Personnel Responsibilities and Lines of Communication

Position	Responsibilities	Lines of Communication
Program Manager R. K. M. Jayanty	Accountable to corporate management for successful accomplishment of the project objectives.	Supervises project. Coordinates project activities with client and subcontractors. Reports to Division Director.
QA Manager James B. Flanagan	Responsible for monitoring all aspects of QA/QC.	Reports to Program Manager. Works closely with technical area supervisors and staff. Performs peer-to-peer coordination with subcontractor QA staff.
Technical Area Supervisors Owen Crankshaw Cary Eaton Lisa Greene Eva Hardison Andrea McWilliams James O'Rourke Max Peterson Edward Rickman Frank Weber	Responsible for maintaining technical quality, data handling and transfer, and identifying and resolving technical problems. Responsible for staff training and assessment.	Reports to Program Manager. Works closely with technical staff and QA Manager.
Technical Staff	Performs technical tasks.	Interacts with other team members. Reports to Technical Area Supervisors.

Position	Responsibilities	Lines of Communication
CHESTER LabNet Paul Duda Rick Sarver Lisa Ball Emmely Briley Jess Mace	Responsible for receiving samples from RTI, performing XRF analyses, maintaining technical quality, data handling and transfer, and identifying and resolving technical problems for staff training and assessment.	Reports to RTI Program Manager.
DRI Judy Chow, OC/EC Barbara Zielinska, SVOC B. G. Cristani D. A. Crow S. D. Kohl N. L. Pennef N. F. Robinson R. J. Tropp J. G. Watson	Responsible for receiving samples from RTI, performing SVOC and OC/EC by IMPROVE method analysis on selected filters, maintaining technical quality, data handling and transfer, and identifying and resolving technical problems for staff training and assessment.	Reports to RTI Program Manager.

A.4.1.2 QA Manager

Dr. James B. Flanagan is the RTI QA Manager for this project. As a member of the Quality Systems Program (QSP) Department, he is administratively independent from the staff performing the project work and data generation. For the purposes of this project, he will report directly to Dr. Jayanty, the Program Manager. Dr. Flanagan will monitor quality assurance/quality control (QA/QC) for the project, investigate problems and recommend corrective actions, perform periodic in-lab and data review audits, host external auditors during anticipated visits, and distribute EPA-provided Performance Evaluation (PE) samples and summarize the results of analysis of PEs.

A.4.2 Analytical Subcontractors

RTI has engaged CHESTER LabNet as a subcontractor to provide limited energy dispersive x-ray fluorescence spectroscopy (EDXRF) services for this program. RTI has also engaged DRI as a subcontractor for OC/EC analysis by the IMPROVE_A method, and SVOC analysis, and determination of OD on selected filters.

All subcontractor laboratories providing analytical services for this program must contribute to this project-specific QAPP and must provide their SOPs for EPA approval. Subcontractors will also be required to analyze EPA-provided PE samples and to undergo a technical systems audit of their facility. RTI will maintain standards and document comparability of laboratories performing the same analyses through an intercomparison program for each type of analysis. Calibration check samples from the same source will be analyzed by both laboratories. At least 5% of the field samples will be analyzed in duplicate by the participating laboratories. Intercomparison results will be summarized in annual quality assurance data reports. Subcontractors will also be required to provide input for the quarterly metadata reports and the annual quality assurance data report.

The capabilities of each subcontractor are briefly outlined in the following subsections.

A.4.2.1 CHESTER LabNet

RTI will send XRF samples to CHESTER LabNet as long as CHESTER LabNet demonstrates that it can meet the quality, sample turnaround, and cost requirements for this program. The initial throughput capacity using the CHESTER LabNet Kevex 770 XRF for Protocol #6 was 25 samples per day. To boost productivity, CHESTER LabNet purchased a second Kevex XRF, numbered 771. Samples were analyzed on both the 770 XRF and the 771 XRF to test for equivalency, and a report titled “Tests of Equivalency for Two XRF Instruments Operated by CHESTER LabNet,” which showed acceptable equivalency of the two XRFs, was submitted to EPA and approved. With these two approved instruments, CHESTER LabNet has a total capacity of approximately 50 samples per day. CHESTER LabNet has purchased a third Kevex XRF for serving its other clients, but this instrument is not used for CSN analyses because no equivalency study has been performed.

RTI and Chester obtain their calibration standards from the same supplier (Micromatter Co). Both labs analyze a multi-element standard that is prepared by Micromatter, containing Si, Ti, Fe, Se, Cd, and Pb at levels of 5-10 $\mu g/cm^2$. The multi-element standard is analyzed with each tray of samples.

A.4.2.2 Desert Research Institute

The Desert Research Institute is the nonprofit research campus of the University and Community College System of Nevada (UCCSN). The main campuses are located in Las Vegas, NV (Southern Nevada Science Park) and Reno, NV (Dandini Research Park), with subsidiary campuses in Boulder City, NV, and Steamboat Springs, CO. DRI’s environmental research programs are directed from three core divisions (Atmospheric Sciences, Earth and Ecosystem Sciences, and Hydrologic Sciences) and two interdisciplinary centers (the Center for Arid Lands Environmental Management and the Center for Watersheds and Environmental Sustainability). DRI's analytical capabilities on this program are described below.

IMPROVE_A OC/EC Analysis for URG 3000N Filter Samples

RTI has subcontracted with DRI to provide OC/EC analysis for filter samples obtained using the URG 3000N sampler following the same method as currently employed by the IMPROVE program. This analytical protocol, known as IMPROVE_A, was developed by DRI using the Atmoslytic 2001 analyzer and was placed in service on the IMPROVE program beginning January 1, 2005. The method is based on the technical requirements given in DRI’s SOP. RTI and DRI have defined data transfer formats and procedures and have developed an SOP for IMPROVE OC/EC analysis. In addition, RTI has purchased an Atmoslytic 2001 analyzer and is in the process of obtaining EPA’s approval to perform OC/EC analyses by the IMPROVE_A protocol.

The DRI instrument consists of essentially the same components as the Sunset Laboratory instrument used by RTI, although the configuration is quite different. The basic components of the system include a sample oven fitted with a laser-photodiode sensor, an oxidizer oven, a methanator, a flame ionization detector (FID), other components used to control oven temperature and gas composition and flows, and a computer workstation running software through which analysis parameters are controlled and data from the FID, photodiode sensor, and oven thermocouples are collected. All carbon volatilized from the filter is converted to CO_2 in the oxidizer, and the CO_2 is converted to methane (CH_4) in the methanator before passing into the FID, where it is measured. The laser emission shines on the quartz filter section in the oven, and some of the light is reflected or scattered back onto a photodiode located on the same side of the filter. The laser-photodiode sensor is used to monitor reflectance of laser light from the filter section during analysis.

Data generated by the IMPROVE_A method will be reported using both the Thermal Optical Transmittance (TOT) and Thermal Optical Reflectance (TOR) methods. TOT and TOR results for certain OC fractions differ, so both will be reported to EPA's Air Quality System (AQS) database under separate parameter codes.

Semivolatile Organics Compound Analysis

RTI has subcontracted with DRI to provide SVOC analysis on selected filter samples. DRI will analyze selected quartz fiber or Teflon filters and back-up sorbent traps for semi-volatile organic aerosol compounds using an extraction procedure that can accommodate multiple filters. DRI will extract semivolatile organic aerosol compounds from the filters and back up sorbent traps. The families of semi-volatile organic compounds (target analytes) to be quantitated for routine analysis are given in **Table A.6.1.** When requested, several filters may be combined for extraction to yield a more concentrated extract solution. Extracts will be analyzed for semi-volatile organic aerosol compounds using gas chromatography/mass spectroscopy (GC/MS) methodology. All analytical runs will be supported by QC analyses including replicate analyses. Sample extracts will be stored at DRI for at least 6 months and up to the life of the contract as requested by EPA.

Table A.6.1. Families of SVOCs to be Quantitated by GC/MS Methodologies

Family	Examples
n-alkanes	n-tricosane, n-tetracosane, n-pentacosane
iso-alkanes	Iso-hentracontane, iso-dotracontane
anteiso-alkanes	anteiso-triacontane, anteiso-hentriacontane
alkenoic acids	Cis-9-n-octadecenoic acid
aldehydes	nonanaldehydes
levoglucosan	levoglucosan
Polycyclic aromatic hydrocarbons	numerous
hopanes and steranes	numerous

Optical Density

RTI has subcontracted with DRI to provide OD (also known as "black carbon") analysis on selected filter samples. DRI will analyze selected Teflon filters for OD as described by Watson and Chow (1988). The densitometer used for the analysis is similar to the integrating plate method used by photographers to evaluate black-and-white negatives. Transmittance is measured before and after filter exposure, and the difference in the logarithms of the transmitted light is proportional to the absorption of the particle deposit. Transmittance is standardized using photographers' neutral-density filters that are commonly used for light attenuation in camera lenses and photographic enlargers. A high correlation between OD and IMPROVE EC has been found.

A.5 Problem Definition/Background

In 1997, the EPA promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations (µg/cubic meter of air) of particles with aerodynamic diameters less than 10 micrometers (the PM_{10} standard) and to particles with aerodynamic diameters less than 2.5 micrometers (the $PM_{2.5}$ standard). To support these standards, a 1500-site mass measurements network and a smaller PM Chemical Speciation Network (CSN) have been established. Additional gravimetric mass and speciated measurements will be required for PM_{10} and PM_{coarse} (defined as PM_{10} minus $PM_{2.5}$ for each species) under the proposed contract.

The ambient air data from the network, which measures solely the mass of particulate matter, are used for NAAQS comparison purposes in identifying areas that meet or do not meet the NAAQS criteria and in supporting designation of an area as attainment or non-attainment. The CSN consists of a set of core sites and additional non-core sites. Chemically speciated data are used to serve needs associated with development of emission mitigation approaches to reduce ambient PM concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM and its components, and evaluating potential linkages to health effects.

RTI will support the CSN by shipping ready-to-use filter packs and denuders to the field sites and by conducting gravimetric and chemical analyses of the several types of filters used in the samplers. This QAPP focuses on the QA activities associated with RTI's role in performing these analyses, as well as in validating and reporting the data.

Prior to operation of the core and additional sites, EPA ran a prototype network, informally known as the "mini-trends" network, in early 2000. This network is comprised of 13 monitoring stations at sites throughout the United States. Each site had two or more $PM_{2.5}$ chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000 to August 2000. RTI currently is supporting approximately 170 sites, including 54 core sites.

Beginning in May 2007, the CSN began operation of 57 URG 3000N samplers, which are used to obtain samples on quartz filters that are comparable to those being sampled by the IMPROVE network. The filter samples obtained using the 3000N sampler are analyzed by the IMPROVE_A method by subcontractor DRI. It is anticipated that the remaining sites in the CSN will be outfitted with URG 3000N samplers during FY09.

This revision of the CSN QAPP includes several new elements not previously encompassed by the CSN program, including PM_{10} and PM_{coarse} filter sampling and the associated gravimetric mass and chemical speciation analyses. New analytical methods incorporated in the proposed contract include inductively coupled plasma/mass spectrometry (ICP/MS) and optical density (OD) analysis of selected filters; and determination of ammonia, nitric acid, and SO_2 collected in the gas phase using denuder technology. The XRF method has been modified to omit 15 rarely seen elements.

A.6 Project/Task Description

- The CSN laboratory contract involves four broad areas:
    1. Supplying each site or monitoring agency with sample collection media (loaded filter packs and, when ordered, denuders) and field data documentation forms. RTI will ship the collection media to the sites or other designated locations specified by the monitoring agencies on a schedule specified by the DOPO.
    2. Receiving the samples from the field sites and analyzing the sample media for mass and for an array of chemical constituents including elements (by EDXRF), soluble anions and cations, and carbonaceous species. Analysis of SVOCs, OD, gas-phase ammonia, ICP/MS, and examination of particles by electron or optical microscopy will be provided for selected samples.
    3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data into the AQS data bank 60 days after initial data reports are first submitted to the DOPO and the states.
    4. Establishing and applying a comprehensive QA/QC system. RTI's Quality Management Plan, this QAPP, and associated SOPs provide the documentation for RTI's quality system.

RTI will provide all the staff, facilities, analytical instrumentation, computer hardware and software, and consumable supplies necessary to carry out tasks from these work areas and will ensure that all contractual specifications are met.

A.6.1 Schedule

The overall contract period extends from January 8, 2009 to January 7, 2014.

A.6.2 Sample Types and Quantities

Table A.6.2 shows the number of samples for the base period of the proposed contract with EPA/OAQPS.

Table A.6.2. Sample Quantities for Base Period January 8, 2009 through January 7, 2010

Line Item	Description	Each	No. Samples
0001*	$PM_{2.5}$ Gravimetric Mass	Each	100
0002*	Elemental Analysis by EDXRF	Each	100
0003*	Sulfate, Nitrate, Ammonium, Water-Soluble Sodium and Potassium	Each	100
0004	Magnesium Oxide/SC Denuder	Each	60
0005a	Organic, Elemental, and Total Carbon (CSN)	Each	5,850
0005b	Organic, Elemental, and Total Carbon (IMPROVE)	Each	13,650
0006	Suite 1-3	Each	19,500
0007*	Ammonia Analysis and Denuder Refurbishment	Each	250
0008*	Nitric Acid and SO2 analysis and Denuder Refurbishment	Each	100
0009*	Semivolatile Organic Aerosol Analysis	Each	10
0010*	Electron Microscopy Analysis	Each	50
0011*	Optical Density Analysis	Each	10
0012*	Organic Denuder Refurbishment	Each	50
0013*	Elemental Analysis by ICP/MS	Each	100

A.7 Quality Objectives and Criteria for Measurement Data

A.7.1 Data Quality Objectives Process

The data quality objectives (DQO) process is a strategic planning approach used to prepare for a data collection activity in order to achieve data of adequate quality to support decision making. The DQO process helps to ensure that the type, quantity, and quality of environmental monitoring data will be sufficient for the data's intended use, while simultaneously ensuring that resources are not wasted collecting unnecessary, redundant, or overly precise data. The formal DQO process consists of seven steps that allow an experimental design to be developed to meet decision criteria specified by stakeholders in the decision, as described in EPA QA/G-4, *Guidance for the Data Quality Objectives Process* (EPA, 1994).

A Speciation DQO Workgroup was established to develop and document DQOs for the $PM_{2.5}$ CSN. The primary DQO, detection of trends in the chemical speciation data, was defined as follows by participants in the EPA workgroup, who acted as stakeholders for the program:

> "to be able to detect a 3%–5% annual trend in the concentrations of selected chemical species with 3–5 years of data on a site-by-site basis after adjusting for seasonality, with power of 0.80." (EPA, 1999a)

Several secondary objectives for data collected at the CSN sites and other chemical speciation sites were identified, but these were not evaluated quantitatively by the workgroup. Four important secondary data uses are as follows:

- Model evaluation, verification, and/or validation
- Emission inventory
- Source attribution
- Spatial and seasonal characterization of aerosol distributions.

The desirable data quality characteristics for these secondary are significantly different from those applicable to trend assessment. For example, during the course of the original two CSN contracts, RTI worked with members of the receptor modeling community to develop uncertainty reporting methods that were consistent with the needs of models such as the Positive Matrix Factorization (PMF) model.

Because no Chemical Speciation Network (CSN) data had been collected when the DQO process was conducted, $PM_{2.5}$ chemical speciation data from the IMPROVE network were used for the assessment. Data from the one urban IMPROVE site, Washington, D.C., were used because the CSN sites are to be in urban locations. This data set was evaluated using a statistical regression model to refine the experimental design and to define goals for measurement quality.

The chemical species considered in the DQO study were limited to sulfate, nitrate, calcium, and total carbon, all of which are included in both the IMPROVE and CSN networks. The analytical methods used in the IMPROVE program are similar to those to be used in the CSN. **Table A.7.1** summarizes the species considered and compares the measurement methods employed by the two programs.

The four analytes that were studied, along with the modeled error components, are shown in **Table A.7.2.** The table illustrates that unexplained random error is much larger than the measurement error for all the analytes considered.

Table A.7.1. Analytes Included in DQO Study

Chemical Species	IMPROVE Method	STN Method	Comment
Elements (calcium)	Proton induced x-ray emission (PIXE)	Energy dispersive x-ray fluorescence (EDXRF)	Relative sensitivity of the two methods needs clarification
Ions (sulfate and nitrate)	Ion chromatography	Ion chromatography	Same method
Carbon analysis (total carbon)	IMPROVE_A method with thermal optical reflectance & thermal optical transmittance (IMPROVE_A/TOR-TOT)	Chemical Speciation Network method with thermal optical transmittance (CSN/TOT)	The CSN & IMPROVE_A methods agree well for total carbon.

Source: U.S. EPA 1998b
Note: Specific analytes shown in parentheses

A.7.2 Quality Objectives for Total Measurement Error

A key conclusion of the DQO study was that the statistical power to detect concentration trends in the chemical speciation data is relatively insensitive to measurement error, up to twice the level seen in the IMPROVE Washington, D.C., data. This is because the “uncontrollable” error components, which are primarily due to natural day-to-day variation in pollutant levels, dominate the random errors that limit the ability of the statistical analysis to detect a trend. Table A.7.2 shows the number of years' worth of data necessary to detect a 5% annual trend using the IMPROVE data set in conjunction with the regression model assuming 1-in-3-day sampling.

Table A.7.2. Years Required to Achieve 0.8 Power with 1-in-3-Day Sampling

Species	Measurement Error = IMPROVE Error × 1
Sulfate	4.1 years
Nitrate	6.3 years
Calcium	4.1 years
Total carbon	3.4 years

Source: EPA 1998.

The DQO study also concluded that with sampling every third day for 5 years, trends greater than 5% (or less than –5%) per year can be detected for sulfate, calcium, and total carbon on a single-site basis. For nitrate, however, the annual trend must exceed ±6.3% to be detected with a power of 80%. The workgroup members concluded that this was not sufficiently different from the 5% goal to require adjustment to the sampling design. Sampling daily instead of every third day provides little improvement in the ability to detect trends; however, the model showed that cutting the sampling rate to every sixth day begins to impair the ability to detect concentration trends within 5 years.

The Speciation Strategic Plan (U.S. EPA 1999b) quotes Measurement Quality Objectives (MQOs) for the overall measurement process that must be achieved in order to meet the DQO for trend detection. These MQOs, which should be interpreted as the total coefficient of variation (CV) attributable to sampling and analysis, are summarized in **Table A.7.3.** Analysis of the IMPROVE data and the model indicated that reduction of measurement errors below levels shown in this table is unlikely to result in any significant improvement in the ability to detect a trend within the parameters specified in the DQO statement. Note that there is no MQO-specified bias because trend identification is insensitive to bias as long as the bias is consistent across a given 5-year time span. In terms of completeness, the trend detection model was found to be relatively insensitive to sampling interval as long as approximately 1-in-3-day sampling is achieved. Thus, 1-in-3-day sampling was implemented at the original trends sites.

Table A.7.3. Recommended MQOs for Total Measurement Error

Analysis	MQO for Total Measurement Error (expressed as % CV)
Ions (anions and cations) by IC	10%
Total Carbon by TOR	15%
Elements by EDXRF	20%

Source: U.S. EPA 1999b

Total measurement error corresponding to the values given in Table A.7.3 may be calculated by combining the individual components of random error using QC data collected by the laboratories, or by statistical analysis of data from sites with collocated monitors. A number of statistical studies of precision, uncertainty, and data quality for the $PM_{2.5}$ CSN data have now been published (Flanagan et al., 2006), indicating that the MQOs shown in Table A.7.3 are being met for ions and total carbon, and for higher-level elements by XRF. However, many elements important as tracer species in modeling applications fail to meet the 20% criterion for total measurement error. A statistical summary of total measurement error results is presented in each annual data summary report posted on the AMTIC PM2.5 Web site.

Work during the first two CSN contracts (2000–2008) has helped to identify some additional quality issues that were incorporated into the program as they were recognized:

- Shipping/handling components of uncertainty – The laboratory component of random error is typically much smaller than the total random error observed with paired field samples. Thus, improving the precision of laboratory measurements beyond a certain point (e.g., better than ±5% for most species) does not appreciably help overall uncertainty. This is reflected in Table A.7.4, which reports the MQOs for total measurement error.
    - DQO/MQO considerations:
        - Develop DQOs and MQOs for total measurement error for all forms of PM and all chemical analyses being performed
        - Investigate procedures for assessing sample handling and transportation issues that may contribute to total measurement error in order to control and minimize this contribution to error
- Sensitivity issues – The majority of the $PM_{2.5}$ sampling for the CSN is being performed using the MetOne SASS sampler, which operates at a flow rate of 6.7 liters per minute and uses 46.2 mm filters. Compared with the IMPROVE program, this relatively low flow rate and large filter size results in a sensitivity deficit of up to 11-fold. This sensitivity difference is immaterial for gravimetric mass and species present in large amounts, such as sulfate, nitrate, and OC. Many trace elements analyzed by XRF

that are usually detectible at high levels include iron, sulfur, and silicon. Inclusion of ICP/MS, a much more sensitive method than XRF, will help identify some of the trace elements but, because of cost, ICP/MS cannot be performed on the majority of CSN filters.

  - DQO/MQO considerations:
    - Develop DQOs and MQOs for sensitivity for all species, taking into account additional data uses such as source apportionment modeling
    - Assess whether the current sampling equipment is providing sampled filters with adequate deposit density
    - Assess whether current analytical techniques (especially XRF) are providing adequate sensitivity for important data uses, and investigate any available ways to increase analytical sensitivity

- OC artifact – The OC artifact is thought to be the result of adsorbed SVOCs from the gas phase and represents a non-particulate source of carbon. With the MetOne sampler, the OC artifact can amount to 2 $\mu g/m^3$ or more, which can bias the results by 20%–30% on a typical sample. Methods for correcting for the artifact are available but can never be perfect. Because of the relatively higher flow and smaller surface area, the OC artifact for samples taken with the URG 3000N or the IMPROVE samplers are much smaller than for those taken with the MetOne SASS. Samples taken with higher flow samplers, such as the $PM_{2.5}$ FRM sampler, will have intermediate magnitude of OC artifact.
  - DQO/MQO considerations:
    - Develop DQOs and MQOs for the accuracy and precision of the OC artifact correction

- Uncertainty definitions – Work with receptor modelers during the first two CSN contracts has highlighted the importance of consistent definitions of uncertainty to be reported to the AQS database. The original formulation of uncertainty was based on the IMPROVE program's propagation of errors approach and relied on uncertainty values provided by the analytical instruments software (for XRF and OC/EC). To meet the needs of receptor modeling, it was important that the uncertainties be calculated in a consistent way across all analyzers. RTI, working with experts in the field of XRF analysis at EPA, UC Davis, and the XRF instrument vendors, developed an approach for harmonizing the uncertainties reported between different XRF instruments. In the process, we also ensured that the total uncertainties for the other CSN analytical techniques (gravimetry, ion chromatography, OC/EC) were comparable with those for XRF and were realistic, based on the collocation results.
  - DQO/MQO considerations:
    - Ensure that DQOs and MQOs are defined in terms that are compatible with the needs of data users

DQOs and MQOs for Speciated PM_{10} and PM_{coarse}

Based on our experience with the $PM_{2.5}$ samples, the process for developing appropriate DQOs and MQOs for PM_{10} should be straightforward. Collocation studies similar to those described for $PM_{2.5}$ (Flanagan et al., 2006) should provide the necessary data for developing and validating uncertainty expressions for all PM_{10} chemical species. For XRF, an additional consideration is the attenuation correction and associated uncertainty for lighter elements, which will be larger than those for $PM_{2.5}$.

Because PM_{coarse} involves subtraction of results from two different filters, there are numerous complications with attempting to calculate accuracy and precision and the associated DQOs and MQOs for PM_{coarse} concentration data. A straightforward approach to calculating precision would be to combine the individual uncertainties reported for the $PM_{2.5}$ and the PM_{10} filter, assuming additivity of variance. This may turn out to be a valid approach for simple species such as gravimetric mass; however, this approach is likely to significantly underestimate the random variability for other chemical species for a variety of reasons. Research based on early monitoring results will be necessary to develop expressions for accuracy and precision and the corresponding DQOs and MQOs applicable to PM_{coarse}.

A.7.3 Measurement Quality Objectives

There are several components of total data variability included in the model used in the original DQO study. Of these, laboratory measurement error is the component that can be controlled and/or quantified most readily through the QA/QC program, even though it is significantly smaller than either the day-to-day variability in environmental pollutant levels (U.S. EPA, 1998) or the errors associated with sampling and handling (Flanagan et al., 2006).

The original set of MQOs for laboratory analyses were developed by considering the MQOs for total error shown in **Table A.7.4** and the known capabilities of the analytical methods to be used. In this table, systematic bias and random errors are aggregated into a single figure that was called “measurement error” in the DQO study. One justification for combining bias and random errors into a single figure is that, over the long time frame of the trends detection study (5 years), bias determinations will tend to fluctuate randomly, so it is appropriate to aggregate them with measurements of random error, particularly when multiple analyzers are used to perform the same analysis, as is done in the OC/EC, XRF, and ion chromatography laboratories.

Completeness is defined as the percentage of samples successfully analyzed divided by the number successfully sampled and returned to RTI. The DQO study found that 1-in-3-day sampling was adequate to meet the objective of trend detection after 5 years. Other sites not included in the trends portion of the network operated on either 1-in-3-day or 1-in-6-day sampling schedules.

Table A.7.4. Laboratory MQOs

Measurement	Measurement Error[a]	Completeness Goal[b]
Cations and Anions	$\pm 10\%$ if $C > 10 \times MDL$[c] or $\pm MDL$ if $< 10 \times MDL$	90%
Carbon Species	$\pm 15\%$ if $C > 10 \times MDL$	90%
Filter Weight	$\pm 10\%$ if $Wt > 6\ \mu g/m^3$	90%
Elements (EDXRF)	$\pm 20\%$ if $C > 10 \times MDL$	90%
SVOCs[d]	$\pm 10\%$ if $C > 10 \times MDL$ or $\pm MDL$ if $< 10 \times MDL$	90%
SEM and Optical Microscopic Examination[d]	N/A	90%
Denuder Analysis for Ions	TBD[e]	90%
Optical Density	TBD[e]	90%
Elements (ICP/MS)	TBD[e]	90%

[a] Measurement error is an aggregate figure that combines systematic bias and random error as described above.
[b] Completeness is based on the number of filters successfully exposed and returned to RTI for the specified analysis. Historically, the CSN laboratories have achieved completeness well in excess of 95% completeness on a continuing basis.
[c] MDL = Method detection limit. Typically determined as three times the standard deviation of seven or more replicate measurements of a reagent blank, matrix blank, or low-level calibration standard; however, other methods for determining the MDL may be used, depending on the analysis.
[d] SVOC and microscopic measurements were not made during the mini-trends portions of the project.
[e] TBD = To be determined as data are gathered under the proposed effort.

A.7.4 References

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- U.S. EPA (1999a). *Particulate Matter ($PM_{2.5}$) Speciation Guidance Document (Third Draft)*, U.S. EPA, Research Triangle Park, NC. January 5, 1999.

- U.S. EPA (1999b). Strategic Plan: Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trend Sites, U.S. EPA, Research Triangle Park, NC, April 16, 1999.

- U.S. EPA (1998). *Data Quality Objectives for the Trends Component of the $PM_{2.5}$ Speciation Network*, U.S. EPA, Research Triangle Park, NC, 1999. Available on AMTIC at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf.

- U.S. EPA (1994). *Guidance for the Data Quality Objectives Process: EPA QA/G-4*, Report No. EPA/600/R-96/055, U.S. EPA, Washington, DC.

- Watson, J.G, and J.C. Chow (November 8, 1988). The 1987–1988 Metro Denver Brown Cloud Study, Vol. II: Measurements. DRI Document No. 8810 1F2. Final Report.

A.8 Special Training Requirements/Certification

It is important that the analytical results produced by each analyst meet MQOs. Attainment of MQOs will be measured by attainment of acceptable recovery and precision from analysis of identified reference samples, "blind" test samples, and previously analyzed field samples.

Analysts new to the CSN program will be required to be experienced with the basic measurement techniques relevant to the analyses that they are to perform. These techniques include the operation of an analytical microbalance, XRF, ion chromatography, GC/MS, and electron and optical microscopy. Determination of OC/EC requires an analyst who has been trained to use the apparatus and to practice good laboratory techniques to avoid contamination of filters and standards.

With experience in the basic methodology, the analyst to be trained (hereafter referred to in Section A.8 as "the analyst") will read and understand the appropriate SOP. Under the direction of an analyst experienced in the method, the analyst will follow the SOP and use the method to analyze reference samples and, if available, samples that have been analyzed previously by an experienced analyst. These samples might include split filters, filter extracts, and whole filters for XRF and electron microscopy. This effort will be continued until the analyst achieves MQOs for recovery (or bias) and precision. The Technical Area Supervisor or mentor will also audit the performance of the analyst, checking such operations as calibration, data treatment, system maintenance, and record keeping. With both acceptable analytical results and a successful systems audit, the analyst will be considered ready to perform program sample analysis. Even then, the analyst will work under the direction of a mentor until the mentor believes the analyst is considered ready to work independently. Ongoing performance will be monitored by the program QA Manager through review of analytical data, which are identified by the analyst.

RTI will require gravimetric analysts to pass a test similar to the certification test administered to analysts working on the EPA's $PM_{2.5}$ Federal Reference Method Performance Evaluation Program (FRM PEP), which RTI helped to develop under another contract.

Permanent RTI employees, including high-level personnel and Technical Area Supervisor, are eligible to attend training courses relevant to the project areas. Both in-house and extramural training opportunities are provided to RTI's employees at its expense. Most employees attend one or more such courses each year. Project staff will be encouraged to attend courses such as manufacturers' training sessions or method-specific courses that are relevant to this program.

The training and acceptable performance will be documented in the analysts' training folder. This will include a record of reading and utilizing the SOP and verification by the Technical Area Supervisor and/or mentor that acceptable method performance has been demonstrated. These folders will include records of all performance standard analyses, formal training, and in-house training and testing.

A.8.1 Current Personnel

RTI believes that no further training is required for current personnel who have performed the chemical and gravimetric analyses in the past. Analysts and other personnel will receive copies of the QAPP and the relevant SOPs necessary to perform their duties. These documents will contain the requirements applicable to the performance of each analyst's job.

Relevant experience of current analytical staff are as follows:

Gravimetric Mass Determination

- **Lisa Greene** – 21 years of relevant experience, including 10 years of experience in determination of gravimetric mass and technical and fiscal management of PM_{10} and $PM_{2.5}$ analytical work for several state air quality agencies and commercial engineering firms.
- **Stacy Doorn** – 13 years of relevant experience, including extensive experience in the preparation and analysis of samples by electron microscopy and over 10 years in the determination of gravimetric mass.
- **Maurice Gerald** – 14 years of relevant experience, including 9 years in the determination of gravimetric mass and 8 months' prior experience working in the Sample Handling and Archiving Laboratory.
- **Okisha Hammond** – 7 years of relevant laboratory experience, including 4 years months in the determination of gravimetric mass.
- **Karen McCombs** – 20 years of laboratory experience, including 9 years in the determination of gravimetric mass.

Ion Analysis

- **Eva Hardison** – 31 years of relevant experience in the technical and fiscal management of ion chromatographic analysis, including 14 years of filter analysis experience for the National Park Service. Also, extensive experience in sample handling, data reduction/analysis, and report preparation.
- **David Hardison** – 30 years of relevant analytical experience, including 9 years in performing ion analysis of filter extracts for the National Park Service, the American Lung Association, the EPA, and the California Air Resources Board.

- **Christine Van Hise** – 13 years of relevant experience in sample handling and preparation, including over 3 years of experience in air filter extraction.

- **Dorrie Pickett –** Over 20 years of relevant experience in sample handling and preparation, including over 2 years of experience in air filter extraction.

Metal Analysis

- **William Gutknecht** – (RTI) 32 years of experience in trace metal analysis, including 4 years of experience in proton-induced XRF (PIXE) and 15 years of experience in portable XRF technology. Technical and fiscal management of principally inorganic analytical programs; extensive experience in data treatment/analysis, QA/QC, and report preparation.

- **Andrea McWilliams** – (RTI) 8 years of relevant experience, including 6 years of experience operating, maintaining, and troubleshooting the ThermoNoran QuanX (EDXRF).

- **Paul Duda** – (CHESTER LabNet) 18 years of relevant experience including 7 years of experience in air filter analysis by EDXRF and 9 years of experience as a LIMS administrator.

- **Richard Sarver** – (CHESTER LabNet) 22 years of relevant analytical experience, including 15 years of experience in environmental air quality analysis, specializing in analysis of air particulates by EDXRF.

Organic/Elemental Carbon

- **Max Peterson** – More than 40 years of relevant experience in separation and analysis of VOCs and SVOCs, including 15 years in source and VOC emission measurements and 11 years of experience in OC/EC analysis and data review, validation, and reduction.

- **Melville Richards** – More than 23 years of relevant experience, including experience in ion chromatography and carbon analysis. Also, 4 years of experience in OC/EC analysis by the current EPA adaptation of NIOSH Method 5040.

OC/EC by IMPROVE Method

- **Judy Chow** – More than 30 years of experience in conducting air quality studies and performing statistical data analysis. Directs DRI's Environmental Analysis Facility (EAF). Supervises filter processing and chemical operations and develops cost-effective, yet accurate, methods for aerosol sampling and analysis. Prepared and revised sections of the U.S. EPA's air quality criteria document that pertained to chemical analysis and source emissions. Co-principal investigator on evaluation of aerosol measurement methods, sampling strategies, and databases for the U.S. EPA's guidance document on network design, continuous particulate monitoring, and aerosol measurement methods.

- **Brenda Cristani** – More than 25 years of experience in data processing involving data management, validation, and report preparation utilizing state-of-the-art software and hardware. Her laboratory experience includes gravimetric, XRF, and atomic absorption analysis of filter samples. Also loads, unloads, ships, and logs filter packs according to specified criteria. Calibrates and tests field and laboratory equipment and, when needed, visits air monitoring field sites to conduct checks on chart recorders, data loggers, gas analyzers, high-volume (hivol) and minivol samplers, and various meteorological systems. Can load and retrieve ambient monitoring data to and from EPA's AQS. Will serve as DRI's Data Technician and be responsible for processing data in formats designated by clients and/or suitable for uploading to AQS.

- **D. L. Trimble** – More than 14 years of experience in ambient air quality measurements and quality assurance. Serves as Laboratory Manager for DRI's EAF Carbon Analysis Laboratory, including data validation, reporting, and analysis of OC/EC measurements.

- **Steven Kohl** – 8 years of experience with scheduling and coordination of laboratory work. Responsibilities include the quality assurance and reporting of data generated by the inorganic analytical laboratory, as well as performing chemical analysis of aerosol samples by x-ray fluorescence. Also manages field studies, maintains a vast array of field sampling equipment, and supervises three laboratory technicians. Before coming to DRI, Mr. Kohl developed immunochemical pesticide assays for use in fiber optic biosensors for environmental monitoring applications for EPA. Mr. Kohl will serve as DRI's EAF Laboratory Coordinator.

- **Norm Robinson –** More than 25 years of experience in model development and database design and implementation. Designs and implements databases and procedures for laboratory information management system and field study and related data.

- **Richard Tropp** – More than 30 years of experience conducting air quality studies, statistical data analysis, and quality assurance. Project Manager for $PM_{2.5}$ FRM laboratory support to the states of Texas and Oklahoma. Provides coordination among laboratory groups, field personnel, contractors, and subcontractors. Provided technical support to EPA in preparing $PM_{2.5}$ regulatory proposal and promulgation packages. Outside reviewer of Section 2.12 of EPA's QA Handbook.

- **John Watson** – More than 30 years in environmental sciences, including the planning and conducting of major air pollution studies. Serves as QA Manager and senior technical advisor for the EAF. Has undertaken reviews of visibility science and regulation and is currently investigating the comparability of existing methods for carbon analysis and ways to obtain better, more useful information.

Microscopy

- **Owen Crankshaw** – 19 years of relevant experience with scanning electron microscopy (SEM) and transmission electron microscopy. Specifically experienced in analysis of PM_{10} and $PM_{2.5}$ samples, including the analysis of Teflon, polycarbonate, and fibrous glass/quartz filters.

Semivolatile Organic Compound Analysis

- **Barbara Zielinska** – More than 30 years of experience in the development, enhancement, and application of collection and analysis methods for trace atmospheric organic species present in both gaseous and particulate phases. Work includes the development of analytical methods for measuring biologically active compounds in primary and secondary particulate organic matter; atmospheric transformations of organic compounds; ozone precursors; and particle-associated and VOC emissions from various sources, including diesel- and gasoline-powered vehicles, wood combustion, and meat cooking. Currently a member of EPA's Clean Air Scientific Advisory Committee (CASAC) and a regular reviewer for the professional journals *Environmental Science & Technology* and *Atmospheric Environment*.

- **Nancy Peneff** – 6 years of experience managing analytical laboratories. Currently the Laboratory Manager of the Organic Analytical Laboratory responsible for coordinating projects, budget review, analysis protocol, and data management. Prior to coming to DRI, managed an inorganic analytical laboratory for plant, soil, and water analysis. Strong analytical background with emphasis in method development and instrument maintenance.

Sample Handling

- **James O'Rourke** – 18 years of relevant experience in sample handling and preparation. Specifically trained in handling and shipping of hazardous materials. Experience in logistics of shipping and receiving large numbers of samples through EPA radon proficiency testing program and American Industrial Hygiene Association Environmental Lead Proficiency Analytical Testing program.

- **Jessie Deal** – 7 years of relevant experience supporting the $PM_{2.5}$ chemical speciation project, which includes handling, packaging, and maintaining records for different types of air filters used for air sampling studies. Serves as assistant supervisor of the sample handling laboratory and oversees operations in Mr. O'Rourke's absence.

Database Development/Management

- **Edward Rickman** – More than 20 years of relevant experience in design and implementation of environmental and QA databases, including a database for EPA's OAQPS $PM_{2.5}$ Performance Evaluation Program and preparation of programs and queries to combine information from EPA's Envirofacts Oracle Data server with additional information from other (off-line) sources. Also experienced in statistical evaluation of test data and analytical methods.

- **Linda Andrews** – 10 years of relevant experience in data management and database design. Participated in various database development efforts, which included designing a relational database; creating necessary data entry forms, queries, reports, and functions; providing technical support or management of data; and creating relationship diagrams and data dictionaries for database documentation. Also participated in creating database programs to process data for use in risk assessment modeling, for statistical analysis, or for further use by external clients.

Quality Assurance

- **James Flanagan** – More than 20 years of relevant experience in data reduction/analysis and QA/QC. Performed numerous QA plan reviews as well as audits of field measurements and laboratory operations. Provided support for a major QA contract for EPA's Air Pollution Protection and Control Division (APPCD).

Denuder Refurbishment

- **W. Cary Eaton** – 36 years of relevant experience in measurement of ambient air pollutants. Experience with use of denuders and cascade impactors. Reviewed manufacturer's applications of candidate samplers for Federal Reference Method (FRM) designation, edited EPA's comprehensive $PM_{2.5}$ QA guidance document, and assisted with workshops for EPA's Performance Evaluation Program for the national FRM $PM_{2.5}$ network and the Speciation Trends Network.

A.8.2 Summary of Experience and Training

The qualifications of each analyst will be maintained in training folders, along with a record of courses taken, special in-house training, and results of performance audits.

Highlights of the present status of experience and training of RTI personnel include the following:

- Gravimetric mass laboratory staff have given instructional workshops and prepared SOPs to train analysts for the $PM_{2.5}$ Performance Evaluation Program.

- The RTI ion chromatographic team has performed air filter analysis for the National Park Service for the IMPROVE program. $PM_{2.5}$ ion analysis has been performed in support of EPA evaluation of $PM_{2.5}$ samplers, for the California Air Resources Board, and for a variety of other clients.

- Three staff members have trained other personnel in the use of single channel $PM_{2.5}$ samplers and in the handling and shipment of filters for the FRM PEP.

- Several members of the RTI staff have been actively involved in evaluating commercially available speciation samplers and have participated in operating them at sites across the country.

- At least three members of the staff have served as sample custodians or sample managers to send and receive filters, prepare denuder surfaces, and send and retrieve COC forms and field data sheets for each of the available speciation samplers.

- RTI XRF operator Andrea McWilliams has successfully completed training courses in the operation and application of the ThermoNoran EDXRF unit and understands the problems associated with the analysis.

- CHESTER LabNet has successfully completed training courses in the operation of XRF units, has participated in numerous audits, and understands the problems associated with the analysis.

- RTI operators of the thermo-optical analysis method for carbon species have shown good agreement with other laboratories through sample analysis intercomparisons and analysis of certified standards.

A.8.3 New Personnel

RTI will hire new personnel as necessary to meet the needs of this program. These personnel will typically be involved with routine, but important, activities such as assembling sample packages in the Sample Handling and Archiving Laboratory (SHAL), receiving exposed samples, and data entry. It is critical that errors in these areas be held to an absolute minimum; therefore, an in-house training program has been implemented to ensure that new personnel or personnel learning a different function are fully proficient in their responsibilities. We will hire new employees for the analytical laboratories in order to maintain analysis schedules.

RTI's approach to assessing and training new hires (and cross-training of existing employees) will be as follows:

- New personnel will be interviewed and their credentials carefully assessed with regard to prior experience and aptitude for the assigned task. Candidates will be interviewed by the Technical Area Supervisor and by at least one other senior-level project participant, such as the Program Manager, QA Manager, or a Technical Area Supervisor in another area.

- RTI regular and temporary personnel to be hired for sample shipping and receiving in the SHAL must have excellent work habits and must be particularly careful and attentive to detail. These individuals must also be comfortable with working under tight deadlines imposed by contractual turnaround times. References will be contacted to verify that the applicant meets these particular qualifications with regard to work habits.

- New hires in the analytical laboratories must have experience or aptitude equivalent to 2 years of experience, but individuals will be assessed on a case-by-case basis by the Technical Area Supervisor. References will be contacted to verify that the applicant has the required laboratory skills and aptitude.

- For individuals hired as permanent RTI employees, a probationary period of 6 months is provided, at which time the employee may be terminated for failing to meet required job standards; temporary employees may be dismissed at any time. The majority of training will be on-the-job and will be provided by the Technical Area Supervisor or by a staffer who has already mastered the task area. The specific SOPs will be the main training material used.

- All SOPs will be written in sufficient detail to allow a new staff member with the requisite training and experience to perform the task. Any departures from the written SOPs will require consultation with the Technical Area Supervisor for that area. Departures from SOPs necessitated by systematic or recurring problems should result in corrective actions, which may include revision of the SOP.

- All new hires will work under close supervision of the Technical Area Supervisor. The individual may work unsupervised only after the Technical Area Supervisor provides a memo to the individual’s training file. Analysts must demonstrate proficiency with analyzing standards and duplicates of previously analyzed samples. These results will be included in the training file.

A.9 Documentation and Records

Table A.9.1 provides a summary of the documentation and records that will be maintained in each functional area for this program. Management records will include monthly data reports, correspondence with the EPA Project Officer, and correspondence and orders from the DOPOs. Consolidated requests from the DOPOs will be received and examined by the Program Manager and will be circulated to all of the laboratories for advanced planning and materials procurement.

Table A.9.1. Management Records

Document Name	Brief Description	Format	Storage Location
Laboratory Request Forms	Used by the laboratories to order materials, schedule shipments, and plan future level of effort (the Program Manager checks the request and distributes it to the laboratories)	Hard copy and electronic	Program files; copies to SHAL and labs
Monthly Data Reports	Monthly data reports to EPA	Electronic	Program Office
Correspondence	Contractual correspondence with EPA and subcontractors	Hard copy	Program Office
Purchase Requisitions	Copies of all approved purchase orders	Hard copy	Program Office
Conference Call Notes	Notes made during conference calls between the Program Manager, DOPOs, and EPA/OAQPS	Hard copy	Program Office
E-mail	All of the Program Manager's project-related e-mail correspondence	Hard copy and electronic	RTI mail server/CD Program Office

A.9.1 QA/QC Records

Table A.9.2 shows the QA/QC records that will be maintained.

Table A.9.2. QA/QC Records

Document Name	Brief Description	Format	Storage Location
Training Files	Records substantiating the training and proficiency of analysts relevant to this program	Hard copy	Program Office
Audits, Questionnaires, and Results	Results of internal QA surveys and audits	Hard copy or electronic	Program Office and QA Office
QAPP	Master version of QAPP, including pending revisions	Hard copy and electronic	Program Office and QA Office
SOPs	Current version of all SOPs	Hard copy and electronic	Program Office, QA Office, and Subcontractor
Intercomparison Study Results	Results validating comparability of EDXRF or OC/EC results if done by two different laboratories	Hard copy and electronic	Program Office and QA Office
Corrective Action Response Memoranda	Results of identified QA problems and their resolutions	Hard copy	Program Office and QA Office

A.9.2 SHAL Records

Table A.9.3 shows the records that will be maintained by the SHAL.

Table A.9.3. SHAL's Records

Document Name	Brief Description	Format	Storage Location
Delivery Order	Instructions from DOPOs for sampling module needs	Hard copy and electronic	Program Office and SHAL
Chain-of-Custody Forms	Forms used to track sample module shipments between RTI and the states	Hard copy, triplicate form (copies 1 and 3 to RTI, copy 2 to field site)	SHAL
Laboratory Chain-of-Custody Forms	Forms used to track groups of aliquots between the SHAL and RTI's internal laboratories or subcontractor laboratories	Hard copy; may be computerized in the future	SHAL and laboratories
SHAL Schedule	Schedules shipments, receipt of containers, and assembly and disassembly of modules according to delivery orders supplied by DOPO	Hard copy	SHAL
Sampling Module Parts Received	Details parts received from states to be used at sampling sites	Electronic	Database
Bin Inventory Form	Lists current inventory of module parts for a specific site stored in a plastic bin in the SHAL	Electronic	Database
Module Assembly Form	Details the assembly of a module for a specific sampling event	Hard copy	SHAL
Container Contents Form	Inventory of modules sent in a shipping container to a specific sampling site	Hard copy	SHAL
Shipment Air Bill	Waybill for transport of containers to sampling site or aliquots to contractor laboratories	Hard copy	SHAL
Incoming Shipment Form	Identifies containers received at the SHAL on a particular date/time	Hard copy	SHAL
Incoming Container Content Form	Details modules received in a container returned from a sampling site	Hard copy	SHAL
Analysis List for Sampling Event	Details requested analysis for a particular sampling event	Electronic	Database
Aliquot Form	Matches filters/pieces of filters to analysis	Hard copy	SHAL
Aliquot Log-Out Form	Lists aliquots that have left the SHAL and have been sent to a laboratory for analysis	Hard copy/notebook	SHAL
Incoming Aliquot Form	Inventory of aliquots being returned to the SHAL from a laboratory	Hard copy/notebook	SHAL
Archive Bin Report	Lists aliquots in a particular storage box sent to archive	Electronic	Database

A.9.3 Analytical Laboratories' Records

RTI and subcontractor analytical laboratories will maintain the generally applicable records listed in **Table A.9.4.**

Table A.9.4. Analytical Laboratories' Records

Document Name	Brief Description	Format	Location
Internal Tracking Forms	Forms used to track sample batches between the SHAL and RTI's internal laboratories	Hard copy and electronic	Returned to the SHAL
Laboratory Notebooks	Includes the following types of notebooks and bound data sheets: ▪ Analysts' notebooks ▪ Instrument maintenance logs ▪ Reagent preparation logs ▪ Materials acceptance tests	Hard copy	Each laboratory
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Each laboratory
Control Charts or Equipment	QC information displayed in sequence to help diagnose problems with analytical instruments; usually include acceptance limits that are periodically recomputed	Hard copy or spreadsheet	Each laboratory
SOPs	Current copies of SOPs relevant to the analyses performed in a particular laboratory	Hard copy	Each laboratory
QAPP	A current copy of this QAPP; the Lab Supervisor must ensure that each analyst has access to a current copy of the QAPP	Hard copy	Each laboratory
Analytical Results Database	Results for each chemical analysis with identifying information	Spreadsheet or DBMS	—
Analytical QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks	Spreadsheet or DBMS	—

A.9.4 Gravimetric Mass Laboratory Records

The gravimetric mass laboratory will maintain records shown in **Table A.9.5.**

Table A.9.5. Gravimetric Mass Laboratory Records

Document Name	Brief Description	Format	Location
Filter Inventory and Inspection Form	Completed upon receipt of filter lots from the vendor; indicates the order to use filter boxes, date inspected, and number of filters rejected	Spreadsheet or hard copy	Gravimetric mass laboratory
Filter Conditioning Information	Indicates the dates filters were conditioned and stability test results	Hard copy	Gravimetric mass laboratory
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Gravimetric mass laboratory
Gravimetric Filter Database	Includes filter ID, initial weighing information (including date, RH, temperature, cassette number), date shipped and received, final weighing information (date, RH, temperature, and weight), and mass loading of the filter	DBMS	Project data server (SQL server DB)
Gravimetric QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks	DBMS	Project data server (SQL server DB)
Weighing Room Environmental Data	Data logger is programmed to record “grab samples” at 5-minute intervals	Data logger spool file or spreadsheet	Project data server
Internal Tracking Forms	Forms used to track sample batches between the SHAL and RTI’s internal laboratories	Hard copy (may be computerized in the future)	Copy retained by gravimetric mass laboratory; original returned to the SHAL
Laboratory Notebooks	Individual analysts’ comments; instrument maintenance logs	Hard copy	Each laboratory
Control Charts	QC information displayed in sequence to help diagnose problems with analytical instruments; usually includes acceptance limits that are periodically recomputed	Hard copy or electronic spreadsheet	Each laboratory

In addition to the records shown in Table A.9.5, the gravimetric mass laboratory will receive a monthly filter order from the SHAL to accommodate program sampling requests. The DOPOs receive the sampling requests from the various state agencies and consolidate these requests into delivery orders, which are sent to the RTI CSN program office. Information derived from the delivery orders is distributed to the SHAL, data management, and the laboratories, so that the SHAL operations, materials (e.g., filters and reagents), and laboratory personnel can be scheduled as necessary. Each month, the SHAL supervisor will calculate the projected number of Teflon filters that will be needed to meet that month’s sampling and field blank requirements. This projection will be sent to the gravimetric mass laboratory via e-mail so that a sufficient number of filters can be ordered in advance.

A.9.5 XRF Laboratory Records

The XRF laboratory will maintain records shown in **Table A.9.6.**

Table A.9.6. XRF Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	XRF Laboratory
"Method" Database	Includes x-ray generation information and other information required to automate the XRF analyses	Computer files	XRF Laboratory
QC Records	Results of calibrations, SRM recoveries, and replicate precision	Computer files	XRF Laboratory
Raw Data Records	Results of PM analyses	Computer files, database files	Instrument PC; database
Laboratory Notebooks	Individual analysts' comments; instrument maintenance logs	Hard copy	XRF Laboratory
Instrument User's Manual	Information for setting up, using, and troubleshooting the XRF instrument	Hard copy	XRF Laboratory or analyst's office

A.9.6 IC Laboratory Records

The IC laboratory will maintain records shown in **Table A.9.7.**

Table A.9.7. IC Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	IC Laboratory
"Method" Database	Contains the information required to automate the analyses	Computer files	IC Laboratory
QC Records	Results of calibrations, SRM recoveries, and replicate precision	Computer files	IC Laboratory and database
Raw Data Records	Results of PM analyses and analysis of selected denuder extracts	Computer files, spreadsheets, database files	Instrument PC, analyst's PC, database computer
Laboratory Notebooks	Individual analysts' comments, instrument maintenance logs	Hard copy	IC Laboratory
Instrument User's Manual	Information for setting up, using, and troubleshooting the IC instruments	Hard copy	IC Laboratory

A.9.7 OC/EC Laboratory Records

The OC/EC laboratory will maintain records shown in **Table A.9.8.**

Table A.9.8. OC/EC Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates for gases and other chemicals used for calibration	Hard copy	OC/EC Laboratory
“Method” Parameter Files	Contains the information required to run the analysis	Computer files	OC/EC Laboratory computers
QC Records	Results of instrument blanks, calibrations, standard recoveries, and replicate precision	Computer files and hard copy	OC/EC Laboratory, supervisor’s office
Raw Data Records	Results of PM analyses (including supporting data that are not uploaded to the database)	Spreadsheets, hard copy, database	Analyst’s PC, supervisor’s office, database computer
Laboratory Notebooks	Individual analysts’ comments; instrument maintenance logs	Hard copy	OC/EC Laboratory
Instrument User’s Manual and/or Manufacturer’s Instructions	Information for setting up, using, and troubleshooting the OC/EC instruments	Hard copy	OC/EC Laboratory

A.9.8 Denuder Refurbishment Laboratory Records

The Denuder Refurbishments Laboratory will maintain records shown in **Table A.9.9.**

Table A.9.9. Denuder Refurbishment Laboratory Records

Document Name	Brief Description	Format	Location
Personnel Training Records	Date and description of training or inspection	Hard copy	Denuder Lab
Denuder Refurbishment Information	Date, number, and type of denuders refurbished and technician name	Hard-copy, notebook	Denuder Lab
SOP	SOPs for coating various types of denuders	Hard-copy, loose-leaf binder	Denuder Lab
Reagent Purity Records	Information for denuders to be quantitatively analyzed	Hard-copy, notebook	Denuder Lab

B.1 Sampling Process Design (Experimental Design)

The experimental design, including design of the sampling network and sampling locations, is outside the program scope and is not addressed in this QAPP. Refer to EPA planning documents available on the U.S. EPA's AMTIC Web site.

B.2 Sampling Methods Requirements

Actual collection of samples is outside the scope of this laboratory QAPP and is not addressed herein. The CSN Field QAPP prepared for OAQPS contains a full description of sample acquisition, including sample COC, which meshes closely with operations of the SHAL. The Field QAPP is available on the AMTIC Web site.

B.3 Sample Handling and Custody Requirements

> **Note:** This section relies heavily on design of RTI's sample handling system, including the SHAL. Please refer to the applicable SOP for more details.

This section describes the sample handling and custody process for all sampling modules to be provided to the sites, as well as sample tracking internally and between RTI and its subcontractors. In this document, the term "sampling module" is used in a generic sense to denote the sampling media and holder associated with a specific sampled air stream in a single speciation sampler. A sampling module is the smallest unit (in one or several pieces) shipped back and forth between RTI and a sampling site.

A sampling module includes denuders (in addition to filter media) and transport hardware if either (or both) is required. All sampling modules and associated sample media will be tracked individually in the database management system (DBMS). An overview of the entire sample handling system is shown in **Figure B.3.1.**

B.3.1 Sample Handling Delivery Order Process

RTI prepares and ships appropriate sampling media (including the required filters) to each state (or sampling site within the state) as needed to meet the sampling schedule for each site covered in the consolidated request received from the DOPOs. The PM checks the consolidated request and distributes it to the SHAL and other laboratories for planning purposes. Based on the schedule defined by all the consolidated requests, RTI schedules and sends modules to the addresses indicated for the state monitoring agencies. Details of the information contained in the consolidated requests, and RTI's interactions with the state air monitoring agencies, will be defined in collaboration with EPA. State personnel collect the required samples and return them to RTI, which logs the samples into its tracking system, performs all required speciation analyses, enters and validates the data, enters data meeting Level 1 criteria into the AQS, forwards all analysis data to the states that requested the analyses, and reports all activities to the DOPOs. Provisions also are made for archiving samples and for resolving technical quality issues and contract dispute issues.

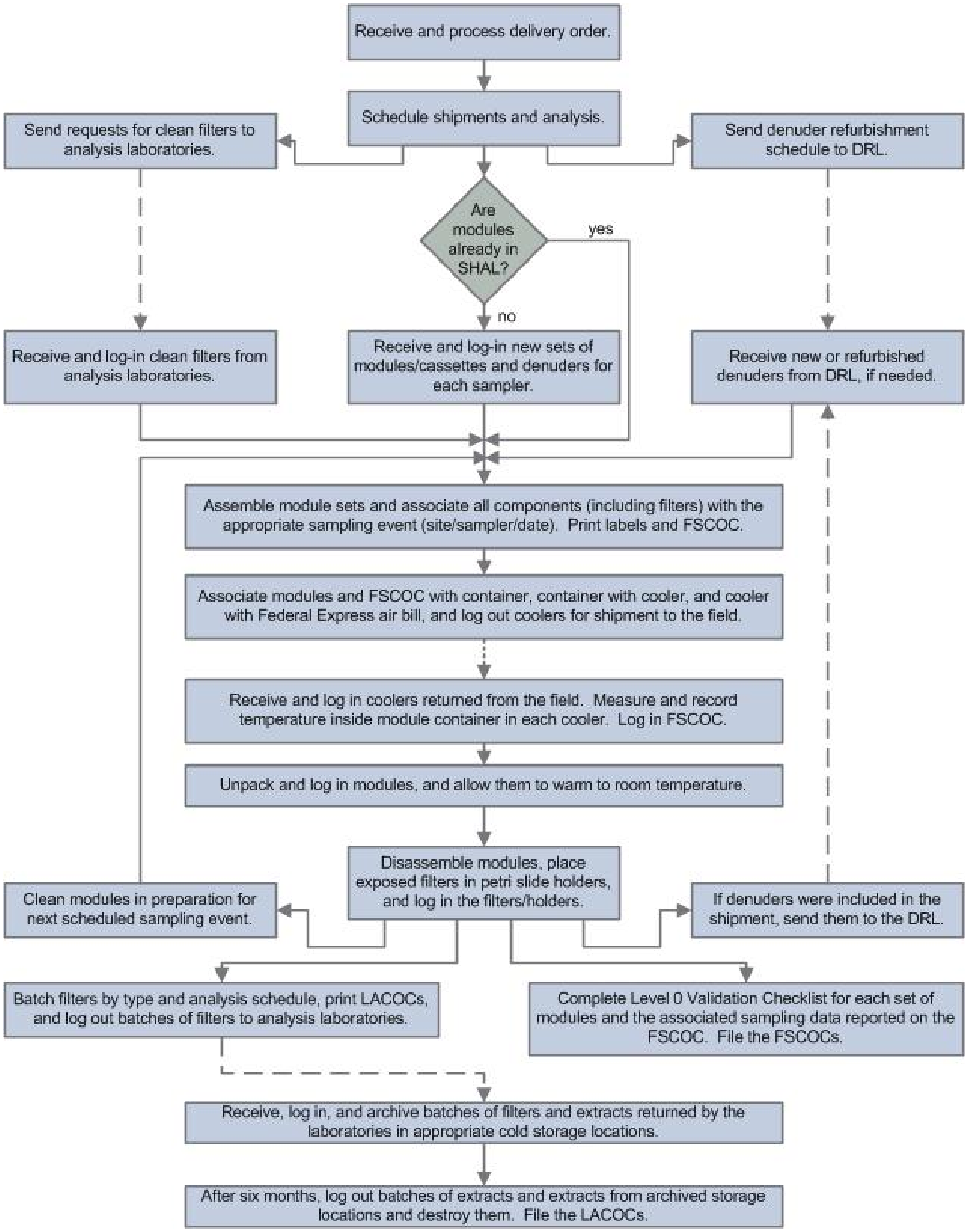


Figure B.3.1. Overview of sample handling and custody system.

The following subsections describe the processes associated with filter and sample handling and archiving, the physical and chemical analyses required for each filter in each type of speciation sampler, and the data handling and analyses required to obtain concentration data of known quality. The sample handling and tracking process is described in more detail in the SHAL SOP.

B.3.2 Chain of Custody

Note: An example of the field COC information sheet is shown in the Field QAPP available on the AMTIC Web site.

RTI will provide COC documentation with all sample shipments to track and ensure that samples are collected, transferred, stored, and analyzed by authorized personnel; sample integrity is maintained during all phases of sample handling and analysis; and an accurate record is maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data to the DOPOs and the state clients.

The COC documentation that accompanies the sampling modules to and from the field will include a three-part carbonless form for sending and receiving samples from the field sites. The COC forms are computer generated so that they are customized for each type of sampler. All media (filters and other types of sampling media, if any) will be listed on the COC form for each sampling event. The COC form will include areas in which the field operators can enter critical data, including the total sample volume for each filter channel.

Internal custody forms will also be used to distribute individual sets of filters to the various laboratories for analysis. These forms are computer generated based on information already entered into the database, such as the assigned aliquot numbers.

B.3.3 Processing System for PM Chemical Speciation Modules

RTI has designated 10 laboratories that are involved in the program, and these are described below:

1. **Sample Handling and Archiving Laboratory (SHAL)**. Personnel in the SHAL will be responsible for assembly of components (including clean filters and refurbished denuders) into sampling modules, shipment of sampling media and modules to the states (or sampling sites within the states), receipt of samples from the states, disassembly and cleaning of sampling modules, distribution of filters (and other sampling media, if applicable) to the individual laboratories for analysis, and final archiving of filters and filter extracts for 6 months. COC and field sampling data sheets are generated by SHAL personnel, who will also log out and log in all filter samples (going to the field or laboratories and returning) and all archived filters and extracts.

2. **Denuder Refurbishment Laboratory (DRL)**. Personnel in the DRL are responsible for refurbishment of all denuders and extraction of denuders employed to collect and quantify acidic and basic gases. The DRL must have a hood and sink for work with volatile solvents and for cleaning spent denuders. The DRL will coordinate with the SHAL to prepare and track denuders as they are needed.

3. **Gravimetric Mass Laboratory (GML)**. Personnel in the GML are responsible for all activities associated with $PM_{2.5}$ gravimetric mass determinations on Teflon filters.

4. **Elemental Analysis Laboratory (EAL)**. Personnel in the EAL are responsible for all elemental (selected elements, sodium through lead, by atomic number) analyses. RTI will analyze the majority of the samples. CHESTER LabNet will assist with elemental analysis support for the contract.

5. **Cations/Anions Laboratory (CAL)**. Personnel in the CAL are responsible for all ion analyses. This will include both anions (sulfate and nitrate) and cations (ammonium, sodium, and potassium) on sample filters and denuder extracts. They are also responsible for acceptance testing and cleaning, if necessary, of nylon and other filters used for collection and measurement of target anions and cations.

6. **RTI Organic Carbon/Elemental Carbon Laboratory (OC/ECL)**. Personnel in the OC/ECL are responsible for total, elemental, organic, and fractions analyses on quartz filters. They will also be responsible for acceptance testing and cleaning, if necessary, of quartz filters.

7. **DRI OC/EC Laboratory**. Personnel in DRI's OC/EC laboratory are responsible for carbon analysis by the IMPROVE method.

8. **Semivolatile Organics Laboratory (SVOL).** Personnel in the DRI SVOL are responsible for measuring individual SVOCs extracted from $PM_{2.5}$ collected on quartz filters and from backup sorbent traps.

9. **Microscopy Laboratory (ML)**. Personnel in the ML are responsible for all optical and electron microscopy (with or without elemental particle analysis).

10. **ICP/MS Laboratory.** Personnel in RTI's ICP/MS laboratory will analyze selected filter extracts as directed.

Figure B.3.2 shows a flow diagram for filter processing by filter type. Teflon filters are used for determination of gravimetric mass and element (sodium through lead) concentrations; some Teflon filters may be analyzed for ions. Quartz filters are used for determination of total, organic, elemental, and fractional concentrations. Nylon filters are used for determination of cations (ammonium, sodium, and potassium) and anions (sulfate and nitrate).

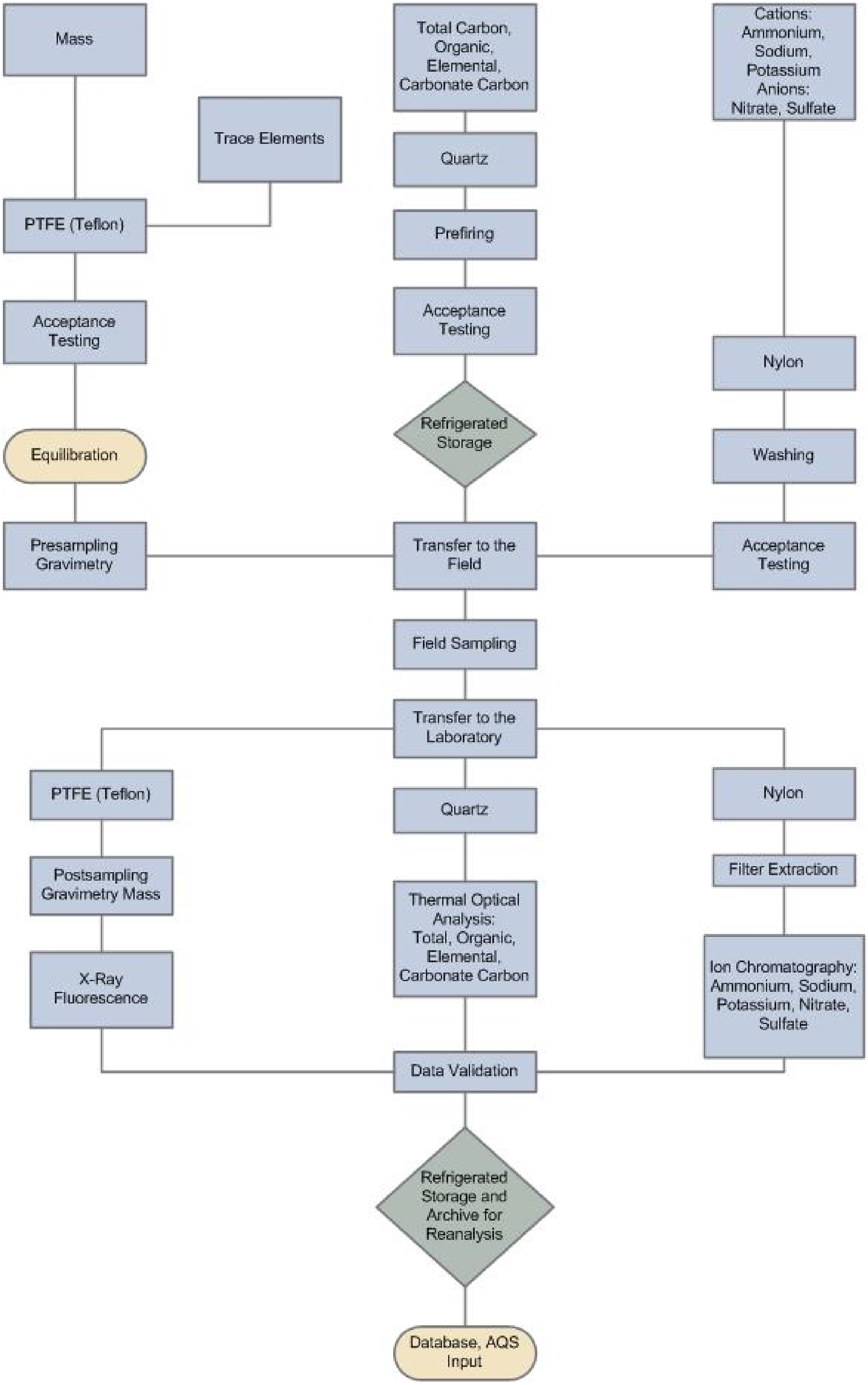


Figure B.3.2. Diagram of RTI filter processing and analysis activities by filter type (arrangement may vary by sampler model).

Figure B.3.3 shows the anticipated movement of filters and extracts through RTI laboratories described above. The focal point for shipping and receiving sampling media and for archiving analyzed filters and extracts is the SHAL. The other laboratories, except for the DRL, are responsible for cleaning and acceptance testing of new filters and for analyses of samples collected on those filters. The main items moving between the various laboratories are shown in the figure, but other pathways are possible.

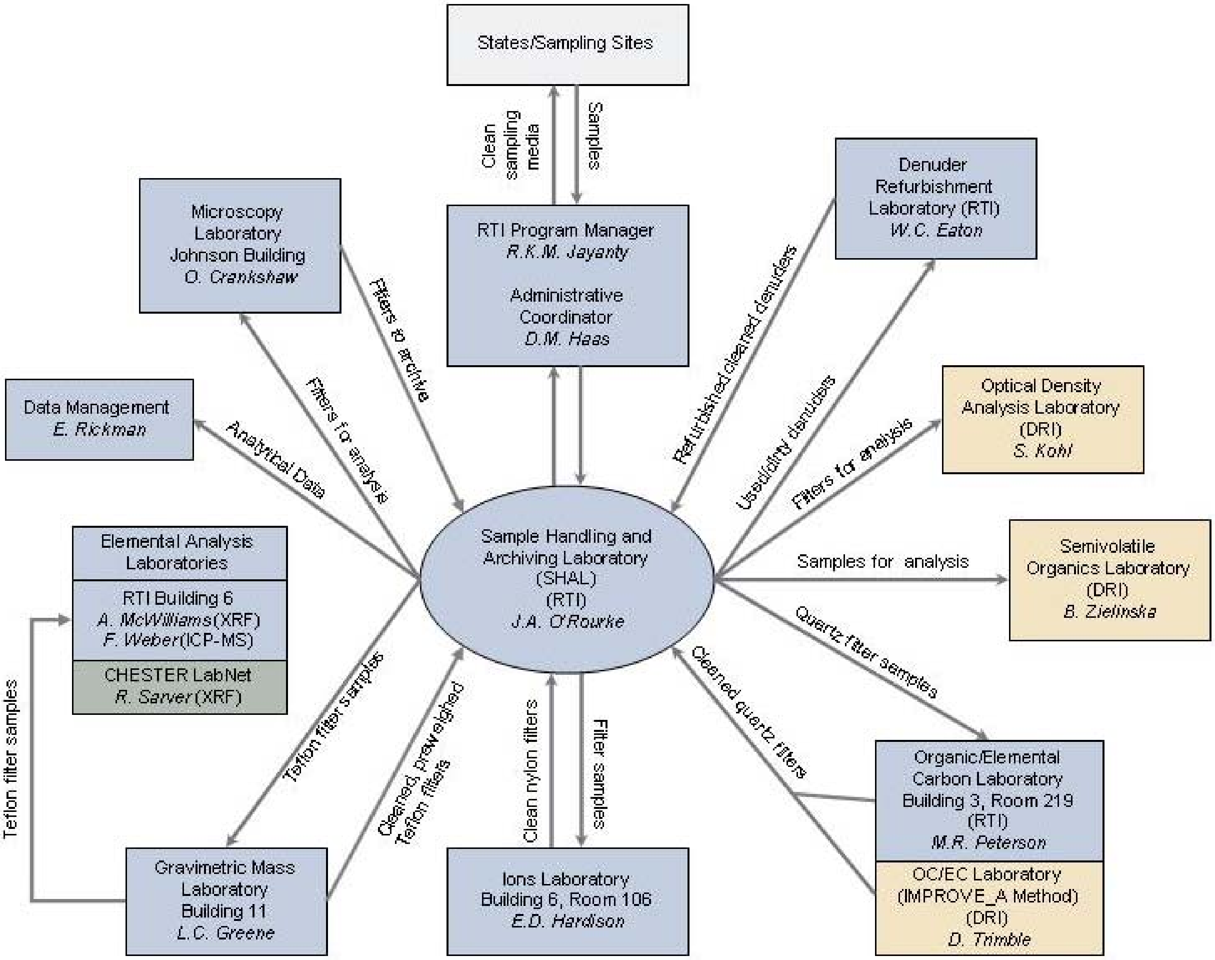


Figure B.3.3. Movement of filters and extracts through RTI and subcontractor laboratories.

It should be noted that following final weighing in the gravimetric mass laboratory, custody of the exposed Teflon filters is transferred to Ms. Andrea McWilliams (Bldg. 7, Room 219). She will distribute filters to two laboratories, CHESTER LabNet and RTI. Analyzed filters are returned to Ms. McWilliams to either archive or send the filters to the CAL.

Table B.3.1 shows the sampling media used in each type of $PM_{2.5}$ speciation sampler, the species collected on each type of filter, and the RTI laboratory (or laboratories) that will measure those species on that filter. All of the sampler models use at least one each of the three types of filters (Teflon, nylon, and quartz) used in the $PM_{2.5}$ speciation program.

B.3.3.1 Assembly of Sampling Modules

Sampling modules sent to the field must be clean, properly assembled with clean and unflawed filters and denuders, and shipped in a timely manner. Personnel in the SHAL will clean and inspect all hardware associated with sampling modules and visually inspect each filter (for a pinhole or crease, evidence of chaffing or flaking, discoloration, or any other defect) and each denuder as each module is assembled. Any items that appear flawed are rejected. SHAL personnel will carefully pack all modules for a given sampler at a given location in the same cooler for shipment to the appropriate destination. All modules are assembled according to the manufacturer’s instructions and with the sampling components requested by the state agencies and approved by the DOPOs. These operations are fully described in SOPs specific to each model of sampler.

B.3.3.2 Shipping to and from the Field

Filter cassettes, sampling modules, and any additional required components are shipped in specially designed insulated shipping containers to each sampling site or other location designated by the states through the DOPOs. Federal Express delivery is used for most shipments.

Scheduling of shipping dates to and from the state agencies is a key part of the SHAL’s operation. RTI will continue to prepare shipping schedules for all sampling locations, and the shipping schedules will be distributed through the DOPOs.

Sufficient commercially available, leak-proof, “blue-ice” gel packs are added to each cooler to maintain a transit temperature at or below 4°C. Each state agency is responsible for freezing the ice packs and packaging the shipment so that it maintains a temperature at or below 4°C. Shipments are returned to RTI overnight by Federal Express as described above. The temperature of each shipment is determined upon delivery at the SHAL using a temperature probe with digital readout. Temperature upon receipt is recorded on a Level 0 validation form.

Table B.3.1. Sampler Component and Laboratory Speciation Analysis Matrix

Sampler			**Mass**	**Elements XRF, ICP-MS**	**Anions[++] SO_4^{-2}, NO_3^-**	**Cations,[++] NH_4^+, Na^+, K^+**	**TC, OC, EC**	**Optical Density**	**SVOC**	**Micros-copy**	**HNO_3, and SO_2 (gas)[++]**	**NH_3 (gas)[++]**
URG 3000N Sequential carbon aerosol sampler	Module 1	Quartz filter					●		●			
SASS	Channel 1	Teflon filter	●	●				●		●		
	Channel 2	Nylon filter with MgO coated denuder			●	●						
	Channel 3	Quartz filter					●		●			
FRM	Each channel[+]	Teflon filter	●	●				●		●		
		Nylon filter with MgO coated denuder			●	●						
		Quartz filter					●		●			
All types	Analytical denuders	Phosphorous or citric acid coated										●
		MgO or Na_2CO_3 coated									●	
PMCOARSE	To be determined											

EC = elemental carbon, HNO_3 = nitric acid, ICP-MS = inductively coupled mass spectrometry, K^+ = potassium ion, Na^+ = sodium ion, NH_3 = ammonia, NH_4^+ = ammonium ion, NO_3^- = nitrate ion, Na_2CO_3 = sodium carbonate, OC = organic carbon, SO_2 = sulfur dioxide, SO_4^{-2} = sulfate ion, SVOC = semi-volatile organic compound, TC = total carbon, XRF = X-ray fluorescence

[+] Three FRM samplers can be used in parallel as three separate channels to collect $PM_{2.5}$ samples for speciation analyses.

[++] Sorbed gases NH_3, HNO_3, and SO_2 are measured by using ion chromatography as NH_4^+, NO_3^-, and SO_4^{-2}, respectively.

B.3.3.3 Disassembly of Sampling Modules

Upon their return to RTI, sampling modules are logged into the database and disassembled by SHAL personnel. Each filter is sealed in a new, clean, labeled petri dish and sent to the appropriate laboratory for analysis. Any denuders used in the module will be refurbished or extracted and analyzed, if required, and all other components will be cleaned prior to reuse.

B.3.3.4 Internal Tracking of Analytical Samples

Figure B.3.4 shows the internal tracking form that is used to transfer batches of filters removed from the sampling modules in the SHAL to the respective RTI laboratories. Several filters are transferred in a typical batch, so there is not a one-to-one correspondence between the external COC form (which corresponds to a set of modules for a single field exposure) and the internal tracking form. In typical use, filters of like type that are received on the same day are listed on a single internal tracking form. These filters need not be from the same source, so long as they are going to the same laboratory for similar analyses. A similar sample request form is used to transfer samples from RTI to its external analytical subcontractors.

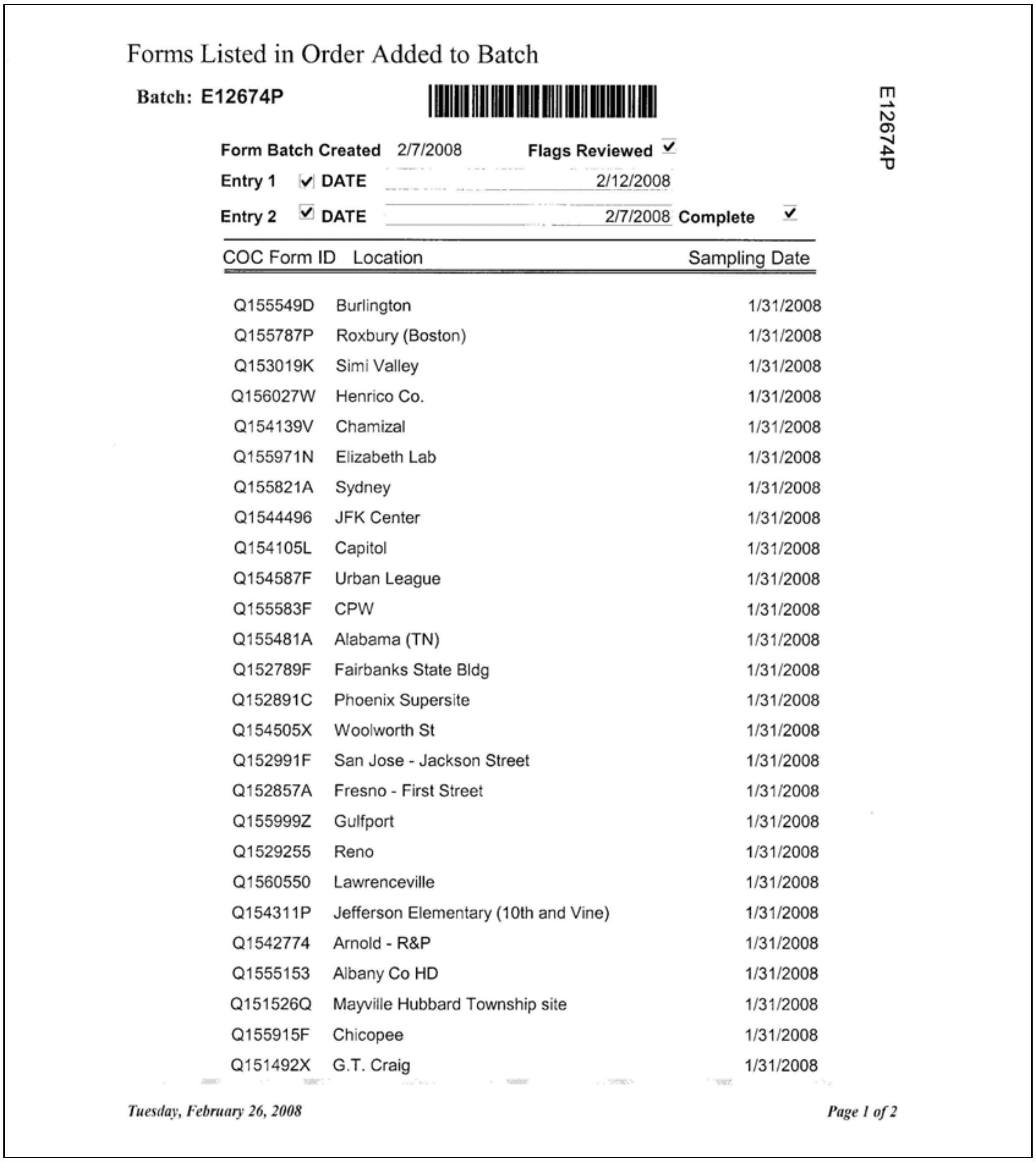
B.3.3.5 Archiving of Filters and Extracts

See *Standard Operating Procedure for Long-Term Archiving of PM Filters and Extracts* for more detailed information.

- After completion of the analyses, the following may remain, depending upon the model of sampler used and the arrangement of filters:

- Teflon filters (following XRF) (filters extracted for ion analysis cannot be archived)
- Teflon filter extracts in 50 mL plastic tubes (following IC)
- Denuder extracts in 50 mL plastic tubes (following IC)
- Nylon filter extracts in 50 mL plastic tubes (following IC)
- Quartz filters (following subsampling for OC/EC analysis)
- Quartz filter extracts in glass bottles (following SVOC analysis)
- Teflon or other filters (following microscopic or optical density analysis).

Quartz filters are archived in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of quartz filters are placed in heavy-duty plastic zippered bags and placed in plastic bins in a freezer maintained at or below –15 °C. Individual filters are indexed for rapid retrieval by Archive Bin ID, Tray ID, and Aliquot ID. Computer-generated reports are available to facilitate retrieval by sample date, site, or state.



Forms Listed in Order Added to Batch

Batch: E12674P

E12674P

Form Batch Created 2/7/2008 **Flags Reviewed** ☑

Entry 1 ☑ **DATE** 2/12/2008

Entry 2 ☑ **DATE** 2/7/2008 **Complete** ☑

COC Form ID	Location	Sampling Date
Q155549D	Burlington	1/31/2008
Q155787P	Roxbury (Boston)	1/31/2008
Q153019K	Simi Valley	1/31/2008
Q156027W	Henrico Co.	1/31/2008
Q154139V	Chamizal	1/31/2008
Q155971N	Elizabeth Lab	1/31/2008
Q155821A	Sydney	1/31/2008
Q1544496	JFK Center	1/31/2008
Q154105L	Capitol	1/31/2008
Q154587F	Urban League	1/31/2008
Q155583F	CPW	1/31/2008
Q155481A	Alabama (TN)	1/31/2008
Q152789F	Fairbanks State Bldg	1/31/2008
Q152891C	Phoenix Supersite	1/31/2008
Q154505X	Woolworth St	1/31/2008
Q152991F	San Jose - Jackson Street	1/31/2008
Q152857A	Fresno - First Street	1/31/2008
Q155999Z	Gulfport	1/31/2008
Q1529255	Reno	1/31/2008
Q1560550	Lawrenceville	1/31/2008
Q154311P	Jefferson Elementary (10th and Vine)	1/31/2008
Q1542774	Arnold - R&P	1/31/2008
Q1555153	Albany Co HD	1/31/2008
Q151526Q	Mayville Hubbard Township site	1/31/2008
Q155915F	Chicopee	1/31/2008
Q151492X	G.T. Craig	1/31/2008

Tuesday, February 26, 2008 *Page 1 of 2*

Figure B.3.4. RTI Laboratory COC form used in tracking.

Teflon filters are archived in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of Teflon filters are placed in heavy-duty plastic zippered bags and placed in plastic bins in a refrigerator or cold room maintained at or below 4°C (but not below freezing). Individual filters are indexed for rapid retrieval by Archive Bin ID, Tray ID, and Aliquot ID.

Filter extracts (nylon or Teflon) are archived for 6 months in extraction vials and grouped in lab batches, which are placed in heavy-duty plastic zippered bags in plastic bins in a refrigerator or cold room maintained at or below 4°C (but not below freezing). Individual extracts are located by Archive Bin ID, Batch ID, and Aliquot ID.

B.3.3.6 Denuder Preparation

Denuders are placed upstream of sampler filters in certain speciation sampling configurations to remove interfering acidic and basic gases and gas-phase SVOCs. The acidic gases of concern to the Chemical Speciation Network include nitric acid and SO_2. The reason for removal of such gases is to preclude their collection on the filter as reaction product artifacts. For example, if nitric acid vapor from ambient air was allowed to reach the nylon filter, it may react with basic substances there or with the filter itself to form nitrate salts; thus the nitrate ion concentration would be higher than that due to nitrate PM alone. In certain instances, it may also be desirable to remove SVOCs from the air stream due to their potential for adsorption or reaction upon reaching the PM collection filter.

RTI will also prepare denuders specially designated for quantitative extraction. These denuders will be prepared with special attention to the purity of the coating reagents, and backgrounds levels of the species to be analyzed (ammonium, nitrate, and sulfate) will be determined for each batch of denuders. Special precautions to ensure low background levels will be taken for denuders that are to be extracted for analysis of ambient gas-phase ammonia, nitric acid, and SO_2.

RTI will provide support for the operation and use of denuders associated with all types of samplers to be used in the speciation network. Denuder specifications for the samplers will be provided upon start-up of this segment of the monitoring program.

The state (or local agency within the state) planning to employ denuders in its PM speciation sampling scheme will inform the EPA Regional Speciation Coordinator of this fact at the same time that a request for analytical services on filters is made. This initial request for denuder use should be made well in advance of the intended date of use to allow for shipment of denuder equipment to the RTI laboratory, denuder cleaning and coating, and QC. The EPA DOPOs will notify RTI's Program Manager of the state's need for denuders (and filters) and details on special filter pack arrangements associated with the denuders. The sampling schedule also will be set. The state must provide a sufficient number of denuders and accessories to meet the demands of their sampling schedule, provide appropriate shipping containers, and carefully pack and ship the new denuders to RTI by Federal Express. Several complete sets of denuders may be required, depending upon the sampling schedule.

Upon receipt of the new denuders and accessories, RTI will clean and coat the denuder devices according to one or more of the following SOPs:

- *Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate*
- *Standard Operating Procedure for Coating Annular Denuders with Magnesium Oxide*
- *Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin*

- *Standard Operating Procedure for Coating R&P Speciation Sampler Chemcomb Denuders with Sodium Carbonate*
- *Standard Operating Procedure for Coating Aluminum Honeycomb Denuders with Magnesium Oxide*
- *Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Measurement.*

All prepared, refurbished, or purchased denuders are sealed airtight and stored in a secure location free of acidic or basic gases and SVOCs. They will then be shipped to the sampling sites for installation on the samplers. The SASS samplers' denuders are installed in the sampling module prior to shipment to the field.

The denuders to be installed at the site sampler are shipped by Federal Express to the requesting state or local agency. Denuders are listed on the COC form that will accompany each shipment to a particular speciation sampler. A record of the number of uses or length of time in use of a particular denuder is maintained by the SHAL so that the denuder is refurbished or replaced according to schedule. All MgO denuders are currently replaced after approximately 30 exposures, and Na_2CO_3 denuders are replaced after each sampling event.

The denuders, COC forms, and field data sheets are returned with the filter samples to RTI from the sampling sites by Federal Express. Upon receipt, the denuders are inspected for damage. The state is responsible for replacement or repair of denuder components damaged in the field; the shipping company is responsible for damage caused during transit. RTI will repair or replace items damaged during handling in its laboratory. The denuders will then be cleaned and/or refurbished for the next round of use according to the established schedule. Unless otherwise directed, RTI will not save extracts from rinsing or cleaning the denuder surfaces and will not analyze the extracts for components. Following cleanup, the undamaged denuders will be refurbished. The newly coated denuders are sealed airtight and stored in a clean, secure location until they are needed.

B.4 Analytical Methods Requirements

B.4.1 Gravimetric Mass Determination

Standard Operating Procedure for $PM_{2.5}$ Gravimetric Analysis describes the procedure to be used for gravimetric mass determination in RTI's laboratory.

B.4.2 EDXRF Analysis for Elements

Standard operating procedures used by RTI and CHESTER LabNet for EDXRF analysis are listed below:

RTI

- *Standard Operating Procedures for X-Ray Fluorescence Analysis of $PM_{2.5}$ Deposits on Teflon Filters*

CHESTER LabNet

- *Standard Operating Procedures for the Sample Receipt and Log In*
- *Standard Operating Procedures for the Analysis of Elements in Air Particulates by XRF (Kevex 771)*
- *Standard Operating Procedures for the Analysis of Elements in Air Particulates by XRF (Kevex 770 and 772)*
- *Standard Operating Procedures for the Kevex Spectrometer Data Generation, Interpretation, and Reporting*
- *Standard Operating Procedure for the Kevex XRF Spectrometer Calibration*

B.4.3 Extraction and Analysis of Anions and Cations

For an overview of RTI's laboratory facility and procedures for extraction and analysis of anions and cations, including nitrate and sulfate, see:

- *Standard Operating Procedure for Cleaning Nylon Filters Used for Collection of* $PM_{2.5}$ *Material*
- *Standard Operating Procedures for* $PM_{2.5}$ *Anion Analysis*
- *Standard Operating Procedures for* $PM_{2.5}$ *Cation Analysis*

B.4.4 Carbon Analysis

RTI's laboratory facility and procedures for organic, elemental, carbonate, and total carbon analysis by the CSN TOT method are detailed in the *Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittal Carbon Analyzer*.

DRI's laboratory facility and procedures for OC/EC analysis by the IMPROVE_A/TOR-TOT method are detailed in the *Standard Operating Procedure for Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples*.

RTI's laboratory facility and procedures for OC/EC analysis by the IMPROVE_A/TOR-TOT method are detailed in three SOPs:

- *Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer*

- *Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a Sunset Laboratory Dual-Mode Analyzer*

- *Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a DRI Model 2001 Analyzer*

While the CSN/TOT analysis and the IMPROVE/TOR-TOT analysis are similar in technical approach, and both require heating ramps under non-oxidizing conditions followed by heating ramps under oxidizing conditions, the two methods are fundamentally different in the way they define carbon fractions. The CSN/TOT analysis is a timed analysis with fixed times at each temperature in the heating profile, and the IMPROVE/TOR-TOT analysis is an event-driven analysis with the sample remaining at a given temperature until evolution of carbon from the filter drops to near zero. A CSN/TOT analysis runs for a total of 12 minutes; an IMPROVE_A/TOR-TOT analysis may take anywhere from 15 minutes to 70 minutes.

The maximum temperatures for the various fractions are also different as are the way so-called "Peaks" are defined. For the CSN/TOT analysis, the five OC peaks are defined as their contributions to OC. For CSN/TOT, the sum of the five OC peaks is always equal to OC. For the IMPROVE_A/TOR-TOT method, the four OC peaks and the three EC peaks are independently calculated without regard to the OC/EC split and pyrolyzed carbon has a negative value if the OC/EC split comes before the addition of oxygen. **Table B.4.1** below describes and compares the carbon fractions measured for both methods and the conditions (e.g., non-oxidizing or oxidizing atmosphere and maximum temperature) under which each fraction is measured.

Table B.4.1. Carbon Fractions Reported

Atmosphere/ Fraction	CSN/TOT[†]		IMPROVE_A/TOR-TOT[‡]	
	Analyte Name	Maximum Temperature	Analyte Name	Maximum Temperature
He&He-O_2/OCT	OC	900°C	OCT	580°C
He&He-O_2/OCR	Not Calculated	N/A	OCR	580°C
He/1st OC Peak	Pk1_OC	310°C	OC1	140°C
He/2nd OC Peak	Pk2_OC	480°C	OC2	280°C
He/3rd OC Peak	Pk3_OC	615°C	OC3	480°C
He/4th OC Peak	Pk4_OC	900°C	OC4	580°C
He-O_2/PCT	Pyrol_C	Varies	PCT	varies
He-O_2/PCR	Not Calculated	N/A	PCR	varies
He-O_2/ECT	EC	920°C	ECT	840°C
He-O_2/ECR	Not Calculated	N/A	ECR	840°C
He-O_2/1st EC Peak	Not Calculated	675°C	EC1	580°C
He-O_2/2nd EC Peak	Not Calculated	750°C	EC2	740°C
He-O_2/3rd EC Peak	Not Calculated	825°C	EC3	840°C
He-O_2/4th EC Peak	Not Calculated	920°C	N/A	N/A

[†] Chemical Speciation Network/Thermal-Optical-Transmittance Analysis, adopted by EPA in 2000.
[‡] Interagency Monitoring of Protected Environments/Thermal-Optical-Reflectance&Transmittance Analysis, adopted as IMPROVE_A in 2005.

B.4.5 Semivolatile Organic Compounds

SVOCs will be analyzed by RTI's subcontractor DRI. The analysis is detailed in DRI's *Standard Operating Procedures for Analysis of SVOC by GC/MS.*

B.4.6 Characterization of Particles by Electron and Optical Microscopy

RTI will provide SEM and optical microscopy for characterization of particulate samples. RTI has extensive experience in the analysis of airborne PM by both optical and electron microscopy techniques, having analyzed a large number of PM_{10} filters by optical microscopy for several state air quality agencies and a significant number of air filters for commercial firms.

B.4.6.1 Scanning Electron Microscopy

SEM can be employed to characterize individual particles collected on a filter. Particles may be sized and the morphology described on an individual basis. The composition of a particle may be determined by EDXRF. Characterization of a large number of particles provides information as to the particle size, distribution, and chemistry of the PM. Any of several filter media can be used to collect particulate material, but smooth-surface filters such as polycarbonate filters are far superior for the purposes of analysis by SEM. The procedures for analysis by particulate material by SEM are described in detail in *Standard Operating Procedure for Sample Preparation and Analysis of* PM_{10} *and* $PM_{2.5}$ *Samples by Scanning Electron Microscopy.*

B.4.6.2 Optical Microscopy

The RTI optical microscopy laboratory is fully equipped with both stereo-binocular and polarizing light microscopes (PLM) capable of both reflected and transmitted light analysis. Photomicrography capabilities allow for documentation of particle characteristics. No RTI SOP currently exists for optical examination of filter media. Procedures will be carried out at the direction of the DOPOs, and reporting criteria and formats will be established at the time of the initial requests.

Analysis by optical microscopy allows for examination of particles having apparent diameters less than 0.25 μm. Optical characteristics such as color, refractive indices, birefringence, and morphology (size and shape) can be determined, which may aid in the identification of particles. The Teflon filter commonly employed in $PM_{2.5}$ sampling is not a suitable substrate for analysis by optical microscopy because the thickness and translucent nature of the filter severely limits the transmittal of light. Additionally, the surface of the filter is highly irregular, making it very difficult to observe individual particles. Other filter media such as mixed cellulose ester (MCE) or polycarbonate provide substrates that are more suitable for analysis by optical microscopy.

B.5 Quality Control Requirements

B.5.1 Quality Criteria for Gravimetric Analyses

All QA/QC procedures and processes employed by RTI in the performance of gravimetric analysis of filters will meet or exceed the requirements outlined in EPA's QA Handbook Guidance Document 2.12 and other criteria applicable to the national gravimetric $PM_{2.5}$ monitoring network. For example, the weighing session software that has been developed by RTI for the CSN program automatically prompts for duplicate and standard weighings to ensure that they are included at the required frequency in each weighing session.

A summary of nine laboratory QC samples that accompany gravimetric measurements and their acceptance criteria is given below.

1. At least two Class 1 working mass reference standards traceable to the National Institute of Standards and Technology (NIST) are weighed at the beginning and end of each weighing session, with weights not to vary by more than 3 μg from the designated value. If the tolerance is exceeded, corrective actions will be taken including reweighing of any filters not bracketed by acceptable standard checks.

2. At least one working standard is weighed after every tenth filter weighed, with the weight not to vary by more than 3 μg from the designated value. If this tolerance is exceeded, corrective actions will be taken as described above.

3. Standard weight measurements are monitored by QC charts (or equivalent) throughout the year to determine if any bias has developed in the weights or the balance.

4. Replicate weighings are made at a frequency of 100% of pre-sampling (tare) filters and 30% of post-sampling filters; if the weights differ by more than 15 μg, the laboratory supervisor for the project will be consulted and corrective action will be taken.

5. At least one laboratory blank is weighed during each weigh session, with the weight not to vary by more than 15 μg from the initial weight. If this tolerance is exceeded, troubleshooting of the entire weighing process will be conducted in coordination with the laboratory supervisor.

6. Field blanks will make up 10% of the total filters analyzed, with post-sampling weights not to exceed initial weights by more than 30 μg. If the weight difference of any of the field blanks exceeds 30 μg, the laboratory blanks are checked. If the laboratory blanks are within 15 μg, the state agencies will be notified to troubleshoot possible contamination in the field.

7. The microbalances are calibrated annually or more frequently, as needed, by a Mettler technician.

8. The primary and working mass reference standards are recertified annually against NIST-traceable mass standards at a state weights and measures laboratory holding a NIST certificate of traceability.

9. The accuracy of the temperature and relative humidity (RH) recorders are verified annually.

B.5.1.1 Gravimetric Disaster Recovery Plan

Raw weighing data, including internal QC checks, are recorded in the gravimetric database application written for the laboratory in Microsoft Access by RTI Data Management personnel. For backup and archiving purposes, the raw data are stored on the RTI chemical speciation program's dedicated database server. Data logger spool files are downloaded directly from each data logger to the server. Database backup and restore procedures are described in greater detail in Section B.10 of this QAPP. Hard copies of raw data will also be printed for backup purposes.

In addition to the program's database backup and recovery plan, the gravimetric mass laboratory will have a severe weather/utilities interruption response plan. This plan will be filed in the Microanalytical Sciences Department's administrative office and will instruct laboratory personnel in the response actions to be taken in the event of power outage, water outage, severe inclement weather, and so forth. The intent of this plan will be to minimize the impact of unavoidable weather events or utilities interruption on laboratory operation, sample throughput, and data quality.

B.5.2 Quality Criteria for Ion Analysis

The quality criteria applicable to analysis of cations and anions are provided in **Table B.5.1.**

B.5.2.1 Ion Disaster Recovery Plan for Data

The Ion Lab supervisor or analyst copies raw data (.txt) and calculated data (.csv) files from the hard drives of each lab computer to a 1GB disk storage partition on an NT file server located in a separate RTI building. Data stored on the NT file server are backed up nightly. Other data security measures include copying data files to the lab supervisor's PC for data analysis, validation, and reporting and frequent backups to CD-R media. At least two archive CDs are burned before any data are deleted from either a lab PC or the NT file server (typically done to free up disk storage space), and the two archive CDs are kept in separate buildings at RTI.

Table B.5.1. QC Criteria for Ion Chromatography (Anions and Cations)

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Multipoint calibration	Daily, before analysis of field samples	Acceptable agreement with previous calibration results plotted on a control chart	Identify and correct the problem before analyzing field sample
Method Detection Limit (MDL)	Annually or after major instrument change	Acceptable agreement with instrument manufacturer's specification	Troubleshoot IC instrument
QC samples prepared with laboratory reagents at concentrations higher and lower than expected sample concentrations (one high, one low)	1) Daily, before analysis of field samples, and 2) After every 10 field samples during a run	±10% of nominal value	1) Identify and correct the problem before analyzing field samples, and 2) Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Commercial, NIST-traceable standard solution	Daily, before analysis of field samples	±10% of nominal value	Identify and correct the problem before analyzing field samples
Reagent blanks	1) Daily, before analysis of field samples, and 2) After every 20 field samples during a run	(1 and 2) less than the MDL for each ion	1) Identify and correct the problem before analyzing field samples, and 2) Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Duplicates (of field samples)	After every 20 field samples during a run	Relative difference less than 10% for concentrations ≥10 times the MDL (less than 100% for concentrations at the MDL)	Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Spiked duplicates	One for every 20 field samples during a run	Spike recovery between 90% and 110%	Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions have been taken

B.5.3 Quality Criteria for EDXRF

B.5.3.1 RTI

QC elements practiced by RTI are shown in **Table B.5.2.**

Table B.5.2. RTI QC Procedures to Analyze EDXRF Elements

Item	Inspection Frequency	Inspection Parameter	Control Limits	Corrective Action
Calibration	As needed	—	—	—
Calibration verification	Weekly	Measure elements on NIST SRMs 1832 and Micromatter QC standards	90%–110%	Investigate and recalibrate; reanalyze any affected filters
Instrument precision	Every tray of samples	Comparison of measured value and value at time of calibration for 6 elements	Relative % of error is $\leq$ 5%	Tray reanalysis
Reproducibility	5%	Duplicate analysis of 5% of batch	Difference of $\leq$ 50% for values with original value $\leq$ 3x its uncertainty	Investigate: and possible reanalysis of entire batch

B.5.3.1.1 XRF Disaster Recovery Plan for Data

Data safety and security are ensured by frequent transfer of computerized raw data from the XRF PC in RTI's Building 6 to portable hard drive media, which is stored in Building 7, Room 219.

B.5.3.2 CHESTER LabNet

QC procedures for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions as performed by CHESTER LabNet are shown in **Table B.5.3.**

Table B.5.3. CHESTER LabNet's QC Procedures Used to Analyze EDXRF Elements

Item	Inspection Frequency	Inspection Parameter	Control Limits	Corrective Action
Calibration	As needed	--	--	--
Calibration verification	Weekly	Measure elements on NIST SRMs 1832 and Micromatter QC standards	90 to 110%	Investigate, possible recalibrate
Instrument precision	Every tray of samples	Comparison of measured value and value at time of calibration for 6 elements	Relative % of error - ≤ 5%	Tray reanalysis
Reproducibility	5%	Duplicate analysis of 5% of batch	Difference of ≤ 50% for values with original value ≤ 3x its uncertainty	Investigate and possible batch reanalysis

The two-sigma (95% confidence level) detection limits in units of ng/cm^2 are calculated from the analysis of a blank Teflon filter as follows:

$$\text{detection limit for element I} = 2\delta_{\text{I}} = \frac{2(2B_i)^{1/2}}{s_i t}$$

where,

B_i = the background counts for element I,
s_i = the sensitivity factor for element I, and
t = the counting livetime.

Theoretically, detection limits may be decreased by simply increasing the counting livetime. In practice, a point of diminishing returns is reached for real-world samples in which the background increases along with the analyte signal. At this point, further improvement in detection limits by increasing the counting time is not possible.

Note: CHESTER LabNet's MDLs are being reported as 3-sigma limits for compatibility with other STN MDLs.

B.5.4 Quality Criteria for RTI OC/EC Analysis

The QC criteria applicable to the carbon speciation analysis in RTI's OC/EC Laboratory are provided in **Table B.5.4.**

Table B.5.4. QC Criteria for OC/EC Analysis by CSN/TOT and IMPROVE_A/TOR-TOT Methods in RTI's OC/EC Laboratory

QC Element	Frequency	Acceptance Criteria	Corrective Action
RTI CSN/TOT Analysis			
Method Detection Limit (MDL)	Annually	MDL $\leq$ 0.5 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples
Calibration peak area	Every Analysis	Within 95%–105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter
Instrument blank	Daily	Blank $\leq$0.3 µg/cm^2	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples
Three-point calibration	Weekly	Correlation Coefficient (R^2) $\geq$0.998 [with force-fit through 0,0]	Determine the cause of the nonlinearity and initiate actions that will identify and solve any problem that may have arisen; then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed
Calibration check	Daily	1) 90%–110% recovery, and 2) Calibration peak area 90%–110% of average for the weekly 3-point calibration	Initiate corrective action, if necessary, to solve the problem before analyzing samples
Duplicate analyses	10% of Samples	1) TC Values greater than 10 µg/cm^2—less than 10% RPD, 2) TC Values 5–10 µg/cm^2—less than 15% RPD, 3) TC Values less than 5 µg/cm^2—within 0.75 µg/cm^2	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag
RTI IMPROVE_A/TOR-TOT Analysis			
Method Detection Limit (MDL)	Annually	MDL $\leq$ 0.6 µg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples
Calibration peak area	Every Analysis	Within 95%–105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter
Instrument blank	Daily	Blank $\leq$0.6 µg/cm^2	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples
Full Calibration [sucrose(aq), KHP (aq), CH_4/He and CO_2/He]	Six Months	Slope [force-fit through 0,0], recovery, and calibration peak area all within 95% to 105% of average slope, average recovery, and average peak area for each run and for each standard.	Determine the cause of the problem and initiate actions that will identify and solve any problem that may have arisen; then repeat the calibration with the standard that appeared to be most different. The individual calibrations for the four standards and their collective results must yield satisfactory results before samples are analyzed
Auto Cal Check	Daily	Peak area for each of the three CH_4/He injections must be within 95% and 105% of the average for the three.	Determine the cause of the problem and initiate corrective action, if necessary, to correct the problem; and obtain acceptable Auto Cal results before analyzing samples.

QC Element	Frequency	Acceptance Criteria	Corrective Action
Calibration check (15 µL sucrose standard)	Daily	1) 90%–110% recovery, and 2) Calibration peak area 90%–110% of average for the weekly 3-point calibration	Initiate corrective action, if necessary, to solve the problem before analyzing samples
Duplicate or replicate analyses	10% of Samples	1) OC or TC ≥ 10 µg/cm^2—less than 10% RPD, 2) OC or TC < 10 µg/cm^2—within 1.0 µg/cm^2, 3) EC ≥ 10 µg/cm^2—less than 20% RPD, 4) EC < 10 µg/cm^2—within 2.0 µg/cm^2	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

B.5.4.1 RTI OC/EC Lab Disaster Recovery Plan for Data

The RTI OC/EC Lab supervisor or analyst copies the raw data (.txt) and calculated data (.csv) files from the hard drives of each lab computer attached to a Sunset Lab analyzer and the Access database of each lab computer attached to a DRI Model 2001 analyzer to a 1-GB disk storage partition on a file server located in a separate RTI building. Data stored on the file server are backed up nightly. Other data security measures include copying all lab data files to the lab supervisor’s PC for data analysis, validation, and reporting and frequent backups to CD-R or DVD-R media. At least two archive CDs or DVDs are burned before any data are deleted from either a lab PC or the file server (typically done to free up disk storage space), and the two archive CDs or DVDs are kept in separate buildings at RTI.

B.5.5 Quality Criteria for Denuder Refurbishments

Quality control steps applicable to acid gas denuder refurbishment are listed below in **Table B.5.5.**

Table B.5.5. QC Criteria for Denuder Refurbishments

QC Element	Frequency	Acceptance Criteria	Corrective Action
Coating solution storage	After each coating session	Sodium carbonate solutions to be refrigerated at ~4°C. MgO slurry to be stored tightly capped while stirring	Prepare fresh coating solution if not refrigerated or if MgO slurry has dried
Reproducibility of MgO or Na_2CO_3 coating	After training session of technicians	For 10 MgO-coated denuders, determine mass applied and strive for 15% RSD	Inspect quality of application; repeat coating of denuders that have low mass applied
Absence of MgO-clogged denuder passage ways	After each coating	Visually inspect each denuder for clogged passage ways	Remove the obstructions; use nitrogen gas to clean debris

QC Element	Frequency	Acceptance Criteria	Corrective Action
Final inspector	After each coating	As applicable, check each denuder for; ▪ Broken glass ▪ O-ring quality ▪ Absence of debris affecting proper seating of denuder	Remove broken denuders from service; replace aged, cracked, or missing O-rings; clean O-ring surfaces with damp lab wipe
Denuder Storage	After denuder coating is dry	To protect denuders from exposure before installation in module, cap or bag them	Reclean and recoat denuders exposed to room air for more than 4 days
Reagent purity	For denuders to be analyzed quantitatively – upon opening new containers of coating material	TBD	Use different reagent source; optionally recrystallize in the laboratory
Denuder lot background contamination	For denuders to be analyzed quantitatively – each preparation lot should have 1 or 2 reextracted	TBD	Reject denuder lot; determine source of contamination; re-make the denuder lot
Field Blank denuder ion background	Minimum of one per shipment	TBD	Investigate source of high background
Denuder extraction effectiveness	For denuders to be analyzed quantitatively –	TBD (90%–110% goal)	Investigate effectiveness of extraction protocol

B.5.6 Uncertainty Determination

Uncertainty values reported to AQS with each concentration record will include components of both analytical and the volumetric uncertainty. The reported uncertainties are estimated “1-sigma” valued (one standard deviation). No blank corrections are assumed other than laboratories’ instrumental baseline corrections, which are an integral part of each analysis. The equations to calculate the total uncertainty for the CSN analytes are included in **Appendix 1**.

B.5.7 Method Detection Limits

The method detection limits (MDLs) for the $PM_{2.5}$ CSN analytes are shown in **Appendix 2** and are reported annually in the data summary reports provided to EPA and posted on AMTIC. MDLs are typically reported as three times the standard deviation of seven or more replicate measurements of a reagent blank, matrix blank, or low-level calibration standard. MDLs for gravimetric mass are determined from net weights (post-weight minus pre-weight) for historical QC blanks and lot stability blanks. MDLs for PM_{10} and PM_{coarse}, and for new analytical methods will be added to this QAPP when they become available. In some cases these may be identical to those for $PM_{2.5}$.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

B.6.1 Gravimetric Mass Laboratory

Two different relative humidity and temperature recording devices are used in the gravimetric mass laboratory to verify that measurements are correct and that variances around the chamber are taken into account. **Table B.6.1** details chamber environment inspection criteria, including how to appropriately document the inspection and troubleshoot if the inspection fails.

Table B.6.1. Inspection Criteria for Gravimetric Mass Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Requirement
Weigh Chamber temperature	Daily	20°–23° C	1) Contact RTI HVAC Department 2) Call service provider that holds maintenance agreement	1) Document in weigh room log book 2) Notify Lab Manager
Weigh Chamber humidity	Daily	30%–40%	1) Contact RTI HVAC Department 2) Call service provider that holds maintenance agreement	1) Document in weigh room log book 2) Notify Lab Manager

EPA Document 2.12 states that filters will not be weighed if the relative humidity and temperature measurements in the weighing environment are not within acceptance criteria (RH = 30%–40% with a control of ±5% and temperature = 20°–23°C with a control of ±2°) for the preceding 24 hours. Critical criteria tables included in March 2000 guidance from OAQPS on the use of data flags for $PM_{2.5}$ AQS data offer slightly relaxed acceptance criteria (RH = 30%–40% with a control of ±5% *standard deviation* and temperature = 20°–23°C with a control of ±2° *standard deviation*). Gravimetric lab personnel will ensure that filters are equilibrated for at least 24 hours before weighing. In the event of protracted chamber downtime that would cause the laboratory holding time to be exceeded, the analyst must decide whether to weigh the filters without the full 24 hours of equilibration, to weigh the filters when relative humidity and/or temperature measurements in the weighing environment have exceeded acceptance criteria, or to wait until the chamber controls are functional, thus exceeding holding time limits. This choice has little impact on overall data validity, as the consequence of each choice is the same: an AQS validity status flag of 2, “operational criteria exceeded.” In each case, the analyst must specify the data flag and insert a brief explanation of the problem in the spreadsheet that is sent to data management.

Table B.6.2 details the weigh room schedule and who will be responsible for performing the maintenance.

Table B.6.2. Gravimetric Mass Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
▪ Multi-point Micro-balance ▪ Internal calibration ▪ Maintenance ▪ External calibration	▪ Daily ▪ Yearly or as needed ▪ Yearly or as needed	▪ Balance Analyst ▪ Mettler Toledo service representative
Comparison of NIST Standards to laboratory working and primary standards	▪ Yearly or as needed	RTI Laboratory Supervisor
Cleaning weigh room	▪ Monthly	Balance Analyst
Sticky floor mat (just outside weigh room)	▪ Monthly or as needed	Balance Analyst
HVAC system preventive maintenance	▪ Yearly	RTI HVAC Personnel

B.6.2 Ion Chromatographic Laboratory

In the ion chromatographic laboratory, several different instruments are routinely tested and maintained**. Table B.6.3** details the items to inspect, how to appropriately document the inspection, and action items if the inspection fails. **Table B.6.4** details the IC maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.3. Inspection Criteria for Ion Analysis Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
IC column back pressure	Each day of use	Column-specific; supplied by Dionex	1) Check for blockage 2) Replace column if necessary	Record pressure in instrument log book
IC background conductivity	Each day of use	Eluent specific; within control limits	1) Check eluent flow 2) Check suppressor 3) Call Dionex tech support if necessary	Record conductivity in instrument log book
Baseline	Each day of use	Steady; no “pulsing”	1) Check for leaks 2) Check for air bubbles in conductivity cell 3) Call Dionex tech support if necessary	Record corrective action in instrument log book

Table B.6.4. Ion Analysis Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Inspection Parameter	Responsible Party
IC system preventive maintenance	Yearly	Check all valves, fittings, flows; replace as needed	Dionex service representative
Check for leaks at valves and column fittings	Daily	Check for leaks	IC analyst
Ultrasonic bath	Monthly	Check for power	IC analyst

B.6.3 EDXRF Laboratory

B.6.3.1 RTI

In RTI's XRF laboratory, the XRF instrument is subjected to routine testing and maintenance. **Table B.6.5** details the items to inspect, documentation to record inspection, and the action items if the inspection fails. **Table B.6.6** details RTI's XRF maintenance schedule and the responsibilities of the person performing the maintenance.

Table B.6.5. Inspection Criteria for RTI EDXRF Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
Energy calibration	Daily	Wavelength alignment of the instrument	This is an automated process	Document in instrument's run log book.
Calibration verification	Weekly	Percent recovery of seven elements on thin-film NIST standards	Adjust instrument calibration factors	Document in instrument's run log book; the results are stored in XRF database.
Ongoing calibration verification	Run with every tray of samples	90%–110% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10μg/cm^2	Re-check instrument calibration and adjust if necessary; re-analyze samples	Document in instrument's run log book
Fast Discriminator (FD)	As needed	FD value is located on the system status; if the FD is set too low, low energy peaks can be lost; if the FD is set too high, the dead time readings can be inaccurate and higher than normal	Service required	Document in service notebook

Table B.6.6. RTI EDXRF Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
Vacuum pump maintenance and oil level check	Monthly, as needed	XRF analyst
Stability test	As needed, depends on Ecal; this test checks for instability due to changes in the x-ray tube output or peak shift both of which will be detected	XRF analyst
State-mandated radiation safety checks	Semi-annually	Safety Officer and XRF analyst

B.6.3.2 CHESTER LabNet

In the EDXRF laboratory, the EDXRF instrument is subjected to routine testing and maintenance. **Table B.6.7** details the items to inspect, how to appropriately document the inspection, and action items if the inspection fails. **Table B.6.8** details the EDXRF maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.7. Inspection Criteria for CHESTER LabNet EDXRF Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
Fundamental calibration	Weekly	Percent recovery of 11 elements on thin-film NIST standards	Instrument recalibration	Document in instrument log book
Ongoing calibration	Every 10 samples	95%–105% recovery of six elements	Reanalysis, check fundamental calibration	Document in instrument log book
Excitation condition check	Every sample	Within analysis uncertainty	Reanalysis	Document in instrument log book

Table B.6.8. CHESTER LabNet XRF Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
Pump maintenance and oil level check	Weekly	XRF analyst
Chiller maintenance and coolant level check	Weekly	XRF analyst
Replenish liquid nitrogen in Dewar	Weekly	XRF analyst

B.6.4 ICP/MS Laboratory

Selected filters will be analyzed by ICP/MS to achieve higher sensitivity than is possible with the XRF method used for the bulk of the filter samples. The list of elements analyzed by ICP/MS is shown in **Table B.6.9.**

Table B.6.9. Elements to be Analyzed by ICP/MS

Aluminum*	Antimony	Arsenic	Beryllium	Cadmium
Chromium	Cobalt	Copper	Barium	Lead
Manganese	Mercury	Nickel	Selenium	Silver

*ICP-MS analysis is not recommended using Whatman Teflon filters due to background levels present in the stiffening ring.

Filter samples are removed from cold storage or received after analysis by XRF. Sample information is entered into the extraction logbook. The filters are loaded into 50 mL, acid-cleaned centrifuge tubes, with the loaded side facing inward. A 25 mL aliquot of extraction solution is added to cover the filter in the tube. The tubes are capped and placed in a heated ultrasonic bath for 3 hours to extract the metals on the filter. The samples are allowed to cool, centrifuged, and a 5 mL aliquot of the supernatant liquid is removed for ICP-MS analysis. The ICP-MS is optimized daily with a tuning solution, and the samples are analyzed against a new calibration curve for each analytical sequence.

Two Thermo X-Series Inductively Coupled Plasma Mass Spectrometers are used for this procedure. Both instruments are equipped with collision cell technology and the following major components:

- Torch box, RF generator, lens stack, quadrapole, and electron multiplier detector
- Personal computer with the Thermo PlasmaLab software
- Vacuum pump and turbo pump
- Refrigerated water recirculator
- Uninterruptible Power Supply (UPS), which supplies the entire instrument, PC, and chiller with 15 minutes of uninterruptible power in full operation and 2 hours of vacuum support in standby mode
- 240-position autosampler housed in a HEPA-filtered enclosure to protect against atmospheric contamination.

Standards are prepared from NIST-traceable, commercially purchased stock solutions. A series of concentrations ranging from 0.25 ppb to 500 ppb along with a blank are prepared to bracket expected analyte concentrations. The range of calibration standards will be adjusted based on the indigenous concentration of individual elements in the samples.

A check standard is prepared from a second source of commercially purchased NIST-traceable stock standards to verify the validity of the calibration curve. The check standard is prepared at a concentration that is not a point on the calibration curve and near the midpoint of the calibration range. The check standard is analyzed following calibration and before the analysis of any samples at a frequency of one per every 10 samples, and at the end of analysis. All sample results to be reported must be bracketed by passing standard checks.

Calibration is performed at the beginning of each analytical run. The correlation coefficient must be ≥ 0.995 for each element. The result for each standard concentration on the curve must be +/– 10% of the expected value for the point to be valid. The initial calibration check, which is prepared from a separate standard source than the calibrants, must pass at
+/– 10% of the expected concentration for each element. The initial calibration blank must be less than the reporting limit for each element. If an element fails to meet the calibration criteria, a new calibration must be run and the associated samples reanalyzed for the given element.

Several different quality control activities are performed as part of the analysis procedure. These activities, their frequency, and the measures of acceptable performance are given in **Table B.6.10.**

Table B.6.10. Quality Control Activities for ICP/MS Analysis Sequences

Activity	Frequency	Measure of Acceptable Performance
Calibration	Every sequence	Correlation coefficient of ≥ 0.995
QC blank	Analyzed after calibration, every 10 samples, and at the end of the sequence	All elements below method reporting limit
QC check sample	Analyzed after calibration, every 10 samples, and at the end of the sequence	90%–110% recovery
MDL	Every 6 months	n/a
Duplicate analysis	One per 20 samples	n/a – flag LDU if > 20%

The detection limit for each element is calculated by analyzing seven replicates of a known standard concentration and multiplying the standard deviation of the replicates by three. The uncertainty for the measurement is the percent relative standard deviation, which is calculated by the instrument operating software for the triplicate readings taken on each sample.

B.6.5 Organic/Elemental Carbon (OC/EC) Laboratory

B.6.5.1 RTI OC/EC Laboratory

In the OC/EC laboratory, the three Sunset Laboratory CSN thermal-optical transmittance (TOT) analyzers and the two IMPROVE_A/TOR-TOT analyzers (a Sunset Laboratory dual mode and a DRI Model 2001) are routinely tested and maintained. **Table B.6.11** details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.11. OC/EC Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
Five OC/EC analyzers	As needed (daily checks are performed on key components)	RTI OC/EC analyst
Analytical balance	Yearly or as needed	Mettler Toledo, Inc., service representative
Muffle furnace	As required	RTI OC/EC Analyst

B.6.5.2 DRI OC/EC Laboratory

In the DRI OC/EC laboratory, the five thermal-optical reflectance (TOR) and five dual reflectance/transmittance (TOR/TOT) analyzers are routinely tested and maintained. **Table B.6.12** details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.12. OC/EC Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
TOR or TOR/TOT Analyzer	As needed (daily checks are performed on key components)	DRI OC/EC analyst
Analytical balance	Yearly or as needed	Quality Control Services (routine) or Mettler Toledo, Inc., service representative (as needed)
Muffle furnace	As required	DRI OC/EC Analyst

B.7 Instrument Calibration and Frequency

B.7.1 Gravimetric Mass Laboratory

The microbalance will be externally calibrated and serviced, if necessary, at least annually or as needed when problems are detected. RTI will keep records on the service dates and calibration results. NIST-traceable standards will be tracked to determine if any bias is entering into the system. These standards will be recertified annually. Control charts based on a standard weight will be maintained to track long-term drift and other time-dependent changes in microbalance performance.

Calibrations in RTI's analytical laboratories are performed on each day of analysis. See the respective SOPs for more details.

B.7.2 Ion Chromatography Laboratory

Multipoint calibration (0.05 to 25.0 ppm) is performed daily. Calibration is followed by analysis of QA/QC samples. Included are:

- QC samples containing anions/cations at concentrations typical of those found in the mid-range of actual filter extract concentrations
- QC sample containing anions/cations at concentrations typical of those found in the lower end of actual filter extract concentrations
- A commercially prepared NIST-traceable QA sample containing known concentrations of anions/cations.

Initially, only the calibration curve from 0.05 to 10.0 ppm is used for the calculation of the anion/cation concentrations. All field sample ion concentrations that exceed 10.0 ppm are recalculated with the 25.0 ppm standard added to the calibration curve.

B.7.3 EDXRF Laboratory

RTI and CHESTER LabNet obtain their calibration standards from the same supplier (Micromatter Co.). Both labs analyze a multi-element standard that is prepared by Micromatter containing Si, Ti, Fe, Se, Cd, and Pb at levels of 5–10 $\mu g/cm^2$. The multi-element standard is analyzed with each tray of samples.

B.7.3.1 RTI

Energy calibration is performed using a copper calibration standard provided by ThermoNoran. This is an automated test to adjust the pulse processor gain so that the detected x-rays appear at the correct energy. Failure to perform this test daily could result in inaccurate quantitative results, misidentification, or failure to detect one or more elements. Peak calibration is performed by analyzing the following thin-film standards:

Purchased from Micromatter, Co. **Table B.7.1** lists the elements and compounds on thin Mylar film that are to be analyzed for the CSN.

Table B.7.1. Elements Present on Micromatter, Co. Standard

Analyte	Analyte	Analyte
Sodium or Chlorine as NaCl	Chromium as Cr metal	Rubidium or Iodine as RbI
Magnesium as Mg metal	Manganese as Mn metal	Strontium as SrF2
Aluminum as Al metal	Iron as Fe metal	Silver or Mercury as Ag-Hg Amalgam
Silicon as SiO	Cobalt as Co metal	Cadmium or Selenium as CdSe
Gallium or Phosphorus as GaP	Nickel as Ni metal	Indium as In metal
Sulfur as CuSx	Copper as Cu metal	Tin as Sn metal
Potassium or Iodine as KI	Zinc as ZnTe	Antimony as Sb metal
Calcium as CaF2	Arsenic as GaAs	Barium as BaF2
Titanium as Ti metal	Selenium as Se metal	Cerium as CeF3
Vanadium as V metal	Bromine or Cesium as CsBr	Lead as Pb metal

Calibration verification is performed weekly by analyzing the following NIST thin-film standards provided by EPA. The expected value and the uncertainties are published with the NIST standards:

NIST SRM 1832 multi-elemental XRF thin film standard certified values are shown in **Table B.7.2.**

Table B.7.2. Certified Values of Elements Present on NIST Standard Reference Material No. 1832

Analyte	Certified Value (μg/cm^2)
	SRM 1832
Aluminum	15.1 ± 0.98
Silicon	35.5 ± 1.14
Calcium	20.1 ± 1.30
Vanadium	4.83 ± 0.49
Manganese	4.62 ± 0.49
Cobalt	1.05 ± 0.06
Copper	2.45 ± 0.16

Re-calibration is performed on an as-needed basis.

B.7.3.2 CHESTER LabNet

Energy calibration is performed using Kevex Standard No. 2036 and the IXRF software calibration option in which a low-energy line is measured at the Al K_2 line (1.487 KeV) and a high-energy line is measured at the Cr K_2 line (8.047 KeV). The program will then assign channel number 149 as the Al peak centroid and channel 805 as the Cu peak centroid, thereby calibrating each channel increment at 10 eV.

Peak calibration is performed by analyzing the following thin-film standards:

1. Micromatter, Inc., vapor deposit of single or two non-interfering elements onto thin mylar film
2. EPA organo-metallic acetate film, usually with two non-interfering elements
3. NIST SRMs 1832 and 1833 multi-element vapor deposits on glass films.

Peaks should be Gaussian-shaped with at least 2,000 counts in the central channel (centroid). Methods for calculating peak location data, calibration factors, and interference factors correction for $PM_{2.5}$ particle size are presented in Chester LabNet SOPs and accompanying discussion.

Recalibration is performed on an as-needed basis. Calibration verification is performed weekly using Calibration Verification Standards (NIST SRMs 1832 and 1833). Control limits are the uncertainties published with the NIST standards; for results outside of control limits, fundamental recalibration of the instrument is performed, followed by reanalysis of the NIST standards.

B.7.4 OC/EC Laboratories

B.7.4.1 RTI OC/EC Laboratory

As shown **in Table B.7.3,** calibration of a CSN/TOT analyzer is checked daily using an external standard and during every analysis using an internal standard. The external standard is prepared by spiking a clean section of quartz filter with 10 μL of a standard sucrose solution, which corresponds to a filter loading of about 21 μgC. The internal NIST-traceable standard is 5% methane in helium. A set of three concentrations of sucrose external standards (10 μL of each, giving a range corresponding to about 4-42 μgC) of filter is run weekly.

Also shown **in Table B.7.3,** calibration of an IMPROVE_A/TOR-TOT analyzer is checked daily using both an internal standard and an external standard and during every analysis using an internal standard. The daily internal standard check consists of automated injections of the internal standard (5% CH_4/He) in a non-oxidizing atmosphere (pure He), an oxidizing atmosphere (2% O_2/He), and at the end of the run. The daily external standard is prepared by spiking a clean section of quartz filter with about 27 μgC in 15-μL of a standard sucrose solution. The NIST-traceable internal standard is 5% methane in helium. A set of five injections (5 to 20 μL, giving a range corresponding to about 9-36 μgC) each of a sucrose external standard and a KHP external standard and six injections (100 to 1500 μL, giving a range corresponding to about 2-36 μgC) each of NIST-traceable external CH_4/He and CO_2/He gas standards are used for a full calibration semi-annually or after significant instrument repairs.

Table B.7.3. RTI OC/EC Instrument Calibration and Frequency

Laboratory	Instrument	Calibration: Frequency
RTI OC/EC Laboratory	CSN/TOT carbon analyzer	▪ Three-point external calibration: run initially to demonstrate linearity; run once a week thereafter ▪ One-point external calibration check: run daily to confirm that FID response has not changed by more than ± 10% since the last three-point calibration ▪ End-of-run calibration peak with 5% CH_4/He: every analysis (counts within 95% to 105% of average for the day)
RTI OC/EC Laboratory	IMPROVE_A /TOR-TOT carbon analyzer	▪ Semi-Annual calibration with four separate standards: separate 6-pt cals with 5% CH_4/He and 5% CO_2/He and separate 5-pt cals with a sucrose solution and a KHP solution (average slopes for the four separate calibrations within 95%-105% of average slope; recovery and internal standard counts for each run within 95%-105% of average for that standard) ▪ Daily Auto Cal check: Injection of CH_4/He standard in He, He/O_2, and end of run (area counts for the 3 injections must be within 95%-105% of the average for the three) ▪ Daily calibration check: mid-level injection of sucrose standard (recovery 90-110%, internal standard counts within 90%-110% of average counts for last full semi-annual calibration) ▪ End-of-run calibration peak with 5% CH_4/He standard, every analysis (counts must be >20,000 and within 95%-105% of average counts for the day)

B.7.4.2 DRI OC/EC Laboratory

As shown in **Table B.7.4,** the DRI carbon analyzers are calibrated in three ways in this order:

1. Semi-annual (or after instrument repair) full calibration using KHP, sucrose, CH4/He, and CO2/He standards;
2. Daily calibration checks using injections of the two gas standards (CH4/He, and CO2/He); and
3. Automatic injection of the CH4/H2 gas standard as an internal standard at the end of each analysis.

Table B.7.4. DRI OC/EC Instrument Calibration and Frequency

Laboratory	Instrument	Calibration: Frequency
DRI OC/EC Laboratory	IMPROVE_A /TOR-TOT carbon analyzer	▪ Semi-Annual: Separate 5-pt cals with 5% CH_4/He, 5% CO_2/He, sucrose solution, and KHP solution (average slopes for the four separate calibrations; new slope 90%–110% of 5% previous slope if no instrument repairs) ▪ Calibration injections of the two NIST traceable gas standards; reverse two cal gases and the carrier gases (O_2/He and He) between morning and afternoon injections (counts should be same) ▪ End-of-run calibration peak with 5% CH_4/He calibration gas performed as part of routine program (counts > 20,000)

B.8 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables are inspected by the laboratory supervisor or laboratory technicians to determine if they are acceptable for use on the project.

B.8.1 Filters

RTI will purchase, inspect, and verify filter lots to be used for the CSN according to specific procedures applicable to each type of filter and for other sampling media such as reagents used to prepare denuders.

RTI will purchase the appropriate number of filters and other sampling media to supply the needs of the monitoring organizations, as directed by the DOPO. The quantity of filters ordered will be sufficient to provide spares to replace defective filters and to satisfy all QA/QC needs (e.g., laboratory blanks and field blanks). Cassettes, if required, will be provided by the state sampling authority responsible for field monitoring. The number of cassettes must be sufficient to allow for shipments to the sampling sites as well as preparation of upcoming shipments from RTI.

Regardless of the filter type or the project's specific analytical requirements, filters of all types must be examined individually prior to use to ensure that one or more of the following defects does not exist:

- **Pinholes.** A small hole or tear in the filter matrix that appears when examined over a light table.
- **Loose material.** Any extra loose material or particulate contamination on the filter surface.
- **Separation of reinforcing ring.** Any separation or discontinuity of the seal between the filter matrix and the outer retaining or reinforcing ring.
- **Discoloration.** Any visible discoloration that indicates problems during the filter's manufacture or packaging.
- **Filter non-uniformity.** Any obvious difference in the spatial uniformity of the filter matrix structure or color. Analytical techniques that rely on the uniformity of aerosol deposition (e.g., XRF) are particularly sensitive to filter defects of this type.
- **Other.** Defined as any other defect (e.g., wrinkling, warping) that might prevent a filter from providing accurate measurement data.

The other acceptance criteria applicable to the different filter types are described in the following sections.

B.8.1.1 Teflon Filters

RTI will purchase the appropriate number of Teflon filters (Whatman, Catalog No. 7592-004) as directed by the DOPOs. The quantity of filters ordered will be sufficient to provide spares to replace defective filters and to satisfy all QA/QC needs (e.g., laboratory blanks and field blanks). Cassettes, if required, must be provided by the state sampling authority. The number of cassettes should be sufficient to allow for shipments to the sampling sites as well as preparation of upcoming shipments from RTI. Acceptance testing of Teflon filters (and other filter types) to be used for ion sampling should be based on analysis of a minimum of 2% per lot (or two filters). Lots must be rejected when the levels of individual anion or cation species exceed 1μg/filter.

B.8.1.2 Nylon Filters

Nylon filters (Whatman, 47 mm diameter, 1 micron pore size) are purchased from Andersen Instruments (Cat. No. 7410-004). These filters will be prepared as follows:

1. Rinse twice in deionized water, approximately one minute per rinse
2. Using TCLP apparatus, rotate for 7 hours in a 2-liter polypropylene jar completely filled with deionized water; drain and repeat for approximately 24 hours
3. Dry in a 40°C oven for ½ to 1 hour.

Nitrate, sulfate, sodium, ammonium, and potassium levels in each lot should be less than 1μg/filter each based on 2% analysis per lot. Prepared nylon filters should be sealed and refrigerated until needed for field sampling.

B.8.1.3 Quartz Filters

The Whatman 47 mm diameter quartz filters and the Pall Tissuquartz 25mm diameter filters are prepared by RTI in-house. The procedure is as follows:

- The 47 mm filters are typically prefired in batches of 100, in a muffle furnace at 900°C for 3 hours. The 25mm filters are prefired typically in batches of 100 for 4 hours.

- The filters are acceptance tested once they have cooled for at least 2 hours, under a low flow of nitrogen in the furnace which has been turned off.

- Either 2% or a minimum of 2, whichever is more, of the filters are randomly selected from the cleaned batch for total carbon testing according to National Institute for Occupational Safety and Health (NIOSH) Method 5040. The results of the acceptance testing show evidence of inadequate cleaning or contamination that may have occurred during transport.

- If any filter analyzed gives, a measured blank total carbon level exceeding 1µg/cm2 for the 47mm filters and 1.5µg/cm2 for the 25mm filters, the filters from that batch will be rejected or recleaned.

- Batches of the 25mm quartz filters that pass the acceptance-testing criterion (≤ 1.5 µg/cm^2 total carbon) are assigned a Batch Number. Batches of acceptance-tested filters are placed individually in petri slide holders, which are placed in a resealable plastic bag labeled with the Batch Number. The resealable plastic bag is stored in a freezer at $\leq -15\,^{\circ}\mathrm{C}$ until the filters are used.

- Batches of the 47mm quartz filters that pass the acceptance-testing criterion (≤ 1 µg/cm^2 total carbon) are assigned a Batch Number, which is used to associate the history of the filters with the batch and to track the batch until the filters are assigned individual identification numbers in the Sample Handling and Archiving Laboratory. Batches of acceptance-tested filters are placed individually in petri dish holders, which are placed in a resealable plastic bag labeled with the Batch Number. The resealable plastic bag is stored in a freezer at $\leq -15\,^{\circ}\mathrm{C}$ until the filters are used.

- Filters are kept in a freezer until just prior to loading into modules.

The reason for the difference in the acceptance criteria is the size of the filter punch used for the analysis: The 25mm diameter filter used for the IMPROVE_A OC/EC method requires a punch that has an area of about 0.5 cm2, and the 47 mm diameter filter used for the CSN/TOT OC/EC method requires a punch that has an area of about 1.5 cm2. RTI will store batches of prepared filters in a freezer until they are needed in preparation for field sampling. Before loading onto the cartridges or modules for field sampling, each quartz filter will be carefully inspected for uniformity in size, shape, thickness, and appearance. Any filters that are visually flawed will be discarded.

B.8.2 Criteria for Other Materials

Other RTI laboratories for Ion Analysis, Carbon Analysis, and Denuder Refurbishment will use the types and quality of reagents, purified water, and other materials specified in the respective SOPs.

B.9 Data Acquisition Requirements (Non-direct Measurements)

This work does not involve the use of any historical databases, literature files, etc. Any supplemental, non-direct measurement data supplied by the monitoring organizations or subcontractors for inclusion in the database will be subject to limited validation to ensure that data have been correctly entered and identified.

B.10 Data Management

This section describes Data Management System (DMS) Quality Control/Quality Assurance (QC/QA) as well as how the DMS promotes overall QC/QA program activities.

B.10.1 Overview

The core of the DMS is a custom database, using Microsoft SQL Server as a relational database server. Custom user programs for data entry and processing were written in Access 2000. To minimize data entry errors, the system imports laboratory data directly from electronic data files produced by laboratory instrumentation systems.

RTI created preset sampling configurations to ensure that samples were scheduled, prepared, and processed consistently. Each sampling event is scheduled for a specific sampling configuration. These configurations specify which sampling media are used by specific sampler channels, what flow rates are appropriate for sampling, which analyses are to be performed on each sampling medium, and how the calculations for each analysis are to be performed.

The system tracks each sampling module, event, and sampling medium with a unique identification number (ID). To prevent data entry errors, barcode readers are used extensively and each ID contains a check digit to reduce errors in manual entry.

Data reports are copied to a separate external Web server for review by the site data contacts. Data revisions are submitted via e-mail and incorporated into the SQL Server database. An AQS-ready data file is then prepared for import into AQS.

B.10.2 DMS Design Features

Careful identification of each sampling module and sampling event is essential in combining the correct analytical results with the correct sampling event. Many features have been designed into the DMS to prevent common data entry errors. Unique identifiers are generated for each sampling event, module, and sampling medium. These identifiers are used to link modules with configurations, sampling events, and analyses. Barcode scanners are used for data entry to reduce the chance of data entry errors. In addition, all identifiers have check digits to permit the data entry programs to immediately catch most manual data entry errors. Database referential integrity also prevents linkage of any sampling module, event, or sampling medium that has not been previously created in the database system.

B.10.2.1 Sample Identifiers

Each item that is tracked by the DMS is assigned a unique identification number (ID). Tracked items include record sheets such as the Field Sampling Chain-of-Custody Form, as well as equipment such as sampler modules, shipping containers, and analysis aliquots in storage. ID numbers that are not automatically generated at the time of data entry (i.e., those that are entered from a local workstation) are obtained from preprinted barcode stickers. The stickers are generated with a unique leading character that specifies the type of item being generated and with a trailing checksum character. The leading character is used by data entry applications to prevent entry of a data item's ID into the wrong field on a form. As an example, a module ID cannot be entered into the aliquot (analytical sample) ID field because module IDs begin with "I" and aliquot IDs begin with "A." The trailing checksum character is used by data entry applications to detect and prevent most common transposition and single character entries. **Table B.10.1** shows the labels currently in use by the CSN Program.

Table B.10.1. Label Identifiers for Tracking CSN Records and Equipment

Prefix	Label Type
Q	Field Sampling Chain of Custody
A	Aliquot
I	Sampler Module ("Inventory")
R	Measurement Request ID
C	Shipping Container (Cooler)
B	Storage Bins
L	Bin Storage Location
H	Aliquot Shipment Batches (to laboratories)
Y	Aliquot Archiving Box

B.10.2.2 Barcode Scanners

Handheld laser scanning barcode readers are used at all SHAL processing stations to read barcode ID labels. These readers are inserted into the client workstation's keyboard connection and provide a rapid and reliable means of entering ID labels used in sample processing.

B.10.2.3 Relational Integrity

SQL Server permits establishment of foreign key constraints between fields in related tables. These constraints provide automatic enforcement of database referential integrity. Enforcement occurs at the server level and is not dependent on application-level programs. Referential integrity constraints prevent entry of a record in a dependent (child) record without a corresponding record in the independent (parent) table. This prevents entry of records that are not linked to other database items. Similarly, an independent (parent) record cannot be deleted while records that depend on that record exist. This prevents the creation of orphaned records.

As an example of referential integrity, laboratory results for a laboratory sample (aliquot) cannot be entered unless the laboratory sample number was previously entered into the Aliquots Table (at the time the sample was created). Thus, attempts to enter laboratory results from other programs or from programs that have incorrect sample identification would be prevented. Attempts to delete an aliquot that has analytical data would also be prevented, as this would orphan the analytical results (i.e., leave results that have no corresponding sample information).

B.10.2.4 Double Entry of Field Data

Sample event information (such as elapsed sample time, volume, barometric pressure, temperature, and sampler QC information) for scheduled events are transmitted from the field on a multi-copy Field COC Form. To prevent data entry errors, information on these forms are double entered and compared by a comparison program. Any discrepancies are resolved before transfer of the double-entered data to the main database.

B.10.2.5 Direct Transfer of Laboratory Data

All laboratory data are sent from the laboratory to the DMS as an electronic file via e-mail. The laboratory data are obtained directly from instrument data system outputs that contain the sample identifier and the measured value. Laboratory personnel add additional QC information during their QC review process. The resulting laboratory data files are directly transferred into the database using custom import programs. This direct transfer prevents data entry errors that could result from manually retyping data into the DMS.

B.10.2.6 Training and Development Databases

Separate training and development databases have been established for operator training and program development purposes, respectively. This permits us to train operators and develop new software without risk of modifying the actual program database. All output (forms, reports, etc.) from these databases contain clear labels to identify them as training or development reports. This prevents their accidental usage in the actual program. In addition, all data entry forms are color coded to clearly identify when a database other than the actual program database is in use. This prevents accidental entry of data into the training or development database when it was intended to be entered into the actual database.

B.10.2.7 Database Backup and Recovery

The information contained in the SQL Server database is backed up to tape on a nightly basis. Tape copies are maintained off site by RTI's IT department. Detailed procedures are covered in RTI's Speciation Data Disaster Recovery Plan.

B.10.3 Automated and Semi-Automated QC Limit Checks for Outlier Detection

The database contains provisions to add data quality flags to most data records. These data flags allow the annotation of data to indicate specific problems and or conditions that might affect data quality. Flags may be added to entire sampling events, individual sampler flow channels, analytical samples (aliquots), or individual analysis results. The flags are expanded during the reporting process so that flags that reflect an entire sampling event apply to all results in that event, flags affecting a sampler flow channel apply to all results using that channel, etc.

A number of automated range checks are currently in place. Outlier checks, also known as "Level 1 checks," are done based on mass balance, anion-cation balance ratios, and other metrics. Assigning the limits for these outlier checks required the development of sufficient historical data to establish a baseline to set appropriate QC limits. **Tables B.10.2** and **B.10.3** show the statistical QC limits that have been developed for $PM_{2.5}$ based on experience during the mini-trends pilot program. The upper and lower limits were based on the 2nd and 98th percentile points on the distributions of the mini-trends data. For blanks, the concentrations were flagged at the upper 95th percentile. Similar validation limits will be developed for speciated PM_{10} and PM_{coarse} when sufficient data has been gathered.

Table B.10.2. Statistical Validation Limits for Routine Data

Percentile	Tail	Validation Test	Sample Type	Limit, µg	Analyte(s)	Outlier Flag
2.0	LOWER	$PM_{2.5}$ Mass Conc.	ROUTINE	2.98	$PM_{2.5}$ Mass Conc.	QL1
2.0	LOWER	Anion/Cation Ratio	ROUTINE	0.86	All ions	QAC
98.0	UPPER	Anion/Cation Ratio	ROUTINE	2.82	All ions	QAC
2.0	LOWER	Mass Ratio	ROUTINE	0.60	All analytes	QMB
98.0	UPPER	Mass Ratio	ROUTINE	1.32	All analytes	QMB
2.0	LOWER	Sulfur/Sulfate Ratio	ROUTINE	0.25	Sulfate ion, XRF	QCR
98.0	UPPER	Sulfur/Sulfate Ratio	ROUTINE	0.45	Sulfate ion, XRF	QCR

Table B.10.3. Statistical Validation Limits for Blanks

Tail	Analyte(s)	Sample Type	Limit µg	Analyte	Outlier Flag
UPPER	$PM_{2.5}$ Mass	FIELD BLANK	50.00	$PM_{2.5}$ Mass	QL1
UPPER	$PM_{2.5}$ Mass	TRIP BLANK	50.00	$PM_{2.5}$ Mass	QL1

The Internal Flags shown in the last column are used to keep track of flagged data within the RTI database and are also shown on the monthly data reports; however, these are not accepted by AQS and must be converted into valid AQS validity status codes and AQS null value codes prior to delivery to AQS. **Table B.10.4** shows how different types of internal flags are converted into AQS codes. There is no one-to-one correspondence between the Internal Flags and the AQS Codes, so the QC reviewer or SHAL supervisor will assign the AQS Codes based on the identified reason for the violation of the screening limits. Because the causes for outliers is often unknown even after careful review of the available documentation, "generic" AQS codes must be used in these cases, as shown in the table.

Table B.10.4. Mapping of Outlier Flags onto AQS Codes

Objective Cause Found for Level 1 Outlier	AQS codes assigned	
	If NOT Invalid (Suspicious)	If Invalid
Lab Error	[1]	AR
Filter Damage	[1]	AJ
Module Assignment Error	(N/A)	AQ or AR
Sampler Malfunction	(N/A)	AN
Unusual Conditions Noted by Operator	[1]	[2]
Unknown Cause	5	AS or AM
Range Checks (Table 10.3)	(N/A)	5

[1] = Use the applicable AQS validity status code
[2] = Use the applicable AQS null value code
(N/A) = Not Applicable

Additional range checks based on fixed criteria are also performed and AQS flags are assigned as shown in **Table B.10.5.**

Table B.10.5. Automated Checks Based on Fixed Criteria

Parameter	Limits	AQS Null Value Code
Exposure Duration, t_{exp}	$23 < t_{exp} < 25$ hrs	▪ AN – Machine malfunction ▪ AQ – Collection error ▪ AV – Power failure ▪ Other code as appropriate
Holding Time before removal from sampler, $t_{pick-up}$	$t_{pick-up} < 48$ hrs	▪ None – As per EPA direction
Average Flow Rate, F_{avg}	Within 10% of target flow rate	▪ AH – Flow rate out of range

B.10.4 Report Preparation and QA Screening

Monthly data reports are screened carefully as described in the following sections prior to delivery to the state monitoring organizations.

B.10.4.1 Data Set Completeness and Integrity

Crosstab Reports showing site locations (rows) and sampling dates (columns) are generated and examined to get an overall picture of data completeness and integrity of data assignments. Missing or anomalous results are investigated and corrected by the data processing staff with the assistance of SHAL and QA personnel. The following crosstab tables are generated to facilitate this screening process:

1. **COC Form number for each event** – Field and trip blanks, routine samples, and unscheduled blanks are displayed in a rectangular table. Missing cells in the table indicate missed exposures or missing data. When empty cells are observed, the data processing manager should be contacted to determine why the data have not

been reported. If an investigation indicates that no data were received, then the SHAL supervisor should be consulted to find out if there was a problem with the shipment.

2. **Total counts of AQS-deliverable records** – Each sampler type should generate a specific number of AQS record counts. Exceptions typically are the result of missing analytical results or of processing records. RTI tries to hold reporting on events until all analysis results have been received. If no additional analysis data are expected for a particular exposure, the data manager will fill the records with "missing data" flags so that the data can be delivered and the exposure purged from the data delivery queue.

3. **Counts of invalid or suspicious analyte records** – Systematic stretches of invalid data for a site may indicate that a site is having problems or that filter shipments to the site should be discontinued.

4. **Sampled date vs. scheduled date** – Any event where these "date" records do not agree is investigated by examining the Field Sample COC (FSCOC) form and by contacting the monitoring agency, if necessary. If a sample was actually run on the wrong date, the data are transmitted to AQS with the date actually run. If the date is incorrect due to a typographical or other error, it is corrected.

B.10.4.2 Entry and Verification of Data Changes from the States

Changes requested by the state agencies are entered into RTI's database by the data processing staff as the comments are received from the respective DOPOs.

When the acceptance period for comments closes for a particular data delivery batch, the text-formatted AQS file is generated. This is checked for integrity using crosstab tables and other simple reporting methods. Record counts per event and sampling date checks are particularly helpful in detecting problems with the record set. After any anomalies are corrected, the AQS text file is regenerated and transmitted to EPA's AQS database as discussed in the next section.

B.10.5 AQS Data Entry

Routine (actual sampled), Field, Trip, and 24-Hour Blank data are currently sent to AQS. **Table B.10.6** summarizes all of the AQS parameter codes applicable to the $PM_{2.5}$ Chemical Speciation analytes. **Table B.10.7** presents the AQS parameter codes for field data parameters. Units for all analytes are micrograms per cubic meter under ambient conditions (i.e., not corrected to standard temperature and pressure). The nominal sampling period is 24 hours. Similar tables for PM_{10} and PM_{coarse} will be developed when the QAPP is finalized or when the parameter codes become available.

The validity status of AQS data is reported in two ways: Data that are qualified in some way but still may be useful for some purposes are assigned Validity Status Codes. These codes, shown in **Table B.10.8,** do not overwrite the data value, which provides data users with the option to include the data item in their analyses. Alternatively, data that are judged to be invalid receive an AQS Null Value Code. In the current AQS system, the Null Value Code overwrites the data value such that the AQS user cannot access the data. The Null Value Codes applicable to the CSN Program are shown in **Table B.10.9.**

Table B.10.6. Analytes and AQS Parameter Codes ($PM_{2.5}$ Only)

AQS Parameter Codes ($PM_{2.5}$)	Analyte	Symbol	Analysis
88301	Ammonium	NH_4^+	Ion Chromatography, Cations
88302	Sodium	Na^+	Ion Chromatography, Cations
88303	Potassium	K^+	Ion Chromatography, Cations
88306	Nitrate	NO_3^-	Ion Chromatography, Nitrate
88309	Nitrate (MASS/nylon)	NO_3^-	Ion Chromatography, Nitrate
88310	Nitrate (MASS/Teflon)	NO_3^-	Ion Chromatography, Nitrate
88403	Sulfate	SO_4^{-2}	Ion Chromatography, Sulfate
88502	Particulate matter 2.5μ	$PM_{2.5}$	Gravimetric Mass
88102	Antimony	Sb	EDXRF (trace elements)
88103	Arsenic	As	EDXRF (trace elements)
88104	Aluminum	Al	EDXRF (trace elements)
88107	Barium	Ba	EDXRF (trace elements)
88109	Bromine	Br	EDXRF (trace elements)
88110	Cadmium	Cd	EDXRF (trace elements)
88111	Calcium	Ca	EDXRF (trace elements)
88112	Chromium	Cr	EDXRF (trace elements)
88113	Cobalt	Co	EDXRF (trace elements)
88114	Copper	Cu	EDXRF (trace elements)
88115	Chlorine	Cl	EDXRF (trace elements)
88117	Cerium	Ce	EDXRF (trace elements)
88118	Cesium	Cs	EDXRF (trace elements)
88126	Iron	Fe	EDXRF (trace elements)
88128	Lead	Pb	EDXRF (trace elements)
88131	Indium	In	EDXRF (trace elements)
88132	Manganese	Mn	EDXRF (trace elements)
88136	Nickel	Ni	EDXRF (trace elements)
88140	Magnesium	Mg	EDXRF (trace elements)
88152	Phosphorus	P	EDXRF (trace elements)
88154	Selenium	Se	EDXRF (trace elements)
88160	Tin	Sn	EDXRF (trace elements)
88161	Titanium	Ti	EDXRF (trace elements)
88164	Vanadium	V	EDXRF (trace elements)

AQS Parameter Codes ($PM_{2.5}$)	Analyte	Symbol	Analysis
88165	Silicon	Si	EDXRF (trace elements)
88166	Silver	Ag	EDXRF (trace elements)
88167	Zinc	Zn	EDXRF (trace elements)
88168	Strontium	Sr	EDXRF (trace elements)
88169	Sulfur	S	EDXRF (trace elements)
88176	Rubidium	Rb	EDXRF (trace elements)
88180	Potassium	K	EDXRF (trace elements)
88184	Sodium	Na	EDXRF (trace elements)
88305	Organic Carbon STN	OC_TOT	OC/EC TOT
88307	Elemental Carbon STN	EC_TOT	OC/EC TOT
88332	PK1_OC STN	PK1_OC	OC/EC TOT
88333	PK2_OC STN	PK2_OC	OC/EC TOT
88334	PK3_OC STN	PK3_OC	OC/EC TOT
88335	PK4_OC STN	PK4_OC	OC/EC TOT
88336	PYROLC STN	PKYROLC	OC/EC TOT
88320	Organic Carbon IMPROVE	OC_TOR	OC/EC TOR
88321	Elemental Carbon IMPROVE	EC_TOR	OC/EC TOR
88322	OH IMPROVE (high temperature OC)	OH	OC/EC TOR
88323	EH IMPROVE (high temperature EC)	EH	OC/EC TOR
88324	O1 IMPROVE	O1	OC/EC TOR
88325	O2 IMPROVE	O2	OC/EC TOR
88326	O3 IMPROVE	O3	OC/EC TOR
88327	O4 IMPROVE	O4	OC/EC TOR
88328	OP IMPROVE	OP	OC/EC TOR
88329	E1 IMPROVE	E1	OC/EC TOR
88330	E2 IMPROVE	E2	OC/EC TOR
88331	E3 IMPROVE	E3	OC/EC TOR
TBD	Aluminum	Al	ICP/MS
TBD	Antimony	Sb	ICP/MS
TBD	Arsenic	As	ICP/MS
TBD	Beryllium	Be	ICP/MS
TBD	Cadmium	Cd	ICP/MS
TBD	Chromium	Cr	ICP/MS
TBD	Cobalt	Co	ICP/MS
TBD	Copper	Cu	ICP/MS
TBD	Barium	Ba	ICP/MS
TBD	Lead	Pb	ICP/MS
TBD	Manganese	Mm	ICP/MS

AQS Parameter Codes ($PM_{2.5}$)	Analyte	Symbol	Analysis
TBD	Nickel	Ni	ICP/MS
TBD	Selenium	Se	ICP/MS
TBD	Silver	Ag	ICP/MS

Table B.10.7. Field Data and AQS Parameter Codes

AQS Parameter Code	Property	Units
68103	Min Ambient Temp	°C
68104	Max Ambient Temp	°C
68105	Avg Ambient Temp	°C
68106	Min Barometric Pressure	torr
68107	Max Barometric Pressure	torr
68108	Avg Barometric Pressure	torr

Table B.10.8. AQS Validity Status Codes

AQS Validity Status Code	Flag Name
IA	African Dust
IB	Asian Dust
IC	Chem. Spills and Industrial Accidents
ID	Cleanup After a Major Disaster
IE	Demolition
IF	Fire – Canadian
IG	Fire – Mexico/Central America
IH	Fireworks
II	High Pollen Count
IJ	High Winds
IK	Infrequent Large Gatherings
IL	Other
IM	Prescribed Fire
IN	Seismic Activity
IO	Stratospheric Ozone Intrusion
IP	Structural Fire
IQ	Terrorist Act
IR	Unique Traffic Disruption
IS	Volcanic Eruptions
IT	Wildfire – U. S.
IU	Wildland Fire Use Fire – U. S.

AQS Validity Status Code	Flag Name
1	Critical Criteria Not Met
2	Operational Criteria Not Met
3	Possible Field Contamination
4	Possible Lab Contamination
5	Outlier – Cause Unknown
6	Data Prior to QAPP Approval
A	High Winds
C	Volcanic Eruptions
E	Forest Fire
F	Structural Fire
H	Chemical Spills & Indust. Accidents
I	Unusual Traffic Congestion
J	Construction/demolition
O	Infrequent Large Gatherings
Q	Prescribed Burning
R	Clean up after a Major Disaster
S	Seismic Activity
T	Multiple Flags; Misc.
V	Validated Value
W	Flow Rate Average out of Spec.
X	Filter Temperature Difference out of Spec.
Y	Elapsed Sample Time out of Spec.

Table B.10.9. AQS Null Value Codes

AQS Code	Flag Name
BI	Sample Lost or Damaged in Shipment
AA	Sample Pressure out of Limits
AB	Technician Unavailable
AC	Construction/repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	Scheduled but Not Collected
AG	Sample Time out of Limits
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (Cannot Calculate)
AJ	Filter Damage
AK	Filter Leak
AL	Voided by Operator

AQS Code	Flag Name
AM	Miscellaneous Void
AN	Machine Malfunction
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	Power Failure (Powr)
AW	Wildlife Damage
AX	Precision Check (Prec)
AY	QC Control Points (Zero/span)
AZ	QC Audit (Audt)
BA	Maintenance/routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration
BE	Building/site Repair
BF	Precision/zero/span

B.10.6 Data Management in the Laboratories

The individual analytical laboratories are responsible for managing their data prior to its entry into the CSN Program’s database. The procedures for data management vary significantly between laboratories and are described in the respective SOPs.

B.10.7 Management and Reporting of Field Audit Data

RTI will provide data entry and reporting support for field calibration and audit data. These will include parameters of flow rate, temperature, pressure, and clock time checks. Details regarding data input and reporting have not been worked out as of the time of this writing, however principles described above will be followed in developing the data management processes and procedures for these new data.

C.1 Assessments and Response Actions

RTI will participate in any laboratory assessment or proficiency program established by EPA, and will maintain any analyst or laboratory certification required for the program.

The QA Manager for this project, Dr. James Flanagan or his designee, will perform periodic technical systems audits of the RTI activities. These audits will cover all aspects of RTI's work, including sample receipt, custody, conditioning, weighing, shipping, data reduction and reporting. These audits are scheduled to be performed annually.

Prior to each audit, a checklist will be prepared, based on this QAPP, the SOPs, and applicable guidance documents. After the audits, the QA Manager will summarize the results in a memorandum to Dr. Jayanty within two weeks. These memoranda will clearly spell out any areas in which corrective action is necessary. If any serious problems are identified that require immediate action, such as a large, systematic analytical bias, the QA Manager will convey these to Dr. Jayanty verbally or through electronic mail the day that such problems are identified. Corrective actions are the responsibility of Dr. Jayanty and will be documented in a memorandum to the file and all relevant project staff, including the QA Manager. The QA Manager will verify the effectiveness of any formal corrective actions and summarize these in memoranda to Dr. Jayanty.

Since these memoranda constitute the corrective action system for this project, all memoranda will be retained in the QA Manager's files, where they will be available for internal or external review.

As SPM, Dr. Jayanty will conduct ongoing informal surveillance of project activities. If new staff members eventually perform some of the activities that others are initially responsible for, the experienced personnel and/or technical supervisors will perform ongoing surveillance of the new persons' work to ensure that the quality of the results is comparable with the previous results.

C.1.1 External Quality Assurance Assessments

RTI's PM speciation laboratories, including subcontractor laboratories, participate in external QA assessments as requested by EPA. On-site audits and assessments are listed below. Reports and findings of these assessments are available in the PM2.5 Speciation Quality Assurance section of EPA's AMTIC website, http://www.epa.gov/ttn/amtic/pmspec.html.

- EPA/NAREL:
    - May, 2007 Technical Systems Audit of DRI's Laboratory

- July 2005 EPA audit of RTI Chemical Speciation Lab Operations
- October 2003 PM2.5 Chemical Speciation Trends Network Lab Audit Report 12/05/03, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/audit03.pdf
- EPA audit of RTI Chemical Speciation Laboratory Operations 03/20/02, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/rtiaudit2.pdf
- A report on the study to evaluate specific laboratory performance as part of the QA oversight of the PM2.5 speciation program 01/30/02, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pememo.pdf
- "Chemical Speciation Laboratory Audit Report", 02/02/01, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/audit.pdf
- "Performance Evaluation Samples for PM2.5 Chemical Speciation Network", 02/02/01, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pesreport.pdf
- "PM2.5 Chemical Speciation Laboratory Audit Report", 09/01/00, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pereport.pdf
- "Performance Evaluation Samples for PM2.5 Chemical Speciation Network", 09/01/00, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/

- The State of Louisiana audits the Gravimetry Laboratory under the Louisiana Environmental Laboratory Accreditation Program. RTI performs PM2.5 filter weighings for the State. The most recent on-site assessment was performed November 13-14, 2008.

C.2 Reports to Management

Within 20 business days from receipt of the sample, the laboratory is responsible for forwarding completed Level 0 and 1 data validation checklists and the results of filter analyses to the appropriate EPA DOPO and State or local contact who submitted the delivery order. Upon approval, the final data set will be released from the laboratory in hard copy and electronic format to the EPA DOPOs, the State or local agency contacts, and to the AQS electronic data base. Draft and final composite annual data summary reports will be issued by RTI to the EPA Project Officer.

The SPM or designee will approve data report summaries sent to EPA. These act as monthly summaries of the data, including the Level 0, Level 1, and Traceability Reports, which are described below.. The SPM and the QA Manager will be notified whenever there is a QA problem and will be apprized of corrective actions taken to solve the problem. The QA Manager will perform yearly technical audits and will submit a report to the project office within two weeks of the audits. Annual determinations of limit of detection, precision, an accuracy and a summary of results of analysis of external performance evaluation samples will also be submitted as part of the Annual Data Summary Report.

The following is a list of regularly scheduled technical and quality-related reports that will be provided to EPA:

1. **Level 0 Validation Report (Checklist)**. Data entry checking of the Custody Forms and Level 0 validation checklist is performed by double entry, with comparison done at RTI. This provides better accuracy than manually reviewing sampler forms to catch errors. Data flags generated during the Level 0 validation process are attached to each data record and are reported monthly to the DOPOs and monitoring agencies as part of regular monthly reporting described in items 3 and 4, below.

2. **Level 1 Validation Report (Checklist).** Cation/anion balance, sulfur/sulfate balance, and reconstructed mass balance reports (spreadsheets) are generated from the DBMS. Other statistical reports are done using data from the DBMS during monthly validation to assist validation personnel in identifying problems. Additional statistical reports are being continuously developed based on experience with the chemical speciation data. Data flags generated during the Level 1 validation process are attached to each data record and are reported monthly to the DOPOs and monitoring agencies monthly as part of items 3 and 4, below.

3. **Monthly Traceability Report.** A report to show traceability between components and analytical results for each sampling event is produced using the DBMS. Electronic copies of this report are prepared and made available to each of the following: the state agencies submitting the delivery orders, the DOPOs, and the EPA Regional QA Laboratory. The information for the monthly traceability report is incorporated into the Monthly Analytical Reports described in the next item.

4. **Monthly Analytical Reports (Electronic and hard copies).** Data for this report are generated from RTI’s DBMS using the field and analytical data and the flags produced during Level 0 and Level 1 validation. RTI has developed SQL queries to produce the reports and spreadsheets. Electronic copies of these reports are made available to the DOPOs, the state agencies submitting the delivery orders, and EPA/OAQPS through RTI's password-protected website. These data users are notified by e-mail of the availability of new data sets as soon as they have been approved by the QA Officer and have been moved to the website.

5. **Quarterly Metadata Summary Reports** of laboratory/field changes and issues that impact data quality will be prepared by RTI with input from its subcontractors. These reports will include a complete listing of field changes

(e.g., sites that shut down or changes to sampler types and dates of operation), laboratory changes (e.g., changes to lab procedures or operations and specific dates for the samples affected); and data collection or analysis issues and dates for samples affected or invalidated. Reports will be chronological and will succinctly describe the issues or changes, and the samples that were affected. One electronic copy of the report will be prepared and delivered to EPA OAQPS for posting on an EPA web site.

6. **Annual Data Summary Report.** RTI worked closely with EPA during the initial $PM_{2.5}$ CSN contracts to develop a comprehensive report responsive to data users' needs without being unnecessarily complex. This report provides a comprehensive overview of performance and summarizes quality issues, corrective actions, data completeness, MDLs, operational problems, blank levels, laboratory QC results, and precision estimated using data from sites where collocated samplers are situated. Other information such as reports of external TSAs and performance audits also may be included as available. An electronic copy of the finalized annual report is posted to AMTIC after EPA approval.

D.1 Data Review, Validation, and Verification Requirements

The following describes RTI's approach to data review, validation, and verification for $PM_{2.5}$ filter analysis. Similar procedures will be developed for the other forms of PM as the new program progresses. The QC criteria given elsewhere in this QAPP will be used as the data validation requirements. Any data that fails routine validation checks will be flagged for review by the monitoring agencies. Large or systematic violations of validation criteria may also trigger a corrective action investigation by the RTI QA Manager.

Analytical data are validated using data from laboratory blanks, calibration checks, standard spikes, and laboratory duplicates. Based on QC verification data, a filter or other sample may be invalidated prior to submitting results to AQS, or the result may be flagged. Reasons for invalidation may include, but are not limited to, damaged filter, laboratory or field blank contamination, balance malfunction, and valid holding times. Table B.10.8 provides the data validity flags currently available for $PM_{2.5}$ data in AQS. RTI will implement any additional or alternative flags that may be defined for $PM_{2.5}$ chemical speciation data.

D.2 Validation and Verification

RTI is responsible for validating analytical data produced in its laboratories. Subcontractor laboratories will apply Level 0 and Level 1 screening to data produced in their laboratories. RTI is responsible for overall, final data review, validation, and verification and for data reporting.

D.2.1 Level 0 Validation

Level 0 data sets contain all available ambient data and may contain nonambient data in the form of QC checks and/or flags indicating missing or invalid data. Any missing data will be retrieved from the source, if available, and any problems related to chain of custody, shipping integrity, sample identifications, and inspections will be rectified to the extent possible. The initial identification of these problems will be the responsibility of the Sample Handling Supervisor, who works closely with the Data Manager and other personnel to document systematic problems and to take or recommend corrective actions. Data will be flagged or invalidated if problems are identified during Level 0 validation but cannot be rectified.

Sources for the information used to screen data for Level 0 validation include the analyst's notes (logbooks and data forms), sample labels, COC forms, package shipping labels, and inspection results for filters and other sample media. Validation flags in the Level 0 data will also include the data flags for items such as power failures, temperature flags, and insufficient data for the averaging period generated by the speciation sampler in the field.

Occasionally, RTI personnel may become aware of an excessive rate of problematic samples from a particular monitoring organization. Such problems might include inadequate packing, excessive numbers of damaged filter media, and incorrectly or inadequately completed forms. RTI will work with the monitoring organization to bring about corrective action. Also, the RTI PM will contact the DOPOs (or the appropriate contact designated by the DOPOs) to inform him/her of the problem.

D.2.2 Level 1 Validation

Level 1 data are reviewed more fully for technical acceptability and reasonableness based on information such as routine QC sample results, data quality indicator (DQI) calculations, performance evaluation (PE) samples, internal and external audits, statistical screening, internal consistency checks, and range checks. Unacceptable long-term performance of the analytical system can also be uncovered in the process of documenting the DQIs of completeness, precision, accuracy, and detection limits, and comparing those indicators with the program's goals or DQOs.

In response to major or systematic problems identified by any of these procedures, corrective actions will be taken and data may be flagged or invalidated. Corrective actions based on Level 1 screening results will include, for example, the following:

- Investigating the specific conditions that contributed to an anomalous results for a single sample or related group of samples
- Contacting the site operator or monitoring agency to find out if there were any meteorological or other conditions that might lead to anomalous results
- Increasing the number of routine instrument checks such as multipoint calibrations, blanks, duplicates, and spikes
- Repeating analyses for the affected samples, if possible
- Reviewing logs and other records for transcription errors and evidence of operational problems or equipment malfunction.

Level 1 screening is conducted primarily after the data have been loaded into the data management system but before the data sets are transmitted to the state agencies for review. Initial screening of data is performed by data management personnel using screening criteria developed by the QA Manager and the laboratory personnel. Data validation flags generated during Level 1 screening are reviewed by the QA Manager; however, the QA Manager often requires input from one of the Technical Area Supervisors to address the problem. Data problems that originate outside the scope of RTI's operations are reported to the appropriate DOPO.

RTI will take any necessary corrective actions on problems identified during Level 0 and Level 1 data review activities and based on input from the state monitoring agencies.

Level 1 designation will be assigned to a set of data after the laboratory has performed all QC activities and has addressed all identified issues. Level 1 data will be transmitted to AQS along with AQS codes generated during the data validation process.

D.2.3 Screening of Subcontractor Data

Although CHESTER LabNet will conduct their own Level 0 and Level 1 screening of the EDXRF data, RTI must further validate its results at Level 0 to ensure a consistent data set. In doing so, RTI will ensure that the sample identifications and COC information from the subcontractor are consistent with RTI's records. This process will consist primarily of comparing the original sample numbers, dates, types, and so on, with the data received from the subcontractor. Of particular importance is ensuring that sample results from the subcontractor match up exactly with data from the other analyses for each exposure. Discrepancies in sample attribution uncovered during Level 0 screening will be investigated and rectified before the data are reported.

RTI will not perform detailed Level 1 screenings on the subcontractor's EDXRF data because this would duplicate efforts already expended. However, data from EDXRF are included in certain Level 1 checks such as reconstructed mass balance and sulfur/sulfate ratio.

D.2.4 Data Corrections

RTI will investigate and attempt to make corrections to all laboratory problems. Corrections to quantitative data such as concentrations will not be applied unless they are defensible and are based on documented information. Questionable data will be flagged appropriately. The following paragraphs briefly discuss the types of data corrections that are typically encountered in this work.

D.2.4.1 Mass

Mass measurements will not be corrected for blank levels. Early in the development of the fine particulate program, a problem was encountered with Teflon filters with rings in which the manufacturer used an adhesive to attach the rings. Solvent continued to volatilize from the adhesive over several weeks, making it difficult to achieve constant weight. The filter manufacturer has since corrected this problem. If any other examples of time-dependent variances in mass measurements are found through analysis of blank filters, RTI will address these in consultation with EPA.

D.2.4.2 Elemental Analysis

EDXRF is subject to interferences and artifacts that are corrected for as follows:

- Escape peaks from secondary targets (e.g., chlorine K∝ from the titanium secondary target, titanium K∝ from the iron secondary target) are corrected by the instrument software.
- Inter-element interference corrections are carried out as described in the XRF SOPs.

- Attenuation corrections for light elements (Na through S) will be applied. The appropriate values for the correction factors differ by particulate size fraction ($PM_{2.5}$ or $PM_{10-2.5}$), and XRF instrumental conditions.
- Filter lot-specific background levels will be accounted for in the instrumental method.

D.2.4.3 Ions

RTI's experience has indicated that artifacts and interferences pose no problem to the analysis of $PM_{2.5}$ ions using state-of-the-art IC systems. High-resolution columns and excellent chromatographic data processing software provide acceptable precision and accuracy. Precision and accuracy results for ions on filters similar to those used in the CSN are included in the ion analysis SOP.

D.2.4.4 OC/EC

This method is subject to a number of potential interferences. RTI will use its best judgment in applying corrections, will fully document any such corrections, and will discuss them with EPA before the data are submitted to AQS.

Carbonates and bicarbonates present in some filter samples may cause interference in the OC/EC analysis. Two alternative procedures may be used to measure carbonate carbon. The first approach includes analysis of a second portion of the filter sample after it has been acidified (i.e., exposed to HCl vapor, which removes carbonate as CO_2) and takes carbonate carbon as the difference between the pre- and post-acidification results. The second approach estimates carbonate carbon by integrating separately the carbonate peak in the thermogram and using the instrument's software to calculate the mass of carbonate carbon volatilized. Carbonate carbon is not generally present in $PM_{2.5}$ on quartz filters at loadings above the absolute error of the measurement; therefore, carbonate carbon was not included in the list of analytes for the current contract.

D.2.4.5 SVOCs

As with IC, state-of-the-art GC/MS provides high resolution of compounds (i.e., accurate qualitative analysis). Artifacts and interferences are more likely to be encountered in the sample extraction and cleanup stages. The following activities should ensure that artifacts such as analyte loss and poor recovery do not pose a significant risk to achieving acceptable analysis results:

- Field blanks
- Method blanks
- Field controls or matrix spikes
- Laboratory controls (spiked sample matrices)
- Method controls (spiked extraction solvent)
- Replicate extract analyses.

D.3 Reconciliation with User Requirements

RTI will ensure that its measurement data meet requirements as expressed in this QAPP and in the Chemical Speciation Guidance documents. RTI and its subcontractors will work closely with EPA to ensure that all important user data characteristics are met. RTI will do the following to ensure that our performance meets contract requirements and client expectations:

- Regular communications between the Program Manager and the DOPOs, the EPA Project Officer, and EPA technical leader. Communications will include conference calls scheduled biweekly or as needed, e-mail and written correspondence, and meeting with EPA/OAQPS personnel in the Research Triangle Park, NC, area.
- An organized system of corrective action notification and follow-through. Significant quality-related problems will be assigned corrective action request (CAR) numbers. The CARs will be tracked by the area supervisor and the QA Manager to ensure that quality problems are addressed in a systematic way. This system will enable the Program Manager to allocate the resources necessary to resolve problems, to prioritize corrective actions, and to track the accomplishment of corrections.

Another key aspect of ensuring the smooth operation of the CSN laboratories is the handling of communications with the various participants in the program. Most programmatic communications with outside participants including EPA/OAQPS, the DOPOs, and the state agencies flow through the Program Manager. The only exceptions to this rule will be dealings on a technical level with EPA personnel (e.g., to define data delivery formats for AQS) and contacts between shipping/receiving personnel at RTI and the state agencies for the purpose of expediting or locating specific shipments. No one at RTI other than the Program Manager is authorized to alter schedules, increase or decrease the number of samples to be analyzed, or change the schedule of shipments to/from a state agency. All such requests must go through the RTI Program Manager.

Appendix 1:
Uncertainty Calculations

Uncertainty values reported to AQS with each concentration record will include components of both the analytical and the volumetric uncertainty. The reported uncertainties are estimated "1-sigma" values (one standard deviation). No blank corrections are assumed other than laboratories' instrumental baseline corrections, which are an integral part of each analysis. The equations below describe how RTI will calculate the total uncertainty for the CSN analytes. A list of symbols is given at the end of this section. Uncertainties for PM_{10} are likely to be determined in the same manner as for $PM_{2.5}$. Uncertainties for PM_{coarse} will initially be determined by statistically combining the uncertainties of the two filters (PM_{10} and $PM_{2.5}$) used to calculate the PM_{10}–$PM_{2.5}$ fraction. The reasonableness of all uncertainties is subject to verification by techniques such as statistical analysis of data from collocated sites.

1.1 General Equation for Uncertainty

The mass uncertainty (micrograms per filter) will be calculated as shown in equation (1) for XRF elements, Ion Chromatography, and OC/EC [mass uncertainties for gravimetric analysis are shown in equations (3) and (4), below]. The use of the *max* function prevents the calculated uncertainty for an exposed filter from being less than the average uncertainty for blanks. In most cases, the first term should be the larger.

$$\sigma_{M\,i,j} = \max\left(\sqrt{\sigma^2_{Ai} + \sigma^2_{Vk} \cdot M^2}\ ,\ \sigma_{Bi}\right) \tag{1}$$

The mass uncertainty is converted to concentration units (micrograms per cubic meter) according to equation (2).

$$\sigma_{C\,i,j} = \sigma_{M\,i,j} \,/\, V \tag{2}$$

1.2 Gravimetric Analysis

Determination of gravimetric mass requires two separate weighings, each of which contributes to the total uncertainty. A 47 mm Teflon filter used in the STN program weighs 145,000 micrograms, while the deposits on the filter are typically on the order of a few hundred micrograms. The total mass of loaded and clean filters is thus approximately the same (i.e., on the order of 145,000 micrograms). RTI has conducted experiments demonstrating that loaded filters have approximately the same repeatability as blank filters. Therefore, a constant value is assumed for the analytical uncertainty, $\sigma_{Ai,}$ used in equation 1, independent of filter loading.

Data obtained from filter lot acceptance blanks have provided a good data set on which to calculate uncertainties for clean filters. The standard deviation of a large population of replicate filter weighings from 2002 and 2003 was determined in order to set the baseline parameters σ_{Ai} and σ_{Bi} in equation 1. These are multiplied by a factor of the square root of 2 to account for the fact that two weighings are involved for each reportable mass concentration value.

1.3 XRF Elements

For XRF elements, an analytical uncertainty value for each analyte is calculated by the manufacturers' software, using an algorithm based on counting statistics for each sample. RTI has found that in order to report more consistent uncertainties for data generated by different analyzers, the manufacturer's uncertainties must be harmonized to ensure that the same components of uncertainty are used. This process is described in two documents that have been prepared by RTI and are posted on the AMTIC Web site:

- Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties – Overview – http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfuncertov.pdf
- Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties – Detailed Discussion – http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfdet.pdf

For the RTI XRF Lab, the XRF software does not calculate an uncertainty for an analyte when the peak and concentration values are zero. The formula shown in equation 3 was developed to calculate an uncertainty when the peak or concentration values are zero. This formula takes into account the background count rate in counts per second (B), livetime (t), and scaling factor (A).

$$\text{Uncertainty} = \text{slope} * A * \text{sqrt}\,(3 * \text{sqrt}\,(B * t) + B * t) / t \qquad (3)$$

1.4 Ion Chromatography

Equation 1 is used for anions and cations (sulfate, nitrate, sodium, ammonium, and potassium), with the analytical uncertainty assumed to be a linear function of concentration, as shown. The intercept at low concentrations, σ_B, is determined from a replicate set of reanalyses of a low-level standard. We attempted to base our initial analytical uncertainty values (σ_{Ai}) on replicate analysis of an up-scale QC standard; however, large and difficult-to-reproduce variability was found, so that we assumed a multiplier, σ_{REL}, of 5% for all analytes and all instruments. Equation 3 is used to calculate the analytical uncertainty, $\sigma_{Ai,}$ as a function of concentration.

1.5 OC/EC

Sunset Labs, which manufactures the OC/EC instrument that was used by RTI for TOT measurements, provides the formulas used by their software to calculate uncertainties, which include constant uncertainty components of ±0.20μgC/cm² for OC and EC and ±0.30μgC/cm² for TC, and a proportional uncertainty component of 5% for all three species. Assuming a filter area of 11.76 cm^2, the constant loadings are 2.35μgC/filter for OC and EC, and ±3.53μgC/filter for TC. See **Appendix 2** to this QAPP for more details. Equation 4 is used for calculating analytical uncertainty for OC/EC.

$$\delta_{Ai} = (\delta_{CONST} + M \bullet \delta_{PROP}) / M \qquad (4)$$

where:

δ_{Ai} = estimated uncertainty of measurement[1] (use in Eqn. 1), micrograms
δ_{CONST} = [constant uncertainty][11.76], micrograms
δ_{PROP} = proportional uncertainty multiplier [5% for OC, EC, and TC]

RTI independently extended the Sunset Laboratory uncertainty estimates to include the OC Peaks. For all reported carbon fractions, the constant and proportional components of uncertainty defined for each fraction below include at least 95% of replicate measurements across three analyzers for 127 filters analyzed over a three-year period in RTI's OC/EC Laboratory.

Carbon Fraction	**Constant Uncertainty Component (δ_{CONST}, μgC/filter)**	**Proportional Uncertainty Component (δ_{PROP},%)**
OC	2.35	5%*OC
EC	2.35	5%*EC
TC	3.53	5%*TC
Pk1 C	2.35	5%*Pk1 C
Pk2 C	2.35	5%*Pk2 C
Pk3 C	3.53	5%*Pk3 C
Pk4 C	3.53	10%*Pk4 C
Pyrol C	2.35	140%*Pyrol C

1.6 Determination of Volume Uncertainty

The relative uncertainty associated with sampled volume and other shipping and handling components of sampling error is often the predominant part of the total measurement uncertainty. However, RTI has no way to determine these, based on any of the field data that we routinely receive. A nominal value of 5%, which is used by the IMPROVE program (see IMPROVE SOP 351, *Data Processing and Validation*), is probably in the right order of magnitude for most of the CSN samplers. More accurate values for relative volume uncertainty would require statistical assessment of field audit results, which have not been consistently available for the CSN in previous years. Studies using data from collocated samplers and other means for assessing whole system variability for both the CSN and IMPROVE networks have shown that the value of 5% is probably an underestimate for the majority of chemical species, though it is reasonably accurate for high-level species that are relatively immune from contamination, such as sulfate and sulfur by XRF.

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[1] Values are consistent with the Expanded Uncertainty concept used for measurements related to health or safety as described in Taylor, B.N.; Kuyatt, C.E. NIST Technical Note 1297: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. Expanded Uncertainty section. Available at http://physics.nist.gov/Document/tn1297.pdf (accessed April 2008).

1.7 Definitions

I = Index for analytes
j = Index for individual sampling events
k = Index for sampler type (SASS, IMPROVE, FRM, etc.)
σ = Standard deviation
M = Analytical mass (micrograms per filter)
V = Sampled volume (cubic meters)
$\sigma_{Mi,j}$ = Std. dev. of mass for analyte I for event j (micrograms per filter)
$\sigma_{Ci,j}$ = Relative standard deviation for analyte I from lab QC samples (dimensionless)
σ_{Bj} = Blank std. dev. from lab QC blanks (micrograms per filter)
σ_G = Std. dev. for replicate gravimetric analyses (micrograms per filter)
σ_{Vk} = Relative std. dev. of sampler volume (dimensionless) [typically 5%]

Appendix 2:
Method Detection Limits

Laboratory method detection limits (MDLs) are reported annually and are subject to periodic updates by the analytical laboratories. Laboratory MDLs can be converted to concentration units (µg/m^3) by dividing by the sampled volume for the respective sampler type and channel. Note that the resulting MDL in concentration units will **not** include any allowance for field uncertainties, including uncertainty in the measurement of volume, contamination, or other field-related issues.

2.1 X-Ray Fluorescence, RTI International

RTI operates three ThermoNoran XRF instruments to analyze CSN filters. Below are the MDLs for the RTI XRF systems. For conversion from µg/cm^2 to µg/filter, the sampled area for the CSN filters is assumed to be 11.3.

Analyte	MDL, ug/cm^2
Aluminum	0.0108
Antimony	0.0357
Arsenic	0.0014
Barium	0.0088
Bromine	0.0015
Cadmium	0.0159
Calcium	0.0041
Cerium	0.0058
Cesium	0.0293
Chlorine	0.0042
Chromium	0.0019
Cobalt	0.0010
Copper	0.0012
Indium	0.0188
Iron	0.0012
Lead	0.0042
Magnesium	0.0097
Manganese	0.0015
Nickel	0.0010
Phosphorus	0.0087
Potassium	0.0034
Rubidium	0.0015
Selenium	0.0017
Silicon	0.0096
Silver	0.0126

Analyte	MDL, ug/cm^2
Sodium	0.0342
Strontium	0.0019
Sulfur	0.0063
Tin	0.0272
Titanium	0.0037
Vanadium	0.0026
Zinc	0.0030
Zirconium	0.0039

2.2 X-Ray Fluorescence, CHESTER LabNet

CHESTER LabNet follows EPA Protocol IO-3.3, Section 12. Reference: *Compendium Method IO-3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy*, U.S. EPA Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH, June 1999.

Two Kevex XRF instruments are used to analyze CSN filters. Below are the MDLs for the CHESTER LabNet XRF systems. For conversion from µg/cm^2 to µg/filter, the sampled area for the CSN filters is assumed to be 11.3.

Analyte	MDL, ug/cm^2
Aluminum	0.0117
Antimony	0.0169
Arsenic	0.0015
Barium	0.0053
Bromine	0.0012
Cadmium	0.0131
Calcium	0.0029
Cerium	0.0050
Cesium	0.0042
Chlorine	0.0078
Chromium	0.0019
Cobalt	0.0020
Copper	0.0023
Indium	0.0140
Iron	0.0033
Lead	0.0041
Magnesium	0.0249
Manganese	0.0024
Nickel	0.0018
Phosphorus	0.0045

Analyte	MDL, ug/cm^2
Potassium	0.0051
Rubidium	0.0013
Selenium	0.0014
Silicon	0.0084
Silver	0.0120
Sodium	0.0509
Strontium	0.0016
Sulfur	0.0042
Tin	0.0156
Titanium	0.0019
Vanadium	0.0015
Zinc	0.0020
Zirconium	0.0024

2.3 Gravimetry

Gravimetric MDLs have been determined by multiple re-weighings of blank filters. A factor of the square root of two has been included in the calculation to account for the fact that each filter must be weighed twice to produce a net result. The RTI gravimetric mass laboratory operates three balances, designated “B,” “C,” and “D,” which are assumed to have the same MDL. No assumptions regarding filter area are required to calculate the MDLs below; however, these MDLs apply only to the 47 mm Teflon filters used by the CSN program.

Instrument	Analyte	MDL, ug/filter
B	Particulate matter	7.200
C	Particulate matter	7.200
D	Particulate matter	7.200

2.4 Anion and Cation Analysis

RTI operates the anion and cation analysis laboratory. Two cation instruments and three anion instruments are currently in operation. These MDLs were determined for the analysis of ions on nylon filters. No assumptions regarding filter area are required to calculate these MDLs.

Instrument	Analyte	MDL, ug/filter
D5C	Ammonium	0.160
D5C	Ammonium	0.160
D5C	Potassium	0.134
D5C	Potassium	0.134

Instrument	Analyte	MDL, ug/filter
D5C	Sodium	0.290
D5C	Sodium	0.290
D6A	Nitrate	0.084
D6A	Nitrate	0.084
D6A	Sulfate	0.120
D6A	Sulfate	0.120
D6C	Ammonium	0.160
D6C	Ammonium	0.160
D6C	Potassium	0.134
D6C	Potassium	0.134
D6C	Sodium	0.290
D6C	Sodium	0.290
S1A	Nitrate	0.084
S1A	Nitrate	0.084
S1A	Sulfate	0.120
S1A	Sulfate	0.120
S2A	Nitrate	0.084
S2A	Nitrate	0.084
S2A	Sulfate	0.120
S2A	Sulfate	0.120
S3A	Nitrate	0.084
S3A	Nitrate	0.084
S3A	Sulfate	0.120
S3A	Sulfate	0.120

2.5 Organic and Elemental Carbon by Thermal Optical Transmission

Organic Carbon/Elemental Carbon (OC/EC) analysis by the Chemical Speciation Network’s thermal/optical transmittance method (CSN/TOT) is performed by RTI. Four analyzers capable of running the CSN/TOT method are operated by the RTI lab. Note that the MDLs reported here for OC, EC, and TC were determined by the manufacturer, and the MDLs for the OC Peaks (Pk1_OC, Pk2_OC, Pk3_OC, Pk4_OC, PyrolC) were determined by RTI. These MDLs are used by the OC/EC laboratory as an upper limit for their periodic redetermination of MDLs. If the MDL determination result exceeds the tabulated value, then corrective action must be taken. Exposed filter area was assumed to be 11.76 cm^2. All of RTI’s analyzers have the same not-to-exceed target MDLs.

RTI CSN/TOT Analyte	MDL, ug/filter
Elemental carbon	2.352
Organic carbon	2.352
Pk1_OC	2.352
Pk2_OC	2.352
Pk3_OC	2.352
Pk4_OC	2.352
PyrolC	2.352

2.6 Organic and Elemental Carbon by IMPROVE_A/TOR&TOT

Organic Carbon/Elemental Carbon analysis by the IMPROVE_A method is performed by DRI. Multiple analyzers are operated by the DRI lab and are not distinguished in the table below. Exposed filter areas were assumed to be 3.53 and 11.76 cm^2 for the IMPROVE and CSN filters, respectively.

Analyte	DRI MDL, ug/filter	
	IMPROVE(a)	CSN(b)
OC	2.895	9.643
EC	0.671	2.234
OH	2.859	9.526
EH	0.424	1.411
TC	3.283	10.937
O1	0.318	1.058
O2	0.600	1.999
O3	1.977	6.586
O4	0.777	2.587
OP	0.565	1.882
E1	0.424	1.411
E2	0.530	1.764
E3	0.177	0.588

(a) IMPROVE filter area = 3.53 cm^2
(b) CSN filter area = 11.76 cm^2

RTI's OC/EC Laboratory serves as a backup laboratory for IMPROVE_A/TOR-TOT analysis. RTI's not-to-exceed target MDLs for IMPROVE_A analytes on all IMPROVE_A analyzers with a deposit area of 3.38 cm^2 (for quartz filter samples collected on the URG 3000N sampler) are given below.

RTI IMPROVE_A Analyte	RTI MDL, ug/filter
OCR	2.03
OCT	2.03
ECR	2.03
ECT	2.03
TC	2.03
OC1	2.03
OC2	2.03
OC3	2.03
OC4	2.03
EC1	2.03
EC2	2.03
EC3	2.03
PCR	2.03
PCT	2.03

Appendix M

Sunset Laboratory Inc. Semi-Continuous OCEC Instrument Manual, Version 6.4.

Sunset Laboratory Inc.

SEMI-CONTINUOUS OCEC
CARBON AEROSOL ANALYZER

A GUIDE TO RUNNING AND MAINTAINING
THE SUNSET LABORAORY
SEMI-CONTINUOUS OCEC ANALYSER

Sunset Laboratory Inc.
10180 SW Nimbus Ave.
Suite J-5
Portland, OR 97223

Introduction

Congratulations; you have purchased the finest Semi-Continuous OCEC Carbon Aerosol analysis instrument on the market today. Sunset Laboratory Inc. has been a leader in the development of the OCEC aerosol analyzer since the early 1980's and has offered commercial laboratory instruments for more than 12 years. Sunset Laboratory has performed much of the instrument development leading to the current state of thermal/optical OC/EC measurement techniques. In addition, Sunset Laboratory has performed literally thousands of OC/EC analyses ranging from mining samples to ambient atmospheric samples. The Semi-Continuous OCEC Analyzer is the latest addition to our growing line of products and services in the field of carbon aerosol analysis.

Theory of Analysis Operation

Sunset Laboratory's Semi-Continuous OCEC instrument has been developed as a field deployable alternative to integrated filter collection with subsequent laboratory analysis. This instrument can provide time-resolved OCEC analyses on a semi-continuous basis with OCEC (organic and elemental carbon) results comparable to the recognized NIOSH Method 5040. As currently performed, a quartz filter punch is mounted in the instrument, then samples are collected for the desired time period. Once the collection is complete, the oven is purged with helium, a stepped-temperature ramp increases the oven temperature to 850 °C, thermally desorbing organic compounds and pyrolysis products into a manganese dioxide (MnO_2) oxidizing oven. As the carbon fragments flow through the MnO_2 oven, they are quantitatively converted to CO_2 gas. The CO_2 is swept out of the oxidizing oven with the helium stream and measured directly by a self-contained non-dispersive infrared (NDIR) detector system. A second temperature ramp is then initiated in an oxidizing gas stream and any elemental carbon is oxidized off the filter and into the oxidizing oven and NDIR. The elemental carbon is then detected in the same manner as the organic carbon.

Three characteristic components of this method are important in the strength of the analysis. The first of these is the optical detection and correction for elemental carbon. Elemental carbon is naturally present in many of these samples from some combustion source such as a diesel exhaust. This black material is a very strong absorber of light, and almost always the only absorber in the red light region. In addition to this elemental carbon in the sample, elemental carbon can be formed from some charring of the organic carbon fraction of the sample as it is pyrolyzed during the initial temperature ramp. This can begin occurring as low as 300 °C depending on the organic components on the filter. This charring of organic carbon could result in an artificially low measurement of the organic carbon and a higher than actual measurement for the original elemental carbon if no correction is made.

The Sunset Laboratory thermal/optical method uses the high light absorbance characteristic of elemental carbon to correct for the pyrolysis-induced error. This is done by incorporating a tuned diode laser (red 660 nm), focused through the sample chamber such that the laser beam passes through the mounted filter in the sample oven. Initial absorbance of the modulated laser beam is recorded. As the oven ramp proceeds, the laser absorbance is monitored continuously by the data system. Any charring of the organic carbon results in an increase in absorbance of the laser. After the initial temperature ramp, when the helium is switched to a He/O_2 mixture, all of the elemental carbon is oxidized off and the laser absorbance is reduced to the background level. When the resulting NDIR data are reviewed with an overlay of the laser absorbance, the point in the second phase oxidizing ramp at which the laser absorbance equals the initial laser absorbance is the split point. Any elemental carbon detected, before this point, is said to have had been formed pyrolytically by charring of the organic carbon. This carbon is subtracted from the elemental carbon area observed during the oxidizing phase of the analysis and is assigned as organic carbon. The primary assumption, for this correction, is that the particulate bound elemental carbons and the pyrolytically formed elemental carbons have the same absorption coefficient. Carefully prepared standard samples suggest that this correction is satisfactory.

The second component of the analysis is the use of a sensitive, linear detector for this measurement. Historically, this has been a flame ionization detector. Recently Sunset Laboratory has introduced is own self-contained flow-through NDIR system. This unit provides results comparable to FID at typical ambient levels. It is a RISC-processor controlled pseudo-dual beam instrument with temperature stabilized source and a linearized signal output. Calibrations are constant for up to a year. NDIR eliminates the requirement for air or hydrogen at the field site significantly reducing the requirements for consumable gases. The conversion to NDIR of the Sunset Laboratory field analyzer represents a significant step forward in reliability and reduced complexity.

The third important component of the measurement system is the incorporation of a fixed volume loop used to inject an external standard at the end of every analysis. This external standard data is incorporated into every data package and is used along with the known carbon concentration in the loop to calculate the analytical results. By having every sample correlated to an external standard injection with each analysis, small variations in instrument performance normalized out resulting in a very stable, repeatable analytical method.

Safety

The purpose of this section is to provide information on the safety precautions that should be taken around the instrument.

Types of safety issues:

1. Laser
2. High voltage wiring
3. Weight
4. Temperature

Laser

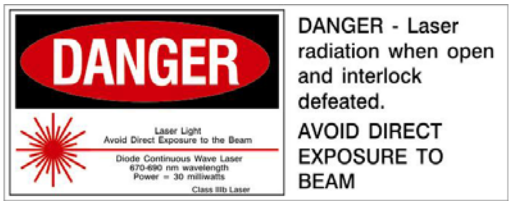
The Sunset Laboratory Semi-Continuous OCEC Carbon Aerosol Analyzer uses a laser diode for the transmission light source during the sample collection and analysis. As such, a report on its configuration has been filed with the Food and Drug Administration; Center for Devices and Radiological Health (CDRH).

Caution: use of control, adjustments, or performance of procedures other than specified herein may result in hazardous radiation exposure.

The Sunset Laboratory Semi-Continuous OCEC Carbon Aerosol Analyzer is classified as a Class 1 Laser Product, which means that there is no laser radiation exposure during operation and maintenance. The interlocked laser system is embedded in the instrument with a closed optical system. The interlock-protected laser shroud covers the laser aperture/photodetector preventing any direct or collateral exposure to the laser system. The attached photodetector head also serves as an additional non-interlocked protective housing covering the laser aperture and sealing the entire system. In order to gain access to the photodetector head to change filters, the operator must remove the protective laser shroud. When this operation is performed, it actuates the interlock shutting down the laser via an electromechanical switch. Once the shroud is removed (and the laser disabled), the operator can safely remove the photodetector head and change the filter. Secondary protection is provided by the instrument housing, which is secured by a series of screws. Some weakly scattered laser light may be indirectly observed during operation but is not measurable above background lighting.

The source laser diode is rated as a Class IIIb product as a standalone unit and emits sufficient optical power to constitute a possible hazard to the human eye if directly exposed to the beam. Therefore, the present Semi-Continuous OCEC analyzer optical system has no user serviceable parts. All repairs and services must be performed by one of Sunset Laboratory's trained technicians.

As a Class I Laser Product, no laser hazard warnings are required on the exterior of the instrument. However, when the maintenance access panel is opened, the first of several laser radiation warning labels are observed. This is located on the laser shroud/interlock housing. It warns that laser radiation may be present if the shroud is removed and the interlock is defeated. This is shown below:



The interlock system can only be defeated by the use of a special override key. The key will only be provided to Sunset Laboratory- trained Service Technicians. No keys will be provided to the user.

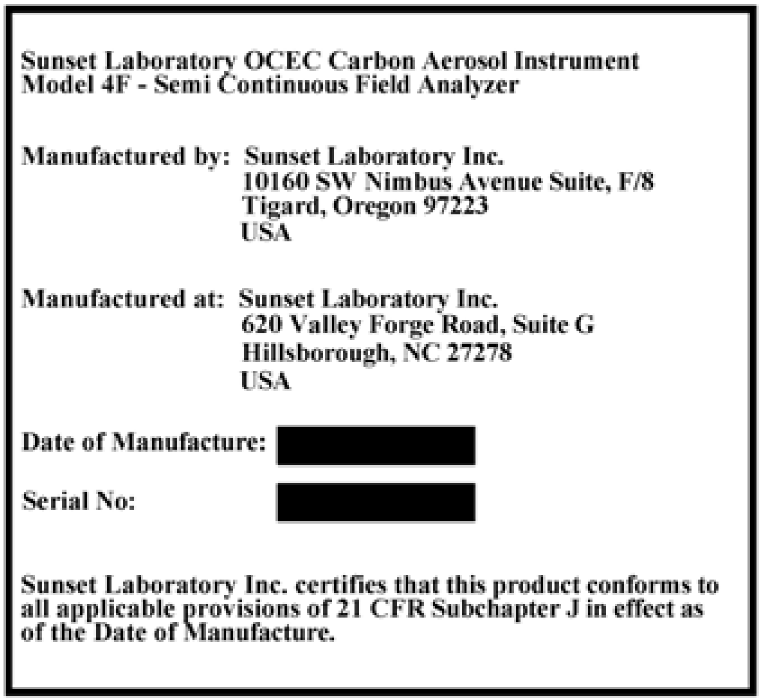
When the laser shroud is removed, two more labels may be observed. The first label is on the aluminum photodetector head, mounted over the end of the optical path, which serves as a non-interlocked protective housing and source detector. This effectively seals off the laser radiation system preventing exposure as long as the photodetector remains installed. The protective housing label, shown below; indicates the type and power of the laser which may be present if the photodetector head is removed with the interlock system defeated.

Should the photodetector (and thus, the associated warning label) be removed, a second warning label located on the mounting plate indicates the open laser aperture. This label also indicates the type and power of the laser diode and warns that direct exposure is possible at the open aperture if the system is opened and the interlock is defeated.

This label is reproduced below:

No hazardous exposure is possible under normal operating conditions and/or maintenance procedures. The protective interlock system shall only be defeated by a trained service technician using prescribed procedures from the factory.

A fourth label, located on the outside of the case on the back, serves as the product identification and product certification as required under 21 CFR 1010.2 and 1010.3. This label, shown below also the instrument serial number, manufacturing completion date and place of manufacture.



Sunset Laboratory OCEC Carbon Aerosol Instrument
Model 4F - Semi Continuous Field Analyzer

Manufactured by: **Sunset Laboratory Inc.**
10160 SW Nimbus Avenue Suite, F/8
Tigard, Oregon 97223
USA

Manufactured at: **Sunset Laboratory Inc.**
620 Valley Forge Road, Suite G
Hillsborough, NC 27278
USA

Date of Manufacture: [redacted]

Serial No: [redacted]

Sunset Laboratory Inc. certifies that this product conforms to all applicable provisions of 21 CFR Subchapter J in effect as of the Date of Manufacture.

Sunset Laboratory Inc. certifies that this product conforms to all applicable provisions of 21 CFR Subchapter J in effect as of the Date of Manufacture. Any effort to defeat the interlock system of service the laser system in this instrument by anyone other than a trained service technician could result in a dangerous exposure to laser radiation. Furthermore, any effort to service, alter or modify the optical system by the user may void the warranty and absolves Sunset Laboratory Inc. of any liability regarding exposure to laser radiation.

High Voltage Wiring

Sunset Laboratory Inc. uses either 115V or 230V AC electric power to operate its Semi-Continuous OCEC instruments. In general, the AC wiring is isolated to the closed area under the instrument cabinet and properly labeled with a "Danger High Voltage" label. Any repair work in this area should only be performed by a trained technician. Every reasonable effort has been made to isolate the AC power from the user. However, no service work should ever be performed on the instrument unless the AC power cord has been unplugged from the AC power inlet.

High Temperatures

In general, the analyzer uses high temperature to analyze for the carbon content of the aerosol samples. Heated zones are marked in bright red warning labels. Avoid contact with these areas. The ovens should be allowed to cool completely before beginning any maintenance or repair work.

Weight

The instrument weighs approximately 30 pounds. Use caution when lifting and moving the device to avoid causing injury.

I Health and Safety Warnings

The Sunset Laboratory Thermal/Optical Carbon Analyzer uses high temperatures (up to 870°C) and laser radiation to perform the required steps in this analytical procedure. Under normal operation, the analyst is protected from exposure to these energy sources. However, during repair or trouble shooting, when the instrument cover is removed, the analyst must take the following precautions:

a) Before attempting any repairs, turn off the power and wait for all heated zones to cool.

b) For most repair work, unplug power to the ovens and avoid contact with any power sources in the oven cabinet.

c) Although the laser source has an interlock protection system, if the interlock is overridden, direct exposure to the laser can occur under certain conditions. Do not look directly at the laser source as permanent eye damage can occur.

d) Use caution when handling all support gas cylinders and regulators. Always have cylinders properly chained to a safety rack.

e) Always wear Safety Glasses and a dust mask when removing and installing the ceramic insulation in the ovens during the installation of heating coils. The insulation does not contain asbestos, however, safe handling of the high temperature insulation should be considered as a good precaution against unknown health hazards.

Customer Provided Hardware Requirements:

1. Power – The Sunset Laboratory Semi-Continuous OCEC Instrument requires a separately fused 120/240V AC power receptacle (15 Amp). The single power line is sufficient to power all phases of the instrument operation. Separate switches are provided to isolate the heated zones from the CPU and blower. This is necessary for testing and troubleshooting.
2. Support Gases – there are five support gases (to be) supplied by the customer along with regulators. These are required to be at the site prior to setting up an installation.
    a. Helium –the main carrier gas is helium. This should be at least 99.999% ultra high purity grade with low moisture, hydrocarbon, carbon dioxide, carbon monoxide and oxygen background. (a GC quality oxygen trap is also recommended for the regulator outlet). CO2 and hydrocarbon content should be less that 1 ppm.
    b. Helium/oxygen – this is a custom blend gas with 10% oxygen and 90% helium balance. It should be ordered with sufficient lead time by the customer to allow for blending by the gas vendor (typically 2-4 weeks). The helium should be the same quality as the main source helium and the oxygen should be 99.999% or better with low moisture, hydrocarbon, carbon dioxide, carbon monoxide and hydrocarbon background. (CO2 and hydrocarbon levels should be less than 1 ppm).
    c. Helium/methane- this is also a custom blend with 5.0% methane and 95% helium balance. Again, this should be ordered with sufficient lead time by the customer to allow for blending by the gas vendor (typically 2-4 weeks). The helium should be the same quality as the main source helium and the methane should be research grade or better with low moisture background.

3. Computer – Sunset Laboratory will typically supply a laptop computer for field operation of the semi-continuous analyzer. It will come with the operating software pre-installed. Training on the operation and use of the software will be provided at the time of initial installation. An un-interruptible power supply (UPS) for the computer (but not the instrument) is also highly recommended to maintain the integrity of the system in the event of a power outage.

    User supplied computers should be at least 500 MHz Pentium II or better with 10 GB hard drive, 256 M memory, 2 serial ports and preferably a R/W CD drive. Laptop computers are preferred for field deployment because they are small and offer temporary battery operation in the event of a power outage. The 2 serial ports are mandatory for the operation of the instrument. Many laptops today offer only 1 serial port (and some with no serial ports). The best solution to this is to obtain a PCMCIA card based serial port(s). These devices are far more reliable (for now) than the USB port serial devices.

Check with Sunset Laboratory for detailed specification and recommendations.

4. Sampling System – The Sunset Labs Semi-Continuous analyzer is equipped with a 3/8” stainless steel ball valve port located on the back of the unit as the sample inlet. Samples are pulled through the ball valve, across the mounted quartz filter, through a mass flow meter and out to the remote sample pump. Initiation of sampling is facilitated through a remote controlled power cord. This can be used to turn on a pump or actuate a 120 VAC solenoid valve to start and stop sample collection. A ballast tank is also provided to prevent filter disruption at the initiation of sampling. Because of the wide range of possible samples and customer sampling requirements, no additional sample introduction components are provided with the basic instrument package. The following components are suggested (or required) to complete the initial installation.
    a. Pump (required) – an oil-less carbon vane pump with a minimum capacity of 24 liters/min at –15 psi vacuum.
    b. ¼” Tubing (required) – sample vacuum ports on the rear of the instrument are ¼” Swageloc tube ports. The customer shall provide sufficient Teflon or nylon tubing as required to reach the ballast tank and pump.
    c. Organic denuder (optional) – organic denuders have been shown to reduce the effects of vapor phase organic adsorption to the cleaned quarts filter. These are currently available as multiple concentric tube and parallel plate devices. Sunset Labs can provide additional advice towards the proper sizing and acquisition of these devices. Sunset Laboratory can provide a parallel plate organic denuder at additional cost.
    d. PM (particulate material) sizing inlet (optional) – most typical sampling operations required some type of particulate sizing inlet such as a cyclone or impactor for controlling the range of particle sizes collected for the sample. These are highly recommended as different size fractions can be contributed from different sources. A carefully controlled sample size fraction will provide much clearer information about the target sample source. Sunset Laboratory can provide an 8 Lpm cyclone sized for the instrument for an additional fee.

Installation

The purpose of this section is to provide information on the installation of the instrument. The instrument will arrive in a custom shipping case at least several days prior to the installation appointment. Sunset Laboratory personnel will coordinate an appointment date and verification of receipt of all of the required components prior to installation. Installation requirements for the instrument itself are relatively minor. It is likely that significantly more effort will be required to design and install a proper sample inlet system to meet experimental requirements.

Installation Sequence

There are six basic steps for the installation and operation of the Sunset Labs Semi-Continuous OCEC Analyzer.

1. Site preparation
2. Instrument placement and integration into the planned sample inlet
3. Hardware connections with support gases and computer
4. Sample filter installation
5. Software installation
6. Calibration and establishment of preliminary sample procedures.

Site Preparation

The suggested installation site should be in a dry, well-ventilated field laboratory with a hard surface work area. The instrument is NOT weatherproof because of the optical requirements of the analysis method. The minimum required workbench area is approximately 3’ by 2.5’ not including space for the computer. The computer is connected to the instrument using 2 serial port cables and should be located such that an easy view of the screen is possible from the instrument. Support gas cylinders can be remotely located for convenience or safety requirements. These should be plumbed with 1/8” tubing run to the proposed installation site with sufficient excess to facilitate easy connections to the flow control system. Recommended tubing is NO-OX^{TM} or copper. These should be properly labeled to prevent confusion during installation and maintenance.

Unpacking

Unless the boxes are badly damaged in shipping and you are directed to do by Sunset Laboratory, it is not recommended that they be unpacked prior to the initial installation as several of the quartz components are very fragile. The Sunset Laboratory Semi-Continuous OCEC analyzer consists of three major sub-system components; the CPU, data acquisition and valve control hardware; the main analysis and sample oven; and the NDIR detector unit. These components are combined into a single unit and shipped in a custom shipping case.

Lifting

The instrument is tightly packed in the custom shipping container to minimize any problematic damage during shipping.

Method

1. With the exception of the instrument, remove all items from the case.
2. Have two people lift the instrument from the case and place in the site for the instrument.

Initial Design and Setup

Prior to receipt and installation, due consideration should be made regarding the experimental requirements for the sampler inlet. The default is 8.0 LPM/ PM 2.5.

These include:

1. PM size speciation (cut point) requirements
2. Pump size requirements
3. Protection of sampler inlet and instrument
4. Humidity control
5. Organic artifacts

PM size (cut point) requirements
Must be addressed with the appropriate system flow and properly designed cyclones or impactors to achieve the desired size speciation.

Pump size requirements
This will likely be determined as a result of bypass plumbing, secondary sampling components, etc. as required to establish the desired PM sampling and cut point requirements. The Sunset Laboratory Semi-Continuous OCEC analyzer typically uses 8 lpm (nominal) for its sample flow with a 3/8” Swageloc tube sample inlet. The pumping system requires a minimum of 15” mercury (vacuum) at 8.0 LPM.

Protection of the sampler inlet and instrument from direct contact with the environmental elements

Protect the sampler inlet and instrument from direct contact with the environmental elements. The instrument is reasonably rugged but is not designed for exposure to the weather (particularly liquid water).

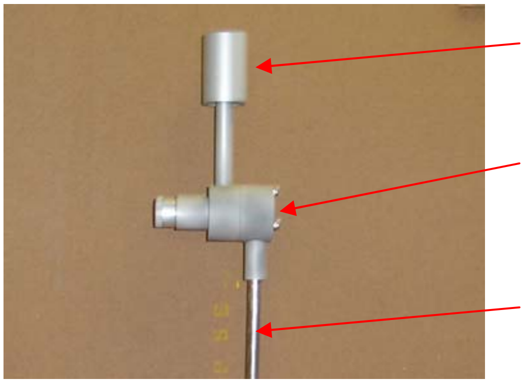
Humidity control
Consideration for the effects of relative humidity need to be made with regards to the sampler inlet and/or the sampling station! If you are sampling in the summer in 90 degree weather and 70% relative humidity outdoors and your sample lines come into an air conditioned instrument room at 70 degrees, condensation could occur in the sample lines with possible problems. *Either the sample inlet lines need to be maintained at a constant RH or the instrument room needs to be maintained at a temperature above the dew point of the sample air!*

Organic artifacts
It has been shown that quartz filters will adsorb organic vapors from the sample air resulting in a positive artifact. Consideration needs to be made as to how this will be addressed through the use of organic denuders or other study experiments to evaluate artifact formation.

Instrument Placement and External Connections

Method

1. Based on preliminary site planning, the instrument should be placed such that there is easy access to the sample inlet (or manifold) with a minimum number of bends in the sample train tubing. The instrument is best suited for placement with the front facing forward for easy access to the laser and filter mount. Locate the instrument to maximize the availability of air flow to the base of the instrument for maximum oven cooling.
2. Install the sample inlet system. The user is required to configure the system consistent with their study design and the sampling site constraints. Fundamentally, the sampling inlet system typically consists of a 2.5 um cut Cyclone for air intake



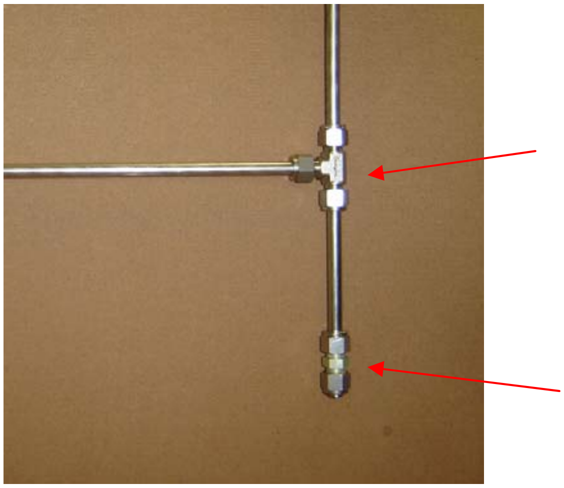
Rain Hat/Air Intake

Cyclone

Transfer tubing (3/8”) SS

and particle size speciation, linked to an organic denuder (note directional flow of air),

and then 3/8 inch tubing into instrument sample inlet.



A good design is to use a “drop out Tee” before the instrument to collect any condensation on humid days.

Check the trap regularly when servicing the instrument especially on humid days.

It is best to use a Teflon ferrules for the connections to permit easy removal of the sample lines at a later date. *Note: Either Copper or S.S tubing can be used. It must be extremely clean from the standpoint of organics such as manufacturing oils. S.S tubing is preferred. If there is any doubt as to cleanliness, the tubing can be cleaned with reagent grade methylene chloride, acetone or methanol and then dried. Alternately, a propane torch can used to heat the length of tubing while blowing* N_2 *through the system to remove any volatile organics.*

3. Connect the vacuum pump line to the back of the instrument marked “vacuum pump”. The vacuum pump should have sufficient capacity to pull at least 16 inches Hg vacuum at 16 lpm. Two different options are available for this configuration:
   a. If using a “house vacuum” type system where the pump is on constantly, the vacuum line should be plumbed into the solenoid valve (provided) on the “VAC” port. The other side of the solenoid valve should be connected to the inlet of the ballast tank. The solenoid valve should then be plugged into the solid state relay control box.
   b. If the pump is to be turned on concurrent with the start of sampling, connect the vacuum pump directly to the ballast tank inlet and plug the pump AC power to the solid state relay control box. The pump can be run on an intermittent or continuous basis depending on sampling and noise requirements.
   c. Plug the solid state relay control box to a 120 VAC outlet of sufficient capacity to support the pump. Large pumps can draw a significant current load. Plug the digital control cable into the instrument on the “Pump SSR” control socket.

4. Place the external temperature thermocouple just inside the cyclone rain hat at a point where the tip is near the sample inlet but out of direct sunlight. Plug the sensor to the “Ambient Temp” socket.
5. Plug the first serial cable into the instrument main board in the top 9-pin female serial port connector (labeled “Com Port”). Plug the other end into the computer serial port. If the computer has a hardware serial port, use that for the main communication port. Note the port number.

6. Plug the second serial cable into second the female 9-pin serial cable labeled "NDIR Port". Plug the other end into the second computer serial port. Note the com port number here too.
7. If you are using a digital data logger such as the ESC data logger, plug the third serial cable into the third serial port on the computer and connect that to the serial port on the data logger. Note this port number as well.
8. 

Hardware Connections with Support Gases

Method

1. There are three support gases: Helium, Helium/Methane, Helium/Oxygen. Be sure the tanks are securely stabilized, the proper stainless steel diaphragm regulators installed, and the proper 1/8" o.d gas lines run to the instrument. Label the lines. All lines should use either GC grade pre-cleaned copper or Alltech "NO-OX" tubing. "NO-OX" tubing should be kept to a minimum length. High quality pre-cleaned copper is the best and is much less expensive than "NO-OX". The helium should also have an oxygen trap placed in the line just prior to the instrument. This will minimize any oxygen in the system.
2. Connect the gases to the respective ports as labeled on the back of the instrument using the provided Swageloc fittings and ferrules.

3. The support gas can then be turned on. Set the secondary regulator pressure to 8 psi initially.

Sample Filter Installation

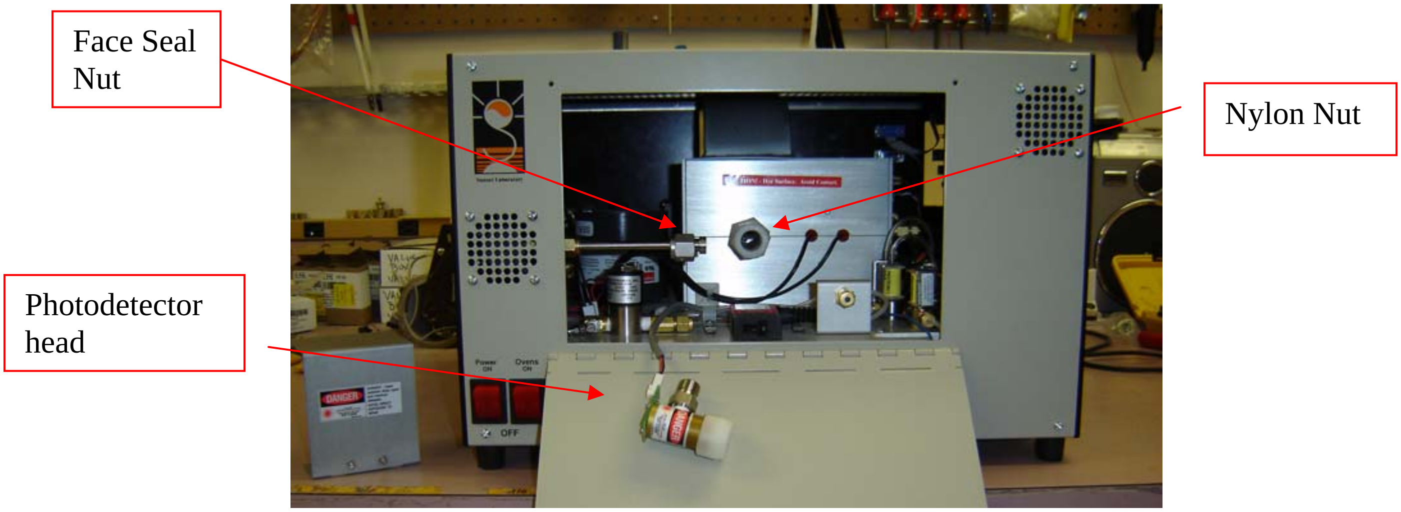
Materials

Philips head screwdriver
Quartz filter
Filter punch
Flat-faced forceps

Method

1. Open filter access panel loosening the finger tight hand screws and opening the access panel.

2. Remove laser shroud by pulling backward away from the instrument until the interlock key and pressure tabs release and the shroud pulls away. This shroud acts as a protective housing for the oven port preventing exposure to the laser system. It has a keyed interlock system which automatically shuts down the laser upon access to this area.



3. To remove the photodetector, remove the stainless steel nut and then loosen the nylon nut with hands. NO WRENCHES! Gently slide the photodetector off the quartz insert. Avoid excess force as the quartz oven can be easily chipped or broken if caution is not observed.

4. 4) The insert is removed or installed by loosening or tightening the front nylon nut on the front oven reducing union. The insert will slide through the union with only slight pressure. Again - no wrenches! While servicing, locate the insert in some secure location that will keep it from falling and breaking. Do not handle the filter end of the insert.

5. Using filter punch, cut a new 17mm quartz filter.

6. Using the flat-faced forceps, gently insert the new filter into the oven port perpendicular to the tube inlet about ¼”. Using the forceps, gently rotate the filter using care not to puncture or bend it. Slide in the filter with the insert at least 1 inch and then install a second filter. It does NOT have to be completely square or rotated

in the oven port at this time.

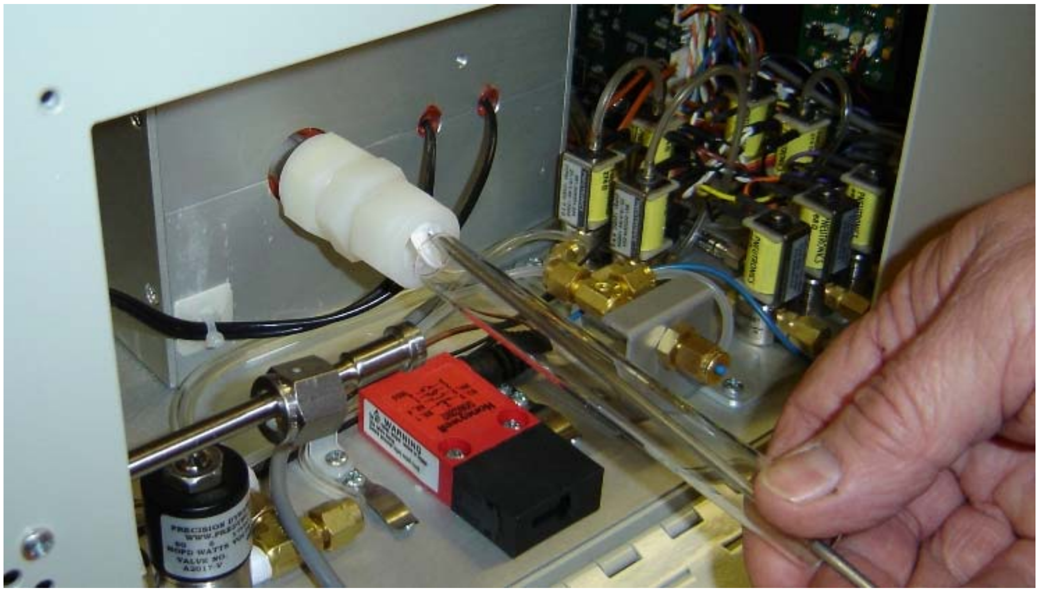
7. Wipe the quartz insert with a clean Kim-Wipe or other lint-free cloth to remove any fingerprints, lent or filter fragments which may be present on the insert.
8. Slide insert in parallel to the oven observing the filter as it begins to square up with the face of the insert and slide into the port. It will offer mild resistance to being pushed into the port.

However, RESIST ALL URGES TO FORCE any aspect of this job. If it does not slide in easily, slip it out and start over. As the insert slides farther into the port, it will press the filter against the seat in the heated zone. Once you can feel the filter begin to seat, hold the insert firmly against the filter and hand-tighten the fitting nut securing it in place. *The most critical period for accidentally breaking or chipping the insert is during the first ½ - 1" of insertion as the piece makes contact with the filter but still can be twisted or rotated off-axis with the oven port. Once the piece has been slid in far enough to limit this motion, the chances for breakage are significantly reduced.*

9. Reinstall the photodetector making sure the face of the o-ring is in place before reinstalling. The fittings should be tightened using hands.

10. Reinstall the laser shroud
11. Filter removal – Filters are removed by using the filter removal tool. The tool has a very sharp barbed point that does not take kindly to being dropped. BE CAREFUL! It is also VERY sharp. Follow sets 1 and 2 to remove the photodetector. With the photodetector removed and the front oven reducing union nut still tight, push the sharp point of the filter removal tool through the filter while it is still held in place.

12. Now loosen the front oven union nut and simultaneously pull out the insert and the filters that are “harpooned” on the removal tool. Set the insert aside careful to note the position so that the same end can be re-inserted into the union when the new filter is installed.



Follow steps 4 through 10 to install a new filter.

Software Installation

The RT carbon analyzer uses two software programs, one to control the instrument and one to calculate (reprocess) the data. The optional computer from Sunset Laboratory will come with the software installed. Existing computers will need to have the software programs as provided on the accompanying CD installed. A PC-type computer is required for operation of the instrument and must have *Microsoft Windows XP Professional; Service Pack 2* installed as the operating system. (Win 2K service pack 4 is still supported but not preferred. Windows VISTA is not supported). Instruments delivered within the United States will be shipped with a new computer with the current software pre-installed and tested. Warranty on Sunset Laboratory Inc. provided computers shall be for 90 days only. Any repairs or damage after the warranty period shall be the responsibility of the purchaser. International purchases may include a computer as an option where allowed by United States export laws.

At a minimum, the computer, whether provided by Sunset Laboratory Inc. or the client, shall include:

1. Windows XP Professional; Service Pack 2. (We currently have no experience with the new Windows Vista operating system. For the time being, we are only supporting XP Professional until the Vista system can be thoroughly investigated and any necessary software changes made to adapt to the new system.)
2. 2 GHz processor or better
3. 512 Mb ram
4. Read/Write CD/Rom
5. 2 serial ports. Serial ports may be directly from the main computer CPU board or USB2.0-to-Serial converter cables. On client provided computers, it is the obligation of the client to configure the serial ports and assure that there are no conflicts between ports or interrupts. We will help where we can but it is your obligation.
6. Small footprint computer case or laptop

Method

1. You must run first the “setup.exe” file provided with the disk (or file upload) in the Setup subfolder under the main Install folder.
2. After you run the setup file, you must then change the format of at least one file and move several others.
3. First, note the location (default) of the new software:

```
C:\Program Files\

\OCEC_Inst_Software\
          \OCECPAR
          \PAR
          \RAWDATA
```

4. When you run the Setup.exe file provided, you will be given the option to locate the control software in another subdirectory. That is acceptable if you are comfortable with that operation in Windows. Location in another directory other than C:\Program Files\ will not affect the performance of the software. We suggest that you use the default setup.
5. In previous additions, the \OCECPAR\ folder had to be located in the main C:\ directory. In the new version, it MUST reside as a subfolder under the OCEC_Inst_Software or the stand alone Calculation software folder. The Setup file will make all of the necessary subdirectories. It will also place the new Instrument Control software and Calculation software in the proper directory.
6. The Setup.exe file will place actual or example files that are required for the operation of your instrument in each of the subfolders. If the software was not sent to you specifically configured for your instrument (probably an upgrade) by a Sunset Laboratory software engineer, then you will have to move and modify two files that currently reside in the C:\OCECPAR\ folder.
7. First, this is what the format of most current “C:\OCECPAR\scinst1par.txt” files look like in most current Sunset Laboratory RT OCEC instruments. Review yours carefully to be sure it matches the format exactly. If not, contact Sunset Laboratory to review any additional changes required.

```
0,0,356.73,-333.83
0,0,351.46,-310.5
0,0,251.71,-236.33
0,0,277.35,-246.83
0,0,292.71,-366.25
-211
1
1
1
1
1
1
1
0.0004143,-0.0628
15850,-.921
-0.0248,-0.0025,-0.1650
-0.0561,-0.0019,-1.122
-0.02,-0.0,-0.0
1
19200
30
0,0,6.041,-5.52
-0.0066,0,-0.0066
120
1.23
19.75
```

```
5
RT3037
```

8. To correct this file; you must make the change shown below. Go to the C:\OCECPAR\ folder and double click on the scinst1par.txt file. It should open up on NOTEPAD. Add the line shown below and save the file in C:\Program Files\OCEC_Inst_Software\OCECPAR\ folder overwriting the example “scinst1par.txt” file installed by SETUP.

```
0,0,356.73,-333.83
0,0,351.46,-310.5
0,0,251.71,-236.33
0,0,277.35,-246.83
0,0,292.71,-366.25
-211
1
1
1
1
1
1
1
0.1           20
1
19200
30
0,0,6.041,-5.52
-0.0066,0,-0.0066
120
1.23
19.75
5
RT3037
RTCalc504.exe
```

9. Add an additional line EXACTLY as the orange line above.
10. Second, you will have to move the current C:\OCECPAR\NDIRpar.txt file to the new \OCECPAR\ subfolder. You can do this by either copying the file using the Contol_C and dropping it into the new \OCECPAR\ subfolder with control_V or by dragging and dropping the file into the new folder. In either case, you will be asked if you want to overwrite the existing file. Generally, the answer is YES although you may want to rename or copy the example file to another location for reference purposes.
11. It is recommended that you leave the other newly installed control files in the new \OCECPAR\ folder. Some older software versions may have extraneous parameter coefficients in these files that could produce operations problems with the new software. These files include:

```
     Valve_table.t
xt
     Valve_set.txt
```

12. If the software fails to operate properly, you can delete these two files and the new software will install default startup files for these two files. The Valve_Set.txt will be modified by the software as the program runs to establish the most satisfactory set points. If the software has trouble with high pressure spikes after about 4 runs through the analysis program, the Valve_table.txt coefficients may have to be modified. Contact Sunset Laboratory Inc. for further information regarding these settings.
13. A new example of SamTimePar1.txt file is also included. The format remains the same as previous versions.
14. Once you have installed these files, you will need to remove the old instrument control and calculation software shortcut ICONS from the desktop and replace them with shortcuts to the new control and calculation software executable files installed by SETUP. Visual Basic 6 will not let us do that for you. Do not drag the actual executable files to the desktop. Be sure you only make a shortcut and drag shortcut Icon to the desktop.

Depending on the version of the control and calculation software you are using, there will be a number of obvious changes in the new code. The major changes include:

- The latest version of the software places the temperature ramp control coefficients into the PAR file so that the user can optimize each ramp for more precise temperature control. Please review examples of the PAR files (old vs. new) for the changes. There are descriptors at the end of the file regarding the settings and how changes are made to improve the ramp controls. Contact Sunset Laboratory Inc. for further details.

- The new version automatically calculates the complete data results files at the end of each data analysis. It will no longer puts out a subset file called “YourFileName.res”. The new files are complete as if you manually ran through the set as currently required in any software version number 8XX or lower. This allows you to log into you computer at some fixed time interval and download complete data sets without running through the calculation routine. You could also have the computer upload results files on a timed basis without attendance. You may still run the calculation software manually at any time to review or re-calculate data as you see fit. The operation is seamless. The calculation algorithm will always be the same for both programs. No more small differences between “Control Software” calculated subsets and full calculation software results.

- The new software has better control of the flows on the of the carrier gases. Adjust your carrier gas inlet pressures to between 15 and 30 PSI for R4 instruments (6 to 8 for R3 instruments). The control software will then optimize the starting points for each mode over the course of several analyses and refine those as conditions change.

- After the system has run for several cycles, you can "AUTOZERO" the gas flows. This is performed by having the system in "IDLE". Check the Valve_Values_Table on the lower screen. When the window pops up, hit the "AUTOZERO Gases" button and wait for the instrument to complete the cycle. It will then save the new zero intercepts in the scinst1par.txt file for current and future reference.

- There is an "Autostart" function that pops up each time the software is started. If left unattended, it will automatically start the instrument up in using the Sample File named SamTimePar1.txt located in the \OCECPAR\ subfolder. This is useful for recovering from a power failure. If the software is installed on a newer desktop, the user can go into the computer setup files available at the startup of the computer and set the power recovery mode to restart the computer after the loss of power. If a shortcut to the RT OCEC software has been placed in the "All Users" startup menu, then the system will recover and Autostart from a hard power failure unattended. Laptops should use one of the newer UPS systems which will keep the laptop operational for up to 2 days after a power failure. The software will recover and restart the instrument in either case once power is restored.

- The new software has a number of new Error Message boxes that pop up in the event of a number of problems that may occur. These include the loss of support gases and the failure to heat as a result of a burned out heating coil.

- Two different options for digital output to a data logger are available. The default is a formatted but not fixed length format while a fixed length format can be selected by checking a box in the lower screen. Contact Sunset Laboratory for more information on this option.

- Several bugs and errors that were a nagging problem with the older software have been corrected. These include the occasional failure to write results files to the disk that were the result of a "Divide by Zero" error. This apparently was embedded in the old calculation routine in the control software. This has been removed.

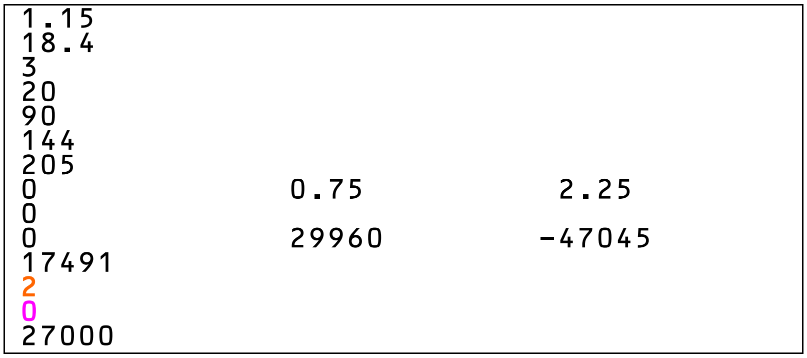
- The use of "0" time collections for QAQC purposes no longer results in the loss of the "Start Analysis" button that sometimes occurred in the older software requiring a restart to clear the flag.

- The new software versions will collect samples up to 24 hours without hanging up.

Serial port configuration - NDIRpar.txt and Scinst1par.txt files

On customer provided computers and software upgrades of existing systems, the serial port designations in the par files for the computer and system must be set up to match the hardware configuration.

1. Scinst1par.txt – This file is the parameter file for the instrument and contains many control and offset parameters to keep the instrument functioning properly. Any changes must be made carefully as errors can cause significant problems with the instrument.
2. As noted in the example file above, the communications port number is located in the line directly above the “19200” number (19th line from the top). Change the serial port number to match the hardware configuration of your computer. NDIRpar.txt example below:



```
1.15
18.4
3
20
90
144
205
0             0.75          2.25
0
0             29960        -47045
17491
2
0
27000
```

3. You will need to change the 10th line to match your hardware serial port (orange) connection to the NDIR.
4. If you are going to use a data logger with serial input, you can send the data through a 3rd serial port designated in line 11(pink). Contact Sunset Laboratory Inc. for more information on the data logger output format.

New Computer Setup Details

1. From Control Panel locate the “Display” Icon
2. Go to “Screen Saver” and set it to “None”
3. In that same screen, there is a “Power” button in the lower right. Click that button.
4. Set the “Power Scheme” to “Always On”. This will by default, leave the hard disks on all the time. You can set it so it turns off the monitor after some period of time that you are comfortable with. This is better than the screen saver mode which can

consume a considerable quantity of memory and cause the software to drop communications.

5. In the “Advanced” tab, it is recommended that you have the computer ask you what to do when you press the “shut off” button.
6. On laptops, have it “do nothing” when you close the top. It should not ever go into “sleep” or “hibernate” mode.
7. If you have purchased a small desktop, you can go into the EEPROM setup of you computer when it starts up by holding the F2 key. In the POWER scheme, you can have it Resume what ever condition is was in the event of a power outage. For example, if it was on (and presumably collecting samples) it would re-boot when power comes back.
8. You should set the computer up so that the default user does not have a password and does not come up in the “Welcome” screen.
9. Go back to the instrument control software folder \OCEC_Inst_Software\ and create a shortcut to the instrument control software. Now in “Explore” go to

```
   C:\Documents and
Settings\
        \All users\
        \Start Menu\
        \Programs\
        \Startup\
```

10. Now drop the shortcut created in step 9 into the \Startup\ folder. Now in the event of a power failure, the computer will reboot to the default user desktop, the Sunset Software will Autostart and the instrument will begin sampling under the default conditions you set up initially. Thus the system can recover from a total power failure without the aide of a UPS system.

Nagging Problems

- Windows still occasionally fails to shut down the NDIR on a normal EXIT from the software. When this happens, the NDIR continues to operate and send data. If you subsequently reboot the computer, on some laptop computers with PCMCIA serial cards, this will result in the installation of a “Serial Ball Mouse” driver that causes essentially all loss of mouse control. In the event that this happens, you should;

    1. Turn off the CPU/Fan switch on the instrument for several seconds to reboot the CPU and NDIR.

2. Shut down the computer. While it is down, pull out the PCMCIA card. Restart the computer. After it completely recovers, then re-insert the PCMCIA card. This should clear the problem driver condition.
3. In the future, if you are going to shut down and reboot (as we suggest every time you service the instrument) then you should also turn off the CPU/fan switch on the instrument to clear it as well. This will prevent the previous problem.

- Occasionally, there are serial communication losses. This is not common but can usually be corrected by setting the serial buffers to a smaller value so that Windows services these more frequently. Ask Sunset Laboratory about how to set these up for your system.

Oven Installation

The main quartz oven has two heated zones: the front oven and the back oven. New instruments will have the oven and heating coils installed, conditioned and ready to operate. The front oven is used to collect and analyze the samples. It is only heated during the analysis phase while remaining at or near ambient temperature during the sampling phase. The back oven contains the MnO_2 oxidizer and is heated to 850^oC during the analysis phase. In order to insure a controlled sample temperature, the back oven is maintained at 500^oC during sampling. The two zones will be delivered pre-configured to perform at the prescribed temperatures and the oven installed. For the procedure for oven installation, see the servicing chapter on page ____.

Laser Installation

The laser is mounted within the optical system and no mounting or adjustment is necessary. For the procedure for the laser setup, see the servicing chapter on page ____.

NDIR Signal

The NDIR serial port is connected to the 9-pin DIN connector located on the back/center of the instrument. This cable is connected to the other serial port on the computer.

1. Go to the “C:\ocecpar\ndirpar.txt” file and type in the correct serial port number (2 – 6). (See section “Files used by the Sunset Laboratory Inc. RT-OCEC analyzer”).
2. When the instrument starts, the “CO_2” signal reported on the screen will begin reporting a CO_2 level after about a minute of software initialization.

Flow Sensor Calibration

The instrument will come with an initial flow calibration from the factory. The flow calibration parameters are contained in the "C:\ocecpar\scinst1par.txt" file. Flow sensor calibration is a multi-step process which must be performed in the correct order. Initial offsets and a calibration check will be performed on-site by the Sunset Laboratory Engineer. Because the sensors work using the carrier gas heat capacity and have been exposed to air during shipment, the initial calibration may change over the course of the first week or so of operation. Thus, the flows should be re-calibrated after the system has been given sufficient time to burn in. Observe the Sunset Laboratory Engineer carefully during this phase of the installation and follow the procedure carefully. If performed properly and the data logged correctly into the instrument parameter file, the observed flow reading on the flow table should be correct (± 5 %) for an extended period. Re-calibration once a year is recommended. The slope values for the sensors tend to remain fairly constant over time but the Zeros do drift. It is recommended that you AutoZero the sensors each week as a routine procedure while servicing the instrument.

Initialization

1. Switch on the CPU/Fan switch to the Main Oven Box only! *Do not turn on the heated zone power yet!*
2. Click on the Semi-Continuous OCEC Startup Icon. The system should begin operation by reporting temperatures and showing flow sensor flow rates.
3. If the system does not start, shut down the software from the PC and restart.
4. If it does not start this time, go into the "C:\ocecpar\scinst1par.txt" file and be sure the serial port setting is correct (1 – 6) for the instrument and try again. (See section "Files used by the Sunset Laboratory Inc. RT-OCEC analyzer"). The instrument software should start and begin controlling the instrument. If you have problems, contact your Sunset Laboratory Representative.

Final Installation Steps

1. Restart the software to initialize the new coefficients. The software will control the flows for each of the sample and analysis modes. The temperature for the "Back Oven" should begin to climb on the software monitor screen. After a short period of time, this will stabilize at their preset default settings: 500°C.

2. After this has been operational for at least 15 minutes, go to the menu and run the “Clean Oven” step. This will heat front oven to clean it out and burn off any residual binder from the heating coil sheathing, clean off the new filters and remove any residual organic material from the front oven. The instrument should now be fully configured and ready to perform the carbon calibrations and begin running samples.

Pre-start Checklist

☐ Install Sample inlet using 3/8 inch tubing. The sequence should be:

1. Air Intake at 2.5 um cut Cyclone
2. 3/8 inch tubing to area of instrument
3. Denuder (note directional flow of air)
4. 3/8 inch tubing into Sample Valve inlet

☐ Install tubing from gas cylinders.

Use clean 1/8 inch copper or S. S. tubing. NoOx tubing may be used, but the length should be kept to a minimum. DO NOT use Teflon because of the diffusion of CO_2 through its walls.

☐ Install tubing to pump.

Use ¼ inch copper or plastic tubing. This does not have to be clean because it is downstream of the sampling filter. Make sure **NOT** to use thin wall tubing that might collapse under vacuum. The sequence should be:

1. ¼ inch tube to vacuum pump
2. ¼ inch tube to Instrument

☐ Connect Control cable of Pump (or Solenoid in Instruments made before June 2010) to 120 VAC control box.

- The 120 VAC Solenoid may be left out and the outlet of the ballast tank connected straight to the vacuum pump, ***however this only applies to instruments made before June 2010 that require a ballast tank***.
- In all cases, the pump itself should be connected to the 120 VAC control box

☐ Connect the 120 VAC Power Cord to the plug on the back of the instrument

☐ Connect the CPU serial cable from the computer to the CPU Serial Port

☐ Connect the NDIR serial cable from the computer to the NDIR Serial Port

☐ Install software

☐ Initialization

Operation

The purpose of this section is to provide information on the use of the instrument.

Software overview

A PC-type computer is required for operation of the instrument and must have Microsoft **Windows XP Professional** (Service Pack 2 or higher) installed as the operating system. **Windows VISTA(updated with all Service Pack 2) and Windows 7 are also compatible and may be used.**

The software for instrument operation and results calculations are designed to run on the included Computerized Display/Data Acquisition System. This software is included with the Base Instrument. The PC based software is currently written in Microsoft Visual Basic 6.0. Software is provided either with a computer supplied by Sunset Laboratory or on an Installation disk. (See software installation section XYZ2)

1. Instrument Operation Application - controls the instrument operation and data collection during sample analysis; saves the raw data for calculations later.

2. Calculation Application - uses the raw data produced from the instrument and calculates organic and elemental carbon, creates a spreadsheet-usable reduced data file of the results and optional prints the individual analysis report.

Controls on the instrument

Essentially all of the control components of the instrument are controlled by the PC. The user can set up most all of the variable features from within the software environment. See section XX below for a complete discussion of the software.

Samples

The analyzer is deployed to the field site. It collects airborne particulate samples on an internally mounted filter and analyzes the sample on a semi-continuous basis. There is no option for replicates without a second sampler. Sample data are stored in raw data files. Additionally, a short result file is printed to a file at the end of each analysis. An optional output can also be transmitted to a data logger equipped with a serial input. The data should be considered irreplaceable and should be backed up on a frequent basis to some sort of permanent media such a CD or tape.

Materials and equipment

See the example Standard Operating Procedure In Section XXX for a detailed discussion of the required materials and equipment for routine sample collection and instrument calibration and maintenance.

Operating parameters

- Quartz Punch Size: 16.5 mm diameter punched using the provided filter punch. Deposit size related to insert inlet size

- Standard Analysis time: ~ 8.5 minutes (not including 2 minutes of purging time). Other methods are possible by change the appropriate parameters

- Sampling Time: pull-down list options ; or file controlled

- Check up the box for “cycle” to continuously measure OC/EC. Then the instrument starts to run on the following minute.

- Check “start analysis” button for 1 cycle measurement.

- Clear the check mark for “cycle” to make the current measurement the last measurement.

- Output Data
  - During sampling, data is averaged every 1 minute.
  - During analysis, data is averaged every 1 second.
  - Data is saved and a complete set of calculations are performed at the end of the analysis.
  - Preliminary EC/TC measurements are calculated and plotted at the end of each analysis.

- Output file can be copied and calculated during sampling, but not during analysis of the current sample. This will result in a “file conflict” error and could terminate the run.

- Windows XP Professional is recommended as computer operating program. Window 98 could cause some problems in the communication between computer and the analyzer. Windows Vista is not currently supported

- Output Data file name is not updated while collecting the sample or analyzing. The measurement data are stored in the file at the end of each analysis. Disruptions in the operation result in the data loss only for the current sample.

Startup and Running a Sample (the Short List)

Before proceeding, assure that the gas lines are properly connected to the back of the instrument and that the gas cylinder valves are all open and the secondary regulator pressures are set from 8 to 10 PSI on Model 3 instruments and 15 – 20 PSI on Model 4 instruments. Also, if there are ON/OFF valves inline for the gases, make sure they are open.

1. Check cylinders for sufficient volume and pressure.
2. Be sure that the serial port cables are installed correctly and the software configured correctly.
3. Turn on the Computer.
4. Turn ON both switches of the Semi-Continuous OCEC Instrument (the back left hand side for Model 3 and lower right front for Model 4). Then start the RTOCEC application program on the PC by clicking on the ICON located on the Desktop.
5. Make sure the computer and instrument CPU link up. Note the temperature boxes and the flows on the flow table. They should start changing as the instrument stabilizes after startup.
6. Check the pressure. In the Off-line Mode it should be in the range of 0.1 to 0.5 psi depending upon flow rates and temperature of the Back Oven. While analyzing On-Line, it should increase to as much as 3.0 psi.. This Oven pressure will change, depending upon flow rates and resistances of the MnO_2 Oxidizer Bed.
7. Check the instrument gas flows on the table to be sure they are stable.
8. Install new filters if necessary.
9. Clean Oven by selecting CLEAN OVEN from the OPTIONS Menu.
10. Enter a sample name in the SAMPLE ID #.
11. Select the proper PARAMETER FILE to be used for analyzing the samples. By default it is “rtquartz.par”.
12. If you desire the raw data to go into an automatically generated file each day, the default ending of “\” is already selected. To have the data go into a file of another name, type the name of the file in the OUTPUT RAW DATA FILE box after the “\” already there. Be sure and end the filename with the extension “txt”(example: yourfilename.txt)
13. Determine how the instrument will be cycled; either by sampling for a fixed time followed by the analysis; or by starting sampling times and pre-determined times and lengths from an external file.
14. Make sure the Cycle Box is checked for continuous operation.
15. Click on “Start”.

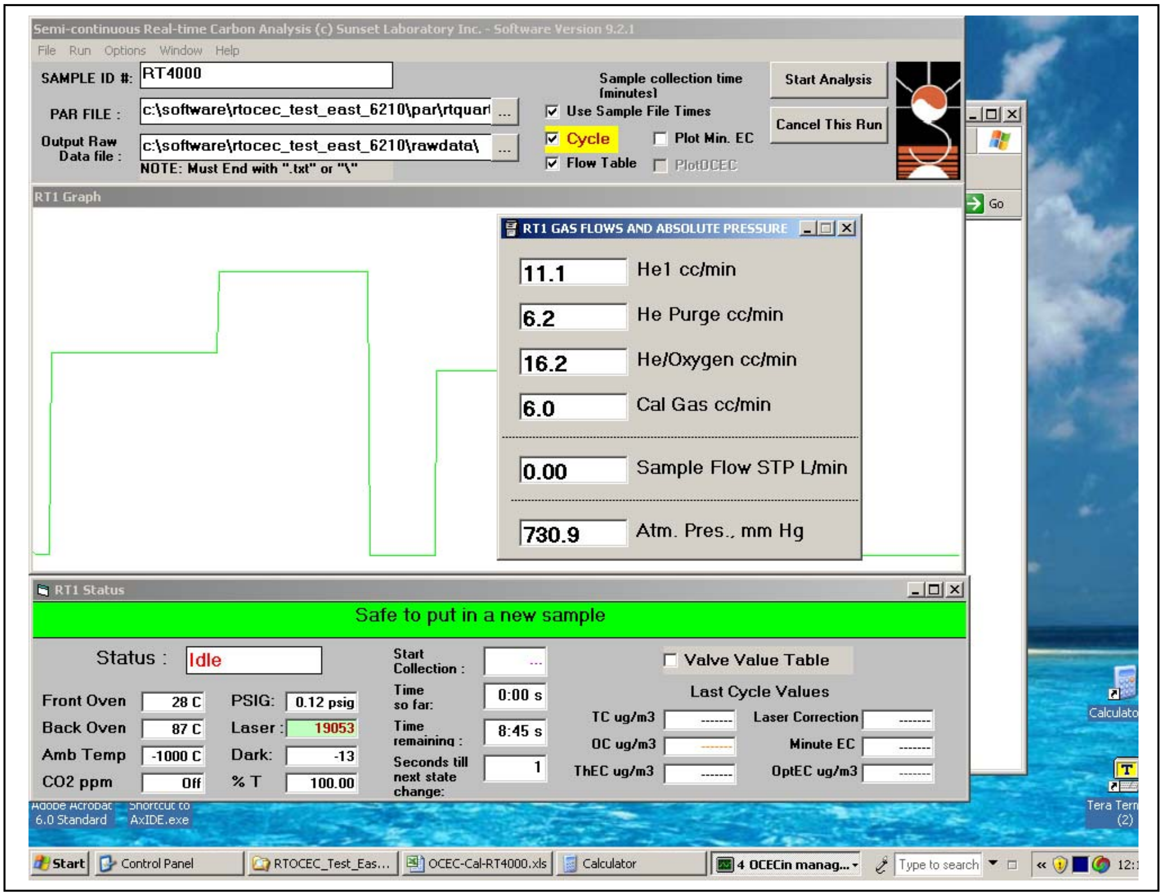
Shutdown

1. If you are intending to return to the Analyzer later in the day or over the next several days click on the upper left “Run” menu and “Exit All Off”
2. Switch off the “Power” switches.
3. Close all of the gases at the regulators on the cylinders.
4. Go have a Beer.

Detailed Software Procedures

The Sunset Laboratory Inc. software is designed to generally be semi-automatic and self-directing. It has numerous error checking routings and error message flags to help in the operation of the instrument. The following section will present clips from software screens to help in the fundamental operation of the instrument.

To initialize the operation of the instrument, the user is instructed to click on the Sunset Laboratory Inc. startup ICON on the Desktop. The following screen will show up on initialization. If no one is present or the system is recovering from a power outage, it will "Autostart" without further attention and operate under default conditions until the user overrides the "Autostart" condition.



SAMPLE ID #: RT4000

PAR FILE : c:\software\rtocec_test_east_6210\par\rtquart

Output Raw Data file : c:\software\rtocec_test_east_6210\rawdata\

NOTE: Must End with ".txt" or "\"

Sample collection time (minutes)

☑ Use Sample File Times

☑ Cycle

☐ Plot Min. EC

☑ Flow Table

☐ PlotOCEC

11.1 He1 cc/min

6.2 He Purge cc/min

16.2 He/Oxygen cc/min

6.0 Cal Gas cc/min

0.00 Sample Flow STP L/min

730.9 Atm. Pres., mm Hg

Safe to put in a new sample

Status : Idle

Front Oven: 28 C

Back Oven: 87 C

Amb Temp: -1000 C

CO2 ppm: Off

PSIG: 0.12 psig

Laser : 19053

Dark: -13

% T: 100.00

Start Collection : ---

Time so far: 0:00 s

Time remaining : 8:45 s

Seconds till next state change: 1

☐ Valve Value Table

Last Cycle Values

TC ug/m3: -------

OC ug/m3: -------

ThEC ug/m3: -------

Laser Correction: -------

Minute EC: -------

OptEC ug/m3: -------

Important details in the Screen

Sample ID location: The default is the instrument Serial Number. The user should type in an ID that will help delineate the sample collection location and time period. The will not change until the user changes it. The use of Commas "," are forbidden in this box.

PAR File: This is the sample analysis protocol. The default is RT-Quartz.par and is a short version of the NIOSH 5040.

Output Raw Data File: This is the folder location of the raw and post-run calculated data. If the user leaves the file format (default) as shown – c:\....\rawdata\ then the raw data and calculated data will be automatically named in the format “SLI_date_code.TXT”and will be changed every day at midnight to reflect the new data. If the user opts to put in their own name, then it will remain until changed by the user. All files are appended and never overwritten to avoid loss of data.

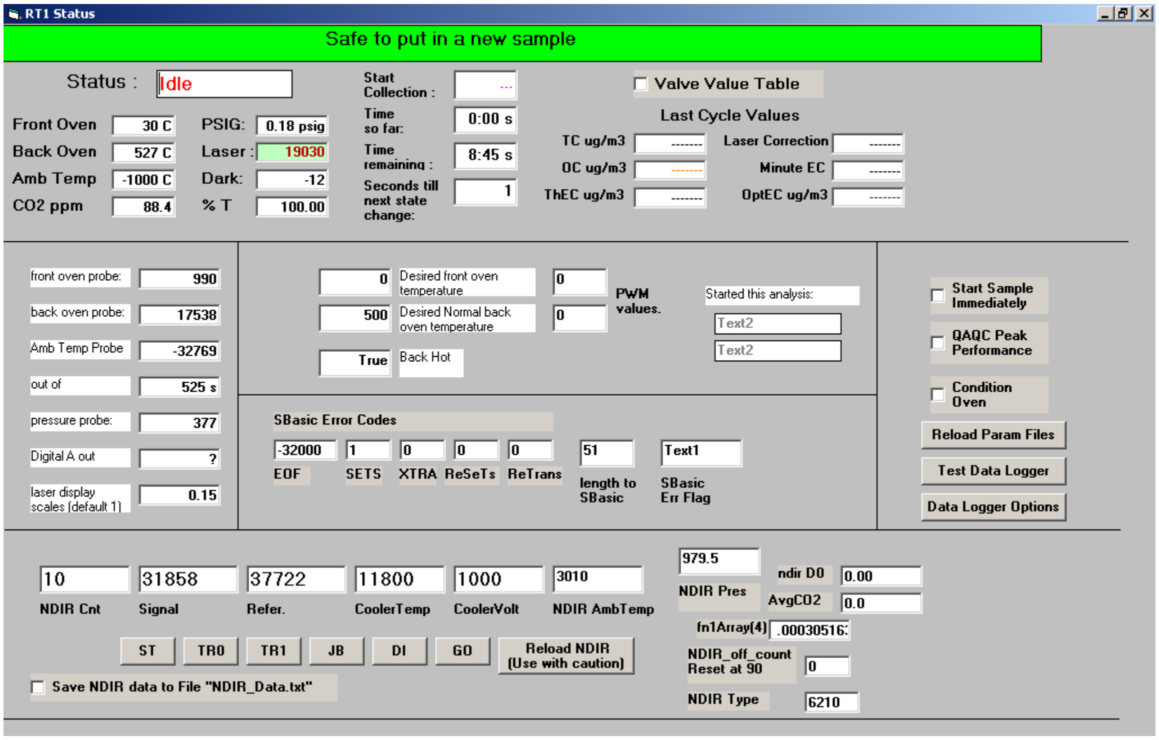
“Use Sample File Times” Checkbox: The default is to use the a file called “SamTimePar1.txt” to define the sample start times. When un-checked, a run time menu will appear that allows the user to choose a fixed collection time. The instrument will collect and analyze samples as fast as possible within this time limits

“Cycle” checkbox: The default is “Checked” and causes the instrument to collect and analyze samples until told to stop
“Flow Table” checkbox: The default is “checked” and causes the Flow rate Table to be drawn on the screen. This can be moved to a position just off of the run-time screen for continuous viewing.

“Plot Min. EC” Checkbox: The default is “Un-Checked”. This box will plot the “once per minute” optical EC during the sample collection on the screen. This is only for user observation. No files are created from the use of this box. A “Minute-EC” file is always created with the data calculation so that the user can observe and plot the Optical EC with every data set.

“Valve Values Table” Checkbox: The default is “Un-Checked”. This box brings up the voltage control valve controls used in the mass flow control of the carrier gases. This is a very powerful tool that will be discussed more thoroughly below.

More instrument parameters and control information is available by expanding the lower RT1 Status screen.


RT1 Status

Safe to put in a new sample

Status : Idle

Front Oven 30 C
Back Oven 527 C
Amb Temp -1000 C
CO2 ppm 88.4

PSIG: 0.18 psig
Laser : 19030
Dark: -12
% T 100.00

Start Collection : ...
Time so far: 0:00 s
Time remaining : 8:45 s
Seconds till next state change: 1

☐ Valve Value Table

Last Cycle Values
TC ug/m3 -------
OC ug/m3 -------
ThEC ug/m3 -------
Laser Correction -------
Minute EC -------
OptEC ug/m3 -------

front oven probe: 990
back oven probe: 17538
Amb Temp Probe -32769
out of 525 s
pressure probe: 377
Digital A out ?
laser display scales (default 1) 0.15

0 Desired front oven temperature 0
500 Desired Normal back oven temperature 0
PWM values.
True Back Hot
Started this analysis: Text2 Text2

SBasic Error Codes
EOF -32000
SETS 1
XTRA 0
ReSeTs 0
ReTrans 0
length to SBasic 51
SBasic Err Flag Text1

☐ Start Sample Immediately
☐ QAQC Peak Performance
☐ Condition Oven

NDIR Cnt 10
Signal 31858
Refer. 37722
CoolerTemp 11800
CoolerVolt 1000
NDIR AmbTemp 3010
NDIR Pres 979.5
ndir D0 0.00
AvgCO2 0.0
fn1Array(4) .00030516:
NDIR_off_count Reset at 90 0
NDIR Type 6210

☐ Save NDIR data to File "NDIR_Data.txt"

The upper segment is the same view as the default startup screen.

The middle and lower segments report many of the data acquisition, serial port and NDIR data inputs. In the event of a problem, your Sunset Laboratory technical representative may ask you to describe input from many of these sections.

Left-Middle Section: A/D raw data inputs

Upper Middle Section: Oven temperature control information
Lower Middle Section: SBasic Error Code, gives serial I/O status and error codes

Right Middle Section: Check boxes and Override buttons.

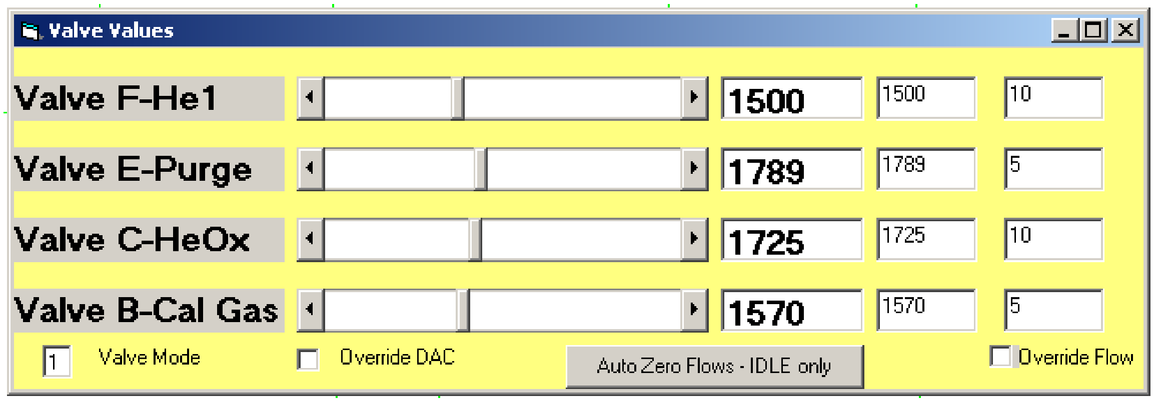
- “Start Sample Immediately”: Default – “Un-checked”; Rarely used. By default, all data collections start at the “Top of the Minute”. Occasionally users will need immediate startup because they are monitoring some process that starts at some “uncontrolled” point. Once “Checked” it will remain until the software is re-started.
- “QAQC Peak Performance”: Default – “Un-checked”; Used to over-ride the back oven temperature. Used when running “Zero time” samples to assure that the back oven temperature is held to 870C. This may be used when running standards or integrated sample punches. It is good practice to shut down the instrument control software and re-start it after running “Zero Time” samples
- “Condition Oven”: Default – “Un-checked”; Used to override the back oven defaults. By first checking the “condition oven” and then “QAQC Peak

Performance” boxes, the user can then highlight the “Desired Back Oven Temperature” value (500 in the screen display) and type in another temperature. This is used to condition a new oven or may be used by the Sunset Lab technician to correct a problem.

- Reload Parameter Files Button – If you make changes such a s flow sensor calibration coefficients, these can be reloaded dynamically by “hitting” this button. You should only do this in the “Idle” mode. This is most useful while performing flow calibrations. Do not use this while collecting or analyzing a sample. The very best way to be sure that all of the parameters are reloaded is by shutting down the software and re-starting.
- Test Data Logger Button – Sends a test string to the appointed data logger serial port.

Lower Section: NDIR Data and control buttons. These should only be used when directed by your Sunset Laboratory technical representative during trouble shooting.

Valve Values Table



Valve F-He1	1500	1500	10
Valve E-Purge	1789	1789	5
Valve C-HeOx	1725	1725	10
Valve B-Cal Gas	1570	1570	5

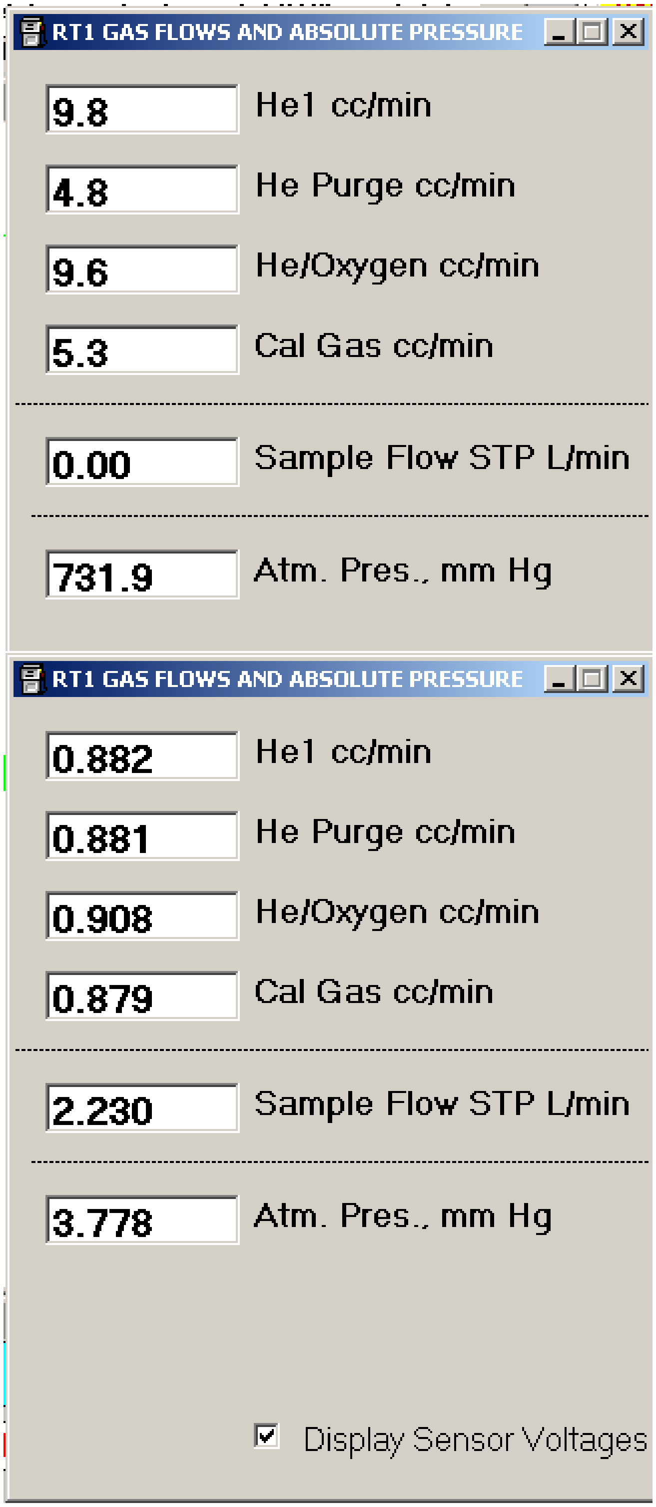
1 Valve Mode
☐ Override DAC
☐ Override Flow

The Valve Values table has several very useful functions. This table has the control valve name for each of the 4 gases used during the OCEC analysis; a "Slider Bar" indicating the relative position of the DAC (digital-to-analog converter) voltage output being applied to the valve to control the gas flow, the DAC position being set by the slider bar, the actual numerical value being sent to the DAC (second column from the right) by the software and the target flow rate of each gas (mls/min) in the right most column.

The user can control the gas flows only when the "Valve Mode" is 1 (i.e "IDLE"). There are 3 control functions the user can perform in this mode;

- Override DAC Checkbox - Default – "Un-checked"; If this box is checked, the user can control the flows by moving the slider bar left and right. This is most often used when performing leak checks. The user can plug a section of the flow system and then momentarily open then close the slider to pressurize that area to see if it leaks. (See leak check procedure).
- Override Flow Checkbox - Default – "Un-checked"; By checking this box, the user can highlight the default flow rate in the box on the right of the target gas and type in a new flow rate. The software will then automatically adjust the DAC output to control the flow at the new flow rate. This is very useful for performing flow calibrations.
- "Auto Zero Flows" Button – By hitting this button in the idle mode, the user causes the software to open up the flows to 50 mls/min for 30 seconds to purge the flow sensors then to shut down the flows for 30 seconds. For the last 15 seconds, the average zero flow voltage for the flow sensors are averaged and the new zero flow voltage is updated in the "Scinst1par.txt" file (See below for file format information). Users are encouraged to "Auto Zero" the flows weekly when they change service the instrument. The zeros tend to drift on the flow sensors while the slopes remain constant. By zeroing the flows regularly, the calibration peaks remain more constant.

Gas Flow Table



RT1 GAS FLOWS AND ABSOLUTE PRESSURE

9.8 He1 cc/min
4.8 He Purge cc/min
9.6 He/Oxygen cc/min
5.3 Cal Gas cc/min
0.00 Sample Flow STP L/min
731.9 Atm. Pres., mm Hg

RT1 GAS FLOWS AND ABSOLUTE PRESSURE

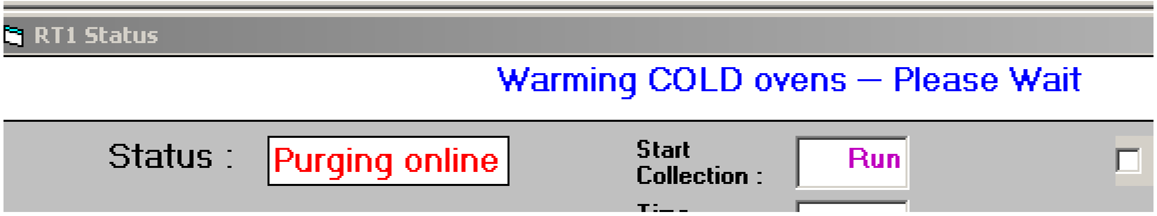
0.882 He1 cc/min
0.881 He Purge cc/min
0.908 He/Oxygen cc/min
0.879 Cal Gas cc/min
2.230 Sample Flow STP L/min
3.778 Atm. Pres., mm Hg

☑ Display Sensor Voltages

The gas flow table is used to monitor the carrier gas flows and to collect data when performing flow calibrations. The default mode is for the gas flow and atmospheric pressure data to be displayed in the actual flow rates or atmospheric pressure. By pulling down the lower edge of the screen, the “Display Sensor Voltages” check box can be exposed (Default – “Un-checked”). When checked, the actual voltage outputs for each device is displayed. These are used to perform flow calibrations. (See Flow Calibration Procedure – Section XYZ).

Error Message Screens

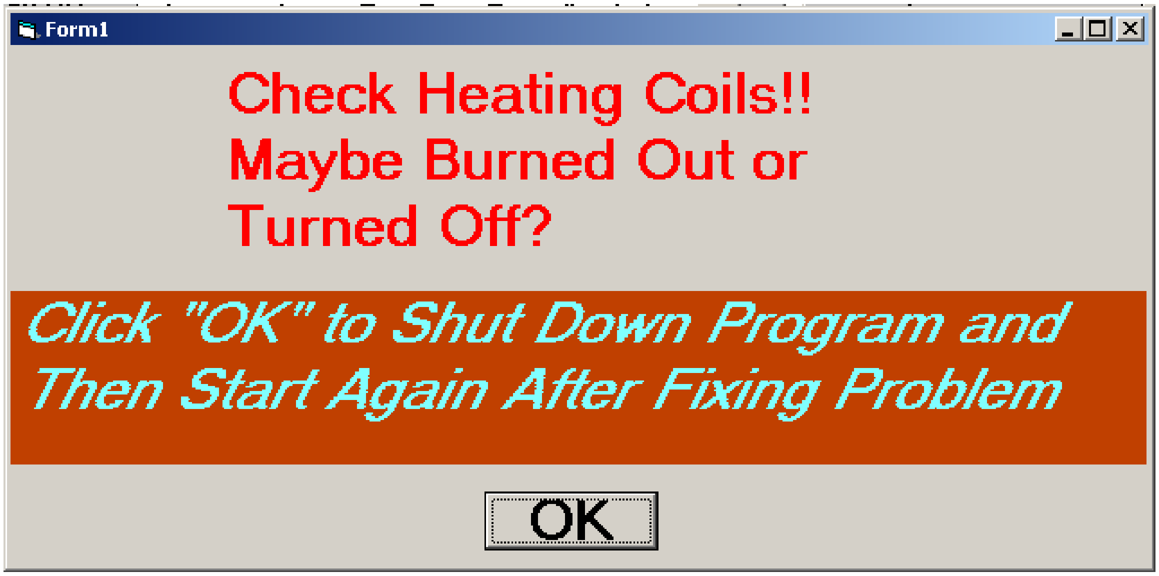
There are a number error message screens that are designed to minimize errors or report problems for users. These generally fall into two classes, 1) Hardware or performance problem related screens, and 2) User Support screens to help minimize errors.



Warming COLD ovens – Please Wait

Purging online

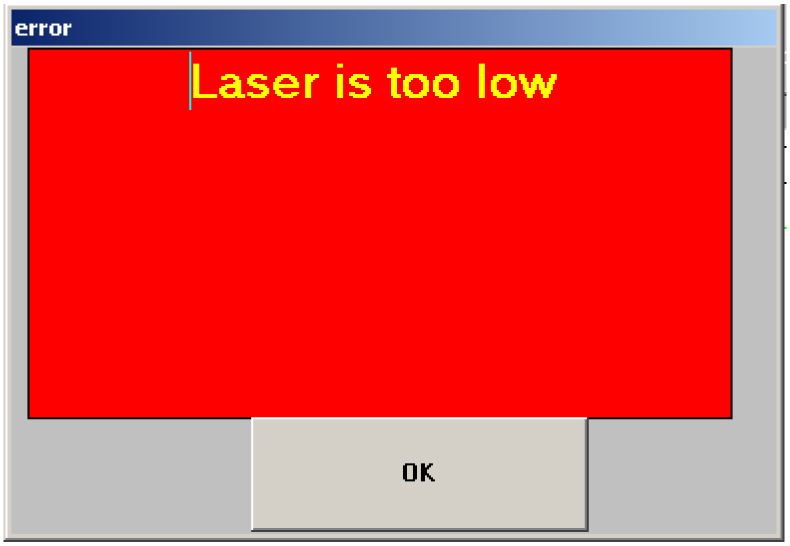
The first Hardware error message is the “Warming COLD Ovens” status bar on the lower status window. Sometimes this will flash for a short period (up to 30 seconds may be acceptable) just before the analysis but reflects that there is a potential problem. If the instrument fails to start and this window is persistently on then this likely means that the back oven heating coil is burned out.



Check Heating Coils!!
Maybe Burned Out or
Turned Off?

Click "OK" to Shut Down Program and
Then Start Again After Fixing Problem

This error message screen pops up when the front coil fails to heat the front oven during an analysis. In most cases, this means the coil is burned out. If the user has set the PID values incorrectly or has set the temperature ramp so short that the temperature could not make 50% of the ramp by the time is switched, then that will also trigger the screen.

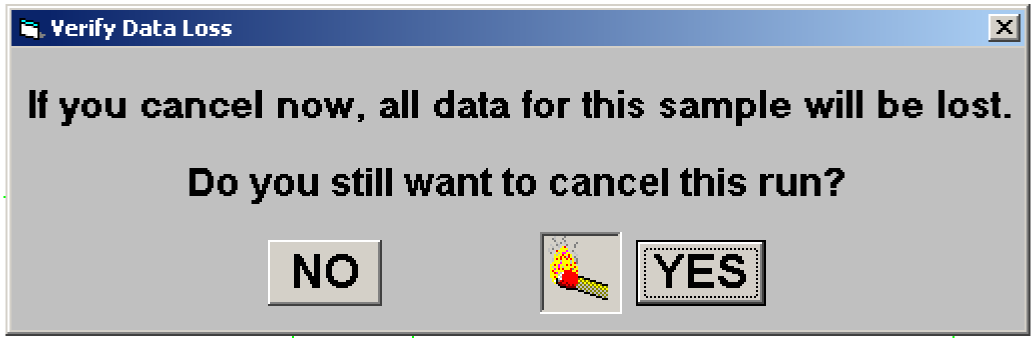


Laser is too low

The “Laser Low” error message most often occurs when the user has just serviced the instrument, replaced the filters and failed to re-insert the interlock key. This can also occur as a result of a hardware failure if the laser has failed or some other event occurs that causes a blockage of the laser beam path or a failure of the photodetector signal

Please enter new sample ID

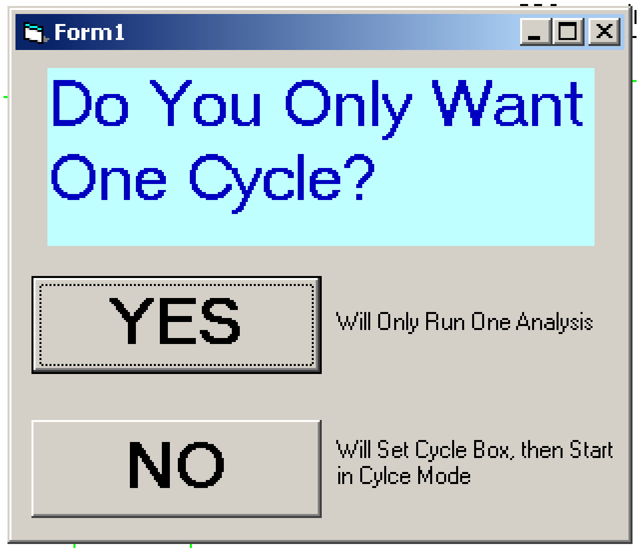
This screen pops up when the user fails to put in the sample ID name. There must be some text string in that Sample ID # box. User may use any type in any text string character except a comma.



If you cancel now, all data for this sample will be lost.

Do you still want to cancel this run?

Verify Data Loss screen pops up if you hit the “Cancel This Run” button on the top of the Start/Stop Form Window. If you stop a sample collection or analysis you will loose the current data set but no prior data sets. This form just requires you to acknowledge that data loss will occur if you continue.

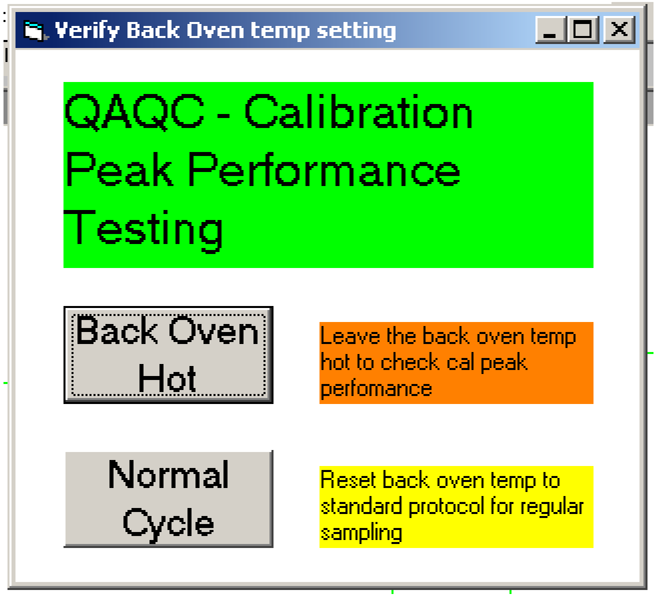


Do You Only Want One Cycle?

Will Only Run One Analysis

Will Set Cycle Box, then Start in Cylce Mode

When the user starts a new run and does not have the “Cycle” Check box checked, then the software requires the user to verify that they only want one run cycle to occur. This helps prevent data loss from failure to have the “Cycle” box checked. This most often occurs after running “Zero Time” or QA samples where the cycle box is usually unchecked.



QAQC - Calibration Peak Performance Testing

Leave the back oven temp hot to check cal peak perfomance

Reset back oven temp to standard protocol for regular sampling

This message screen pops up if the user has been running “Zero Time” samples or QA samples and has the “QAQC Peak Performance” check box checked. The for forces the use to verify that they wish to continue to leave the box checked. This would be undesirable in the event that the QA work was complete and the user was ready to continue with normal cycle testing.

Note: It is good practice to shut down the instrument, control software and computer routinely at the end of QA testing and instrument servicing to assure that all variables and check boxes are cleared and that the computer memory manager is re-set to minimize the possibility of the computer going into the Page Swapping mode or from Data loss if the control software is not properly setup for normal operation. This is best insured by restarting everything from scratch.

Note: If an error occurs when trying to save the data to this file (for example, if the file happens to already be OPEN by another application), then the raw data will be stored in a default file at the C: hard drive level, called "C:\OCEC_RawData.txt". This is to assure there is no lost data.

File Formats

The Sunset Laboratory Inc. analyzer uses several parameter files to set up and maintain control of the system during operation. These are used for flow, temperature, sampling and analytical method control. Earlier file formats are not compatible. Contact Sunset Laboratory Inc. for conversion of older files to the latest file format. Examples of these files and what each line means are provided below:

1. **c:\ocecpar\scinst1par.txt –** This file contains temperature and flow calibrations as well as several general settings.

0,0,398.24,-340.93 : ‘ He1B3, He1B2, He1B1, He1A
0,0,396.22,-345.13 : ‘ HeBkFB3, HeBkFB2,HeBkFB1,HeBkFA
0,0,261.12,-226.6 : ‘ HeOxB3, HeOxB2, HeOxB1, HeOxA
0,0,328.89,-286.18 : ‘ CalB3, CalB2, CalB1, CalA
0,0,284,-260.1 : ’ PresB3,PresB2,PresB1,PresA (AtmPres)
1 : ‘ Pressure zero offset (Oven Pres)
134 : ‘ FID offset (No Longer Used)
1 : ‘ Front oven temp offset (raw a/d)
1 : ‘ Back oven temp offset
1 : ‘ methanator oven temp offset (N/A)
60 : ‘ Sunset minute coefficient
1 : ‘ Ambient temp offset
600 : ‘ Pressure transducer coefficient
.3,15 : ‘ Back ov power coefficient, time constant
1 : ‘ Com Port Number
19200 : ‘ baud rate
10 : ‘ delay seconds after reset
0,0,6.1,-5.5155 : ‘ SamB3,SamB2,SamB1,SamA SampleFlow
-0.0066,-0.0000,-0.0066 : ‘ PID for mass flow control valves
120 : ‘ AC input voltage
1.24 : ‘ Punch Area, sq cm
19.3 : ‘ Calib Const, ug C
4 : ‘ Transit Time, seconds
RT-4000 : ‘ Instrument Name
RTCalc513.exe : ‘ Name of the calculation software

NOTE: No text descriptors are allowed on the lines as shown here. All lines must be in the correct order and have exactly the correct number of commas or TABS. The above presentation format is shown for clarity only. Any errors can result in an out of control condition of the instrument. Only make changes with the guidance of Sunset Laboratory.

2. Data control for the NDIR system is through the file called **“c:\ocecpar\ndirpar.txt”**. It has the real-time calculation coefficients as well as the serial port numbers for acquisition of the real-time NDIR-CO$_2$ measurements and Data Logger Port, if any. These are shown as follows:

1.23 : Actual filter deposit size in cm^2
18.5 : Calibration loop constant in ugC
5 : transit time in seconds
30 : First peak begin time
90 : Second peak begin time
150 : Third peak begin time
210 : Fourth peak begin time
0,29828,-45387,15958 : NDIR Calibration Coefficients

```
0,.75,2.25,0                    : OptEC cal coefficients
5                               : NDIR serial port number
0                               : Data logger serial port # (0 if none)
12500                   : NDIR Source Temperature Coefficient
.00002                  : NDIR slope correction (Model 6210 only)
```

3. This file is also used by the RTOCECCalc program and must exist in a file on the C:\ hard drive called **“c:\instpar\”** while running it also. Note that the final number represents the Serial COM Port number which is connected to a Data Logger. If no Data Logger is connected, this value should be set to 0 (zero).

4. Another significant file is the one called **“C:\ocecpar\valve_table.txt”**. This file contains the control coefficients for the mass flow control system.

```
0,0,0,0,0,0,0,0,0,0,0, 1.0                  : Sample valve
100,5,0,0,5,5,5,5,0,0,5, 0.95               : CalGas Valve
50,0,5,0,0,0,0,15,0,15,25, 0.95             : Helium Oxygen
0,0,0,0,0,0,0,0,0,0,0, 1.0                  : Helium3
50,5,0,0,25,15,5,5,5,5,5, 0.95              : Helium purge
30,65,5,0,90,90,65,50,65,50,40, 0.95        : Helium 1
0,0,0,0,0,0,0,0,0,0,0, 1.0                  : Hydrogen (N/A)
0,0,0,0,0,0,0,0,0,0,0, 1.0                  : Air (N/A)

' table values are in mls/min and correspond to the following
' operation modes
'max-change,idle,standby,collect,purge offline,purge
online,Helium,oxygen,CalHe,CalOx,clean oven, % reset
```

The first number is the raw DAC value for maximum allowed change per cycle while the next numbers are the flow settings (mls/min) for each control mode.

Control of the sample-time is made by either the pull-down menu setting on the instrument screen or by a sampling-file containing the actual start times and length of collection. The pull-down menu system simply runs the instrument as fast as it can collecting for a desired sample time and then analyzing the samples. The “Use Sample File Times” method will start at desired times and collect for a fixed number of minutes, then allow a period of time to purge, analyze and cool the oven.

5. This file is called **“c:\ocecpar\SamTimePar1.txt”** and consists of a start time (24 hour clock 00:00 – 23:59), and sample time in minutes. It does not have a fixed number of lines nor does it have to be in sequential order. HOWEVER, you must allow proper time for the purge time, sample analysis and cool down before beginning another sample. If you do not allow enough time, the system will skip a segment and wait for the next occurring start time. An example file is given below for collections starting on the even hours for two hour cycles.

```
0:00,105                : No text allowed here but this is 105 minute
2:00,105                : sample, 12 minute analysis, 2 min purge and
4:00,105                : one minute extra cool down time
6:00,105
8:00,105
10:00,105
12:00,105
14:00,105
16:00,105
18:00,105
20:00,105
22:00,105
```

*Make sure there is **absolutely nothing** on (including carriage returns and blanks) on or below this line. If so, the software will find a variable "mismatch" and default to the non-file mode or fail to run more than one cycle.*

6. Operating analysis files are given as "name.par" files in the \PAR\ folder of the operating software. The default method is RTQuartz.par and is shown below:

```
Helium, 10, 1               : No other text is allowed on these
Helium, 65, 325             : lines. Helium is the carrier gas
Helium, 50, 475             : the center number is the time in
Helium, 50, 600             : that mode in seconds
Helium, 90, 870             : the last number is the target
Helium, 40, 0               : temperature.
Helium, 15, 550             : a zero in the last number means
Oxygen, 30, 550             : turn on the cool down blower
Oxygen, 45, 625
Oxygen, 45, 700
Oxygen, 45, 775
Oxygen, 90, 870
CalibrationOx, 150, 0
' All done!
' The last entry *must* be "go offline and turn blower on".
Offline, 1, 0
' end.
```

Note that there MUST NOT be any commas (",") in the description or comment sections.

Data Analysis

The purpose of this section is to provide information on the OC/EC analysis program, assist in determining what values are appropriate, and provide remedial action for problems.

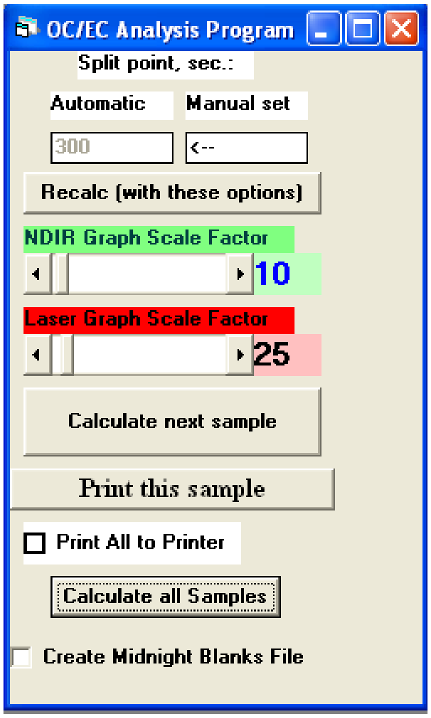
OC/EC Analysis Program

The Sunset Laboratory OC/EC Analysis Program is used to calculate the results from a sample set after the data are stored under the base file name. The data are summed over the range to yield the total carbon results. The overall carbon response is based on a multi-point external calibration. The external methane standard for every cylinder is calibrated against the external multi-point calibration. The external methane standard is run at the end of every sample. This known amount is used to normalize the response factor for each sample. This essentially cancels out small drifts in detector response over time. The software determines an initial NDIR response baseline prior to the desorption and analysis. The area at each point along the thermogram curve minus the baseline is multiplied against the calibration response to determine the carbon. The automated OC/EC split point is calculated from where the laser absorbance in the oxidizing phase of the EC analysis matches the initial absorbance measured when the sample was first inserted into the oven. Carbon observed before the split point is considered organic carbon and carbon after the split is considered elemental carbon. The analyst has several options in computing the results from a set of experiments. These should be exercised with caution based on the extent of the analyst's experience. The analysis program can batch process all of the sample data sets in a file without further review. It is recommended that the analyst study each individual data set as it is processed to look for any anomalies. During the processing, the analyst can calculate carbonate (if evolved as a single peak) by using the manual integration feature in the program. When re-integrating, the program draws a baseline between the designated points and calculates the peak area. The program will then automatically call this area carbonate and subtract it from the initial area for organic carbon (which includes carbonate, if present). There is no option for validating the presence of carbonate (as there is with integrated sample filters) because all of the sample is consumed during the analysis. If necessary, the OC/EC split point can be manually set (reassigned) by moving the cursor to the desired point. The software will calculate the split based on that point. This decision is based on the analyst's experience and information about the sample.

Method

1. Click on the designated calculation software file RTCalc*xxx*.exe. This can be found in the primary control software folder on the C drive or the shortcut Icon on the Desktop.

2. The software will automatically open the raw data folder. Select a sample file to be analyzed. An uncalculated sample will be specified as the samplename.txt at the end.
3. Selecting a sample will then open up the OC/EC analysis program.
4. On the left-hand side of the screen is the icon that is shown below. From here, the split point can be changed, the scale factors can be changed, the sample can be calculated, the sample can be printed, and all of the samples can be calculated.



Split point, sec.:

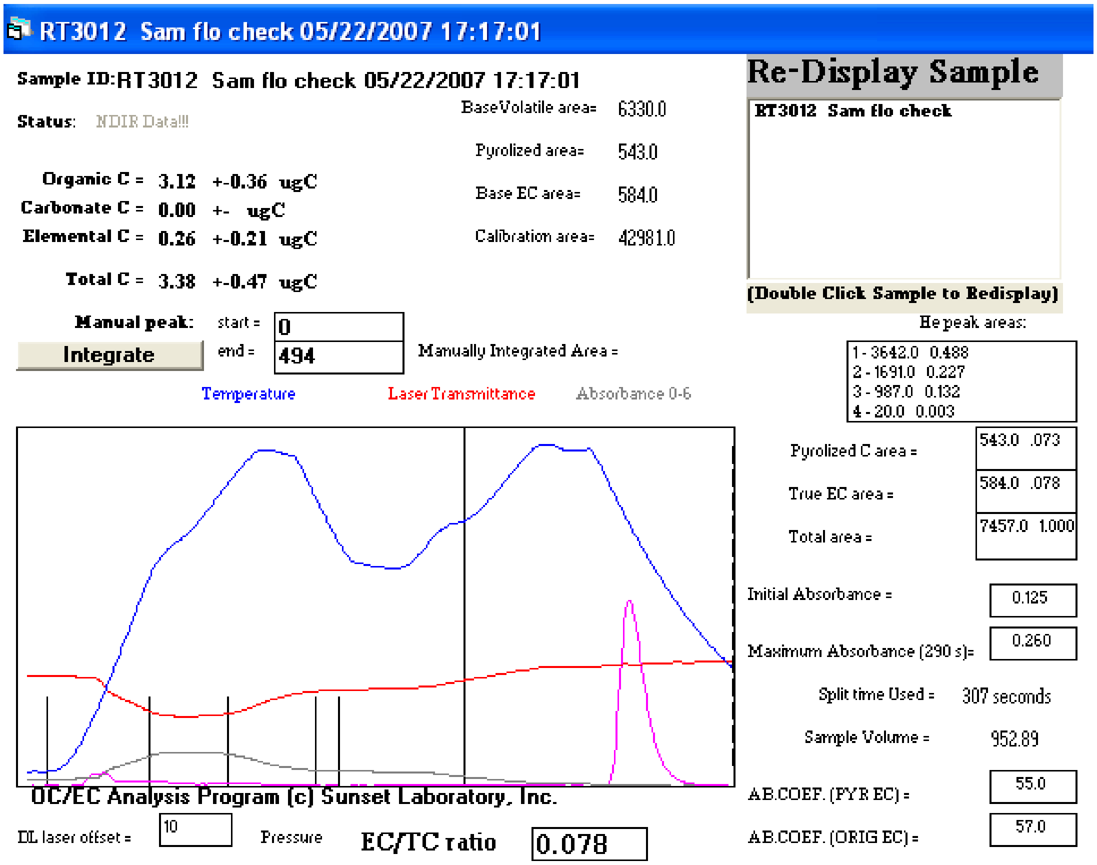
Automatic: 300

Manual set: <--

NDIR Graph Scale Factor: 10

Laser Graph Scale Factor: 25

5. Once the specifications are adjusted, press calculate sample. A screen will come up that looks like below.



RT3012 Sam flo check 05/22/2007 17:17:01

Sample ID: RT3012 Sam flo check 05/22/2007 17:17:01

Status: NDIR Data!!!

Organic C = 3.12 +-0.36 ugC
Carbonate C = 0.00 +- ugC
Elemental C = 0.26 +-0.21 ugC

Total C = 3.38 +-0.47 ugC

BaseVolatile area= 6330.0
Pyrolized area= 543.0
Base EC area= 584.0
Calibration area= 42981.0

RT3012 Sam flo check

Manual peak: start = 0
end = 494
Manually Integrated Area =

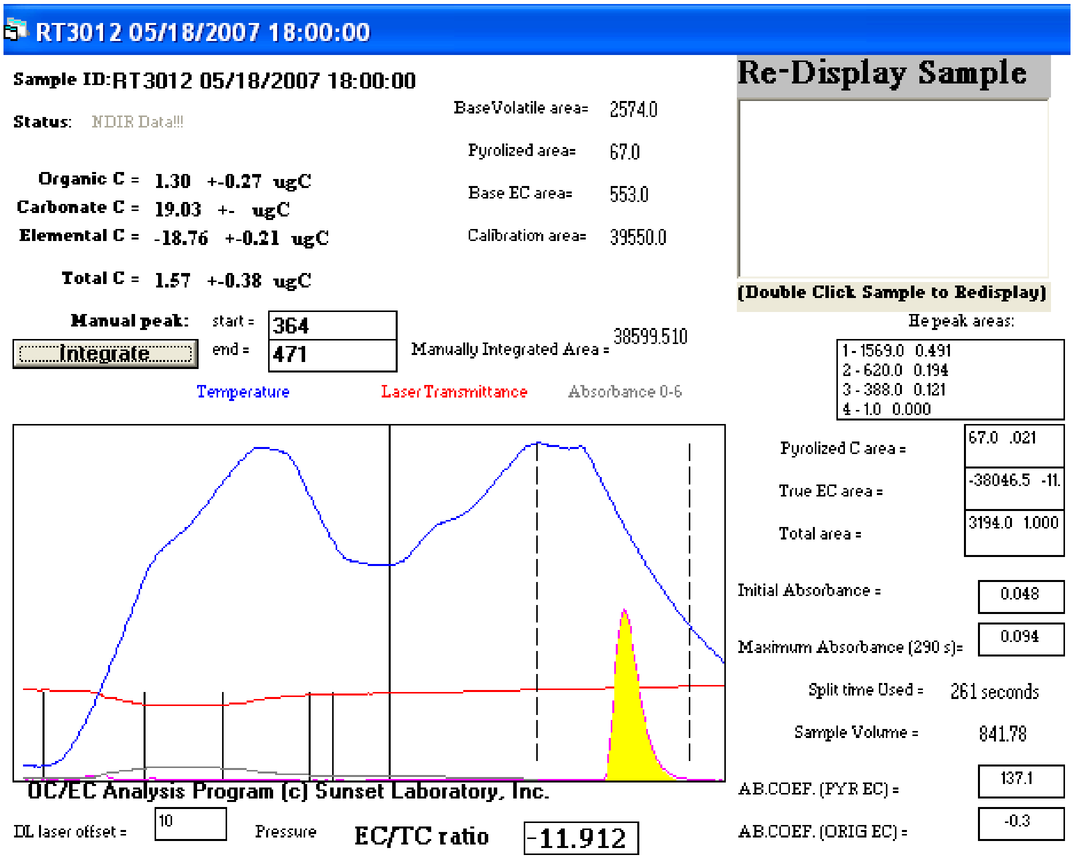
He peak areas:
1 - 3642.0 0.488
2 - 1691.0 0.227
3 - 987.0 0.132
4 - 20.0 0.003

Pyrolized C area = 543.0 .073
True EC area = 584.0 .078
Total area = 7457.0 1.000

Initial Absorbance = 0.125
Maximum Absorbance (290 s)= 0.260
Split time Used = 307 seconds
Sample Volume = 952.89
AB.COEF. (PYR EC) = 55.0
AB.COEF. (ORIG EC) = 57.0

DL laser offset = 10
Pressure
EC/TC ratio 0.078

6. If there is carbonate in the sample, the results can be changed to accommodate this. Place the cursor in the start box and press the right arrow. This will cause a dotted line to move to the right. Move this line until the beginning of the desired curve. Then place the cursor in the end box and press the left arrow until the second dotted line moves to the end of the curve desired. When the curve of carbonate is enclosed in the dotted lines, press the integrate button. The screen will then look like below. The curve for the carbonate is in yellow. The software has updated the organic carbon, carbonate, and elemental carbon on the screen.



Sample ID:RT3012 05/18/2007 18:00:00

Status: NDIR Data!!!

Organic C = 1.30 +-0.27 ugC
Carbonate C = 19.03 +- ugC
Elemental C = -18.76 +-0.21 ugC

Total C = 1.57 +-0.38 ugC

Manual peak: start = 364
end = 471

BaseVolatile area= 2574.0
Pyrolized area= 67.0
Base EC area= 553.0
Calibration area= 39550.0

Manually Integrated Area = 38599.510

He peak areas:
1 - 1569.0 0.491
2 - 620.0 0.194
3 - 388.0 0.121
4 - 1.0 0.000

Pyrolized C area = 67.0 .021
True EC area = -38046.5 -11.
Total area = 3194.0 1.000

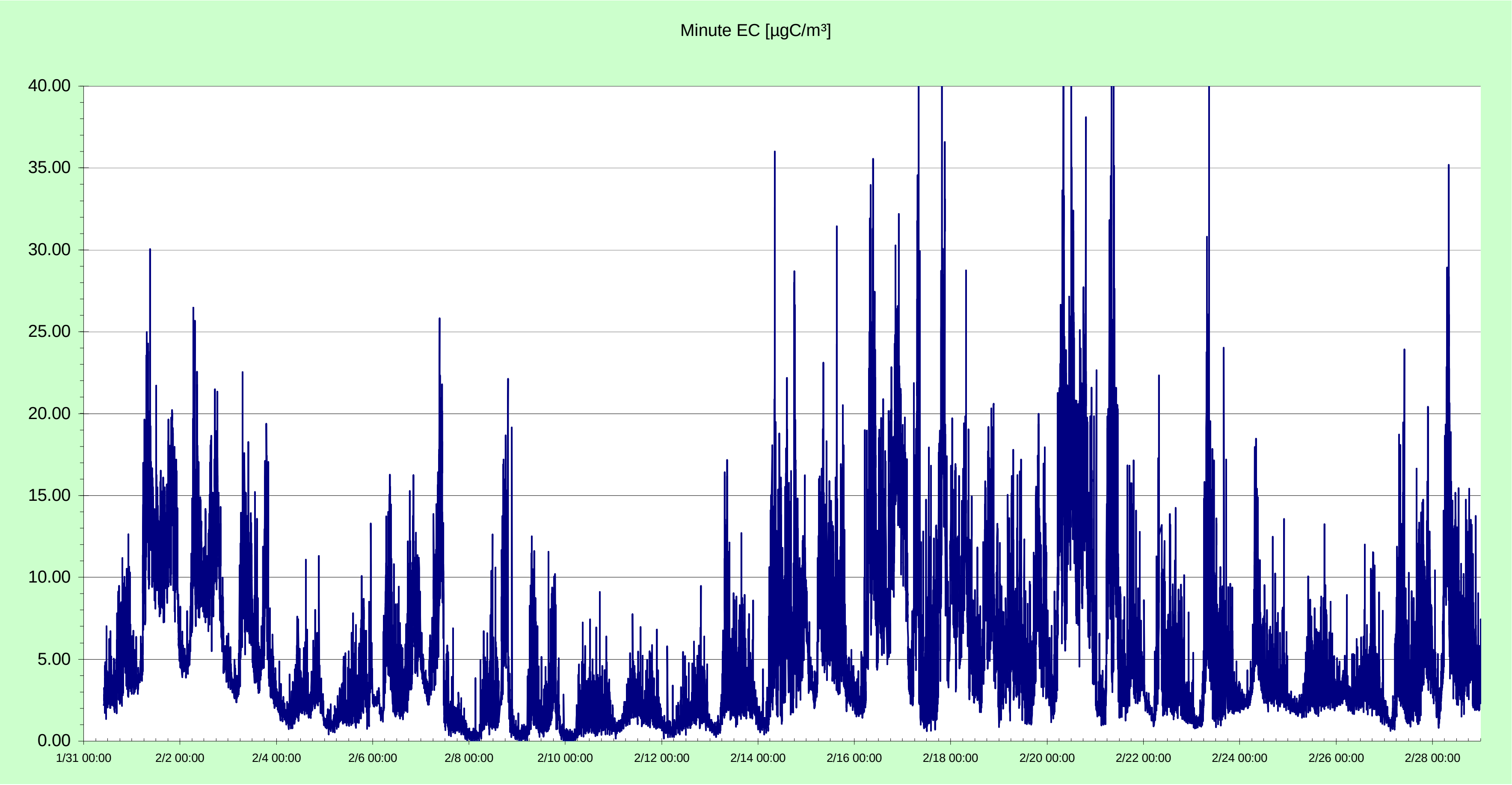
Initial Absorbance = 0.048
Maximum Absorbance (290 s)= 0.094
Split time Used = 261 seconds
Sample Volume = 841.78
AB.COEF. (PYR EC) = 137.1
AB.COEF. (ORIG EC) = -0.3

DL laser offset = 10
Pressure
EC/TC ratio -11.912

7. Once a sample set has been calculated, the results can be found in the instrument’s main subfolder on the C drive. Click on the raw data file. Under the raw data file, there will be sample sets with different specifications at the end. For each sample set there are four different files: thesamplesetname.txt, thesamplesetname_BlanksRes.txt, thesamplesetname_MinuteEC.txt, and thesamplesetname_Res.txt. An example is:

18may07w.txt
18may07w_BlanksRes.txt
18may07w_MinuteEC.txt
18may07w_Res.txt

8. To show a spreadsheet on the elemental carbon every minute, left click on the MinuteEC.txt and select open with excel. To show this graphically, highlight column B and select the scatter plot connected with lines. This will show a visual reference of micrograms of elemental carbon over time. An example of this is shown below.


Minute EC [µgC/m³]
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
1/31 00:00
2/2 00:00
2/4 00:00
2/6 00:00
2/8 00:00
2/10 00:00
2/12 00:00
2/14 00:00
2/16 00:00
2/18 00:00
2/20 00:00
2/22 00:00
2/24 00:00
2/26 00:00
2/28 00:00

9. To look at tabulated calculated data, open up the Res.txt file by left clicking and selecting open up with excel. The analysis software automatically stores the data in a spreadsheet format for compilation. Calculated errors are based on long-term historical data for replicates and instrument blanks. Over the course of hundreds of replicate runs, the relative standard deviation is typically 5%. True instrument blanks measured by running previously run filters without re-opening the oven report an average of 0.2 µgC/cm^2 background. Thus, the reported error is obtained by multiplying the carbon yield of the sample in µgC/cm^2 by 0.05 for the typical sample and instrument variability and adding 0.2 µgC/cm^2 from the typical instrument background. The spreadsheet consists of 45 different columns of data. A sample of a spreadsheet is provided over the next couple of pages. Because the spreadsheet does not fit across one page, it is separated and can be read fully by reading across one table then moving down to the next table.

Sunset Laboratory OCEC Results

Date Calculated: 05-22-2007

Sample ID	Thermal OC (ugC/M3)	Thermal EC (ugC/M3)	OptOC (ugC/M3)	OptEC (ugC/M3)	TC (ugC/M3)	Start Date/Time	Mid-time of Collection	Sample Volume
RT3012 Sam flo check	5.82347	0.360093	5.711938	0.471625	6.183563	########	########	473.8758
RT3012 Sam flo check	3.27235	0.278052	3.098515	0.451888	3.550402	########	########	952.8942
RT3012 Sam flo check	3.359359	0.427345	3.198953	0.587751	3.786704	########	########	946.8041
RT3012 Sam flo check	3.35509	0.500301	3.397363	0.458028	3.855392	########	########	947.2269
RT3012 Sam flo check	2.70024	0.463761	2.858173	0.305827	3.164	########	########	947.8253

OC(ug)	OC unc	EC(ug)	EC unc	CC(ug)	CC unc	TC(ug)	TC unc	EC/TC ratio	CalConst	Punch Area	calibration area	transit time
2.759601	0.33798	0.17064	0.208532	0	-	2.930241	0.446512	5.82E-02	19.5	1.21	38511	5
3.118203	0.35591	0.264954	0.213248	0	-	3.383158	0.469158	7.83E-02	19.5	1.21	42981	5
3.180655	0.359033	0.404612	0.220231	0	-	3.585267	0.479263	0.112854	19.5	1.21	37447	5
3.178032	0.358902	0.473899	0.223695	0	-	3.651931	0.482597	0.129767	19.5	1.21	37527	5
2.559355	0.327968	0.439564	0.221978	0	-	2.998919	0.449946	0.146574	19.5	1.21	37486	5

Split time(sec)	Manual split?(sec)	Init.Abs.	Abs.Coef.	Atm.Pres.mmHg	OCPk1,ug C/cub m	OCPk2,ug C/cub m	OCPk3,ug C/cub m	OCPk4,ug C/cub m
300	<--	6.19E-02	43.90194	770.5	4.098868	1.164694	0.368642	3.85E-02
307	<--	0.124812	56.99961	769.7	1.734017	0.805113	0.469927	9.52E-03
294	<--	0.175418	52.45912	770.5	1.733029	0.902539	0.523044	1.32E-02
290	<--	0.13679	34.92628	771.6	1.746666	0.860716	0.54693	7.13E-03
254	<--	9.03E-02	24.84818	772.4	1.524099	0.770556	0.377595	7.68E-03

Pyrolized C/cub m	True EC/cub m	Optical EC (ugC)	OptEC ABS	OptABS Coef	Opt Coef X^3	Opt Coef X^2	Opt Coef X^1	Opt Coef X^0
0.14532	0.360093	0.223492	8.00E-02	43.29061	0	0.75	2.25	0
0.258531	0.278052	0.430601	0.150603	42.31993	0	0.75	2.25	0
0.189748	0.427345	0.556485	0.192101	41.76977	0	0.75	2.25	0
0.194196	0.500301	0.433857	0.15169	42.30535	0	0.75	2.25	0
2.03E-02	0.463761	0.28987	0.10294	42.97	0	0.75	2.25	0

[redacted]

CO2_ndirC3	CO2_ndirC2	CO2_ndirC1	CO2_ndirC0	Laser Correction
0	47155.84	-77722.8	31000	0.955328
0	47155.84	-77722.8	31000	0.954584
0	47155.84	-77722.8	31000	0.954806
0	47155.84	-77722.8	31000	0.952456
0	47155.84	-77722.8	31000	0.953333

Column Name	Column Description
Sample ID	Name of sample
Thermal OC (ugC/M3)	Amount of thermal organic carbon
Thermal EC (ugC/M3)	Amount of thermal elemental carbon
OptOC (ugC/M3)	Amount of optical organic carbon
TC (ugC/M3)	Amount of total carbon
Start Date/Time	Date and time at which sample started running
Mid-time of Collection	Time in which the collection is halfway
Sample Volume	Volume of sample
OC(ug)	Amount of organic carbon
OC unc	Organic carbon uncertainty
EC(ug)	Amount of elemental carbon
EC unc	Elemental carbon uncertainty
CC(ug)	Amount of carbonate carbon
CC unc	Carbonate uncertainty
TC(ug)	Amount of total carbon
TC unc	Total carbon uncertainty
EC/TC ratio	ratio of the Total carbon the elemental carbon. Indicative of the degree of diesel in the sample
CalConst	constant for the methane carbon in the fixed calibration loop
Punch Area	Area of your filter punch
calibration area	Area of the calibration peak
transit time	time in seconds determined for the individual instrument as the time offset between the laser signal (which is essentially real time and the FID signal which occurs after the sample carbon transits through the oxidizer oven, methanator oven and associated tubing. The FID results are shifted in time that many seconds so that the data correspond to the observed laser signal.
Split time(sec)	laser computed split time between OC and EC
Manual split?(sec)	split time that can be set by the analyst if they choose
Init.Abs.	Apparent absorbance based on the initial laser signal and final laser signal after analysis
Abs.Coef.	Apparent absorption coefficient of the EC on the filter based on the Thermally measured EC and the Initial Abs.
Atm.Pres.mmHg	local apparent atmospheric pressure at the time of analysis

OCPk1,ug C/cub m OCPk2,ug C/cub m OCPk3,ug C/cub m OCPk4,ug C/cub m	The Peaks are based on the area under the peak during each of 4 temperature ramps under helium. Some people claim they can get source data from evaluating the peak ratios
Pyrolized C/cub m	carbon associated with Pyrolysis as determined by the laser split point
True EC/cub m	
Optical EC (ugC)	Apparent EC on the filter based on a fixed absorption coefficient and the apparent absorbance (init Abs)
OptEC ABS	Apparent absorbance based on the initial and final laser reading during the thermal analysis
OptABS Coef	Absorption coefficient calculated from the absorbance the calculated elemental carbon
Opt Coef X^3	Coefficient for the polynomial fit of the Optical EC
Opt Coef X^2	Coefficient for the polynomial fit of the Optical EC
Opt Coef X^1	Coefficient for the polynomial fit of the Optical EC
Opt Coef X^0	Coefficient for the polynomial fit of the Optical EC
CO2_ndirC3	Coefficient for the polynomial fit of the NDIR
CO2_ndirC2	Coefficient for the polynomial fit of the NDIR
CO2_ndirC1	Coefficient for the polynomial fit of the NDIR
CO2_ndirC0	Coefficient for the polynomial fit of the NDIR
Laser Correction	Correction factor based on the laser attenuation as a function of heating. Begin Int - beginning integration point

Acceptance Criteria

Parameter	Number	Limit
Single point external standards	1 per week	Calculated ± 5.0 %
Instrument blanks	1 per week	Value ± 0.3 µg C
Multipoint external standard set	1 per 100 samples	Calculated ± 5.0 %

Remedial Action

External standard out of range - *carefully prepare and re-run two standards. If standards are still uniformly out range then:*	▪ Check gas flows (see maintenance chapter on page ____) ▪ Check for leaks (see servicing chapter on page _____) ▪ Check system temperatures (see maintenance chapter on page ____) ▪ Re-make stock solution. Re-run samples (See operation chapter on page ____) ▪ Perform multipoint calibration and update calibration parameter file (see calibration chapter on page ____)
	▪ Check for leaks (see servicing chapter on page ____) ▪ Check system pressure (see maintenance chapter on page ____) ▪ Check oxygen trap (see servicing section on page ____) ▪ Check gas lines to be sure no Teflon is used
External methane standard out of range	▪ Check carrier gas flow rates. Recalibrate if necessary (see maintenance chapter on page ____) ▪ Check system pressure (see maintenance section on page ____) ▪ Check for leaks (see servicing chapter on page ____)

Maintenance

The purpose of this section is to supply you with information that will help keep the instrument in top condition. The information provided includes a maintenance timeline, routine inspections, sample filter replacement, denuder filter replacement, cleaning cyclone protocol, and flow sensor calibration. The instrument requires virtually no routine maintenance over extended periods of time. Proper care of the instrument will result in reliable performance and an extended lifetime. For warranty information see appendix.

Maintenance Timeline

Daily	Check the instrument for error flags that show hardware problems
Weekly	Run calibration check (for protocol see calibration chapter on page ____) Replace sample filters (see protocol on page____) Routine inspections (see section on page ____)
Monthly	Replace denuder filters (see protocol on page ____) Clean Cyclone (see protocol on page ____)
Semi-annual	Re-calibrate flow sensors (see protocol on page ____) Clean sample inlet components (See section on page____)

Routine Inspections

The instrument should be checked regularly for:

1. Temperature stability
2. Gas Cylinder pressure
3. Oven pressure
4. Carrier Gas flows (autozero weekly)

5. Laser

Temperature
The temperature stability of the front and back ovens are of concern for the instrument. Temperatures can be read from the software screen. The back oven temperature should read approximately 870^{o}C during analysis and 500^{o}C during sampling. The front oven temperature profile is a function of the protocol being used. It should track the ramps as closely as possible. See section XYZ on setting the temperature profile control coefficients.

Cylinder pressure
The secondary pressure on the cylinders should read 7-8 PSI (.483-.552 Barr, 48.26-55.16 kPa) on Model 3 instruments and 20 – 30 PSI on Model 4 instruments. The cylinder should be changed if the primary pressure is 100 PSI or below.

Oven pressure
Oven pressure can be read from the software under PSIG. The oven pressure for the instrument should typically range from 1.0-1.7 PSI. Check for leaks if out of range.

Gas flows
Check gas flows on computer output and verify that they are within required set points on the table below according to the mode the instrument is in.

Valve	**Max-change**	**Idle 1**	**Standby 2**	**Collect 3**	**Purge offline 4**	**Purge online 5**	**Helium 6**	**Oxygen7**	**CalHe 8**	**CalOx 9**	**Clean oven 10**	**Multiplier 11**
Sample valve	0	0	0	0	0	0	0	0	0	0	0	0
Cal gas	150	5	0	0	15	15	15	15	0	0	5	0.95
He/Ox	75	10	5	0	0	0	0	15	0	15	25	0.95
He3	0	0	0	0	0	0	0	0	0	0	0	0
He purge	75	5	0	0	25	15	5	5	5	5	20	0.95
He1	50	10	5	0	100	75	65	50	65	50	40	0.95
H2	0	0	0	0	0	0	0	0	0	0	0	0
air	0	0	0	0	0	0	0	0	0	0	0	0

If the flows do not comply with the table, perform an autozero and flow calibration. Also see the leak check protocol in the servicing chapter on page ______.

Laser
When a sample path is clear and has a dry sample, the transmittance should be in the range of 10,000- 20,000, depending on the sample thickness.

Replacing Sample Filters

Materials
Quartz filter
Filter punch
Flat-faced forceps
Filter removal tool

Method

1. Open filter access port using the finger tight nuts on the door panel.

2. Remove laser shroud by pulling up on back on the panel.. This shroud acts as a protective housing for the oven port preventing exposure to the laser system. It has a keyed interlock system which automatically shuts down the laser upon access to this area.

3. To remove the photodetector, remove the stainless steel nut and then loosen the nylon nut with hands. Gently slide the photodetector off the quartz insert. Avoid excess force as the quartz oven can be easily chipped or broken if caution is not observed.

4. Place the photodetector on the oven plate.

5. Push the filter removal tool through the filter and pull it out concurrently with the insert.
6. Using filter punch, cut a new 17mm quartz filter.

7. Using the flat-faced forceps, gently insert the new filter into the oven port perpendicular to the tube inlet about ¼”. Using the forceps, gently rotate the filter using care not to puncture or bend it. Slide in the filter with the insert at least 1 inch and then install a second filter. It does NOT have to be completely square or rotated in the oven port at this time.

8. Wipe the quartz insert with a clean Kim-Wipe or other lint-free cloth to remove any fingerprints, lent or filter fragments which may be present on the insert.
9. Slide insert in parallel to the oven observing the filter as it begins to square up with the face of the insert and slide into the port. It will offer mild resistance to being pushed into the port. However, RESIST ALL URGES TO FORCE any aspect of this job. If it does not slide in easily, slip it out and start over. As the insert slides farther into the port, it will press the filter against the seat in the heated zone. Once you can feel the filter begin to seat, hold the insert firmly against the filter and hand-tighten the fitting nut securing it in place. *The most critical period for accidentally breaking or chipping the insert is during the first ½ - 1" of insertion as the piece makes contact with the filter but still can be twisted or rotated off-axis with the oven port. Once the piece has been slid in far enough to limit this motion, the chances for breakage are significantly reduced.*

10. Reinstall the photodetector making sure the face of the o-ring is in place before reinstalling. The fittings should be tightened using hands.
11. Reinstall the laser shroud

Injection Port Septum

The gas injection port is used for syringe injection of gas standards for QAQC performance monitoring of the instrument. Early instruments simply used a Swageloc nut and GC septum on the port while later instruments included a needle guide. The needle guide greatly improved the overall performance and reduced leaks from the septum. All users are encouraged to contact Sunset Laboratory Inc. for the needle guide upgrade. The septum should be replaced after every 10 injections or if there is any evidence of a leak. The most obvious indication of a leak is if you note a significant drop in the instrument pressure when inserting or removing the syringe needle during an injection. The septa are ¼” OD GC septa and can be purchased in bulk from Restek (Part No. 27128). The needle guide can be obtained from Sunset Laboratory Inc.

Materials
New septa
Needle guide insert
Small screwdriver

Method

1. Shut down the instrument software
2. Remove the Swageloc nut and septum from the injection port
3. Use the small screwdriver to pry out the septum
4. Make sure that the needle guide in correctly inserted into the Swageloc nut with the guide tip in the hole and the flat surface facing the septum.
5. Carefully insert the septum so that it remains squarely in the nut.

6. Screw the nut back onto the port until you just feel the septum begin to seat on the face of the port. Turn an additional ½ turn. Do not over tighten the nut as this will cut and core out the septum causing it to fail quickly

Replacing Denuder Filters

Under continuous use, Sunset Laboratory Inc. recommends that the parallel plate filters be changed at least once a month to minimize the possibility of VOC breakthrough. If an increase above typical adsorbed VOC is observed on quartz backup filters, then the carbon filters should be changed immediately. Filter sets are available from Sunset Laboratory Inc. or they can be cut as needed by the customer. The bulk filter material is supplied by Schleicher and Scheull, Inc., Reference Number 10320163, Phone Number 1-800-645-2302. The strips can be cut with a good quality paper cutter to the dimensions of 1.25” x 8.0” (The bulk material is 8” x 10” so a 1.25” wide strip can be cut from the 8” side minimizing the number of cuts necessary to produce the desired size.). Fifteen strips are necessary for each replacement set.

Materials
Philips head screwdriver
New filter material

Method

1. To change the filters, remove the denuder from the sample train and place on a flat surface.
2. Unscrew the front plate and set aside on the table.
3. Slide out the parallel plate insert tray and place on the table.
4. The filter plates are stacked in the tray and separated by 2 mm spacer rods. Remove all of the filters and spacers.
5. Discard the old filter material.
6. Install the new filter strips in the reverse order separating each with a spacer rod on each side. Be sure to place a strip in the bottom of the tray against the aluminum surface and last strip at the top of the tray so that when it is re-inserted into the denuder that there is no exposed aluminum surface in the parallel plate sector of the denuder.
7. Carefully re-insert the tray being sure that the top filter is not dislodged as the tray slides into the outer shell. Also be sure that the flow direction indicated matches the outside direction arrow.

8. Re-attach the front cover with the o-ring properly seated. When tightening the screws, assure that they are uniformly tightened to affect a good seal. The end plate does not have to be so tight that it contacts the outer shell.

Cleaning Cyclone and Inlet tubing

The sampling inlet of all sampling systems needs to be cleaned periodically. The cyclone inlet accumulates the larger particles from the sample air stream. There are also some vapor phase losses to the walls of the cyclone and connective tubing. All of this must be cleaned periodically (6 months) to minimize high blanks and adsorbed vapor artifacts.

Materials
1/8” Allen wrench
Methanol, acetone or methylene chloride
small brush such as a gun cleaning brush and cloth
clean, high pressure air or nitrogen source

Method
1. Remove cyclone from sample inlet by pulling it. Be careful not to damage the o-rings.
2. Lift the rain hat off the cyclone.
3. Unscrew the dust port
4. Disassemble the cyclone body by removing the three screws using Allen wrench.
5. Take small brush, methanol, or high pressure device and clean the body
6. Reassemble
7. Disassemble the tubing.
8. Rinse with methanol
9. If possible, swab with a brush or cloth
10. Blow dry with high pressure clean air or nitrogen. Even better, heat with a heat gun while flushing with gas.
11. Reassemble everything.

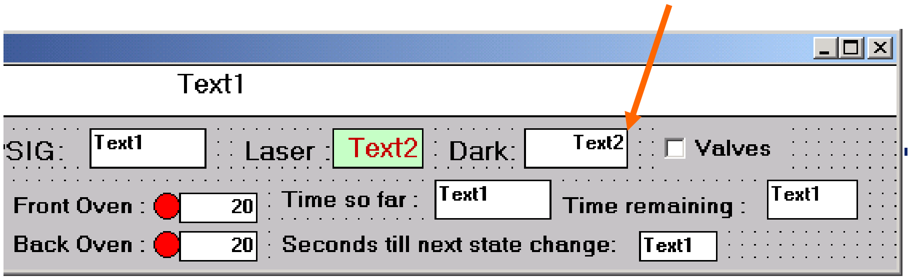
Flow Sensor Calibration

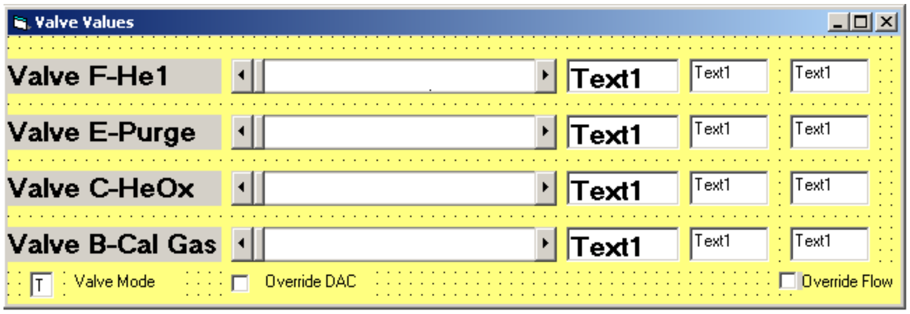
Flow sensor calibration is multi-step process which must be performed in the correct order. If performed properly and the data logged correctly into the instrument parameter file, the observed flow reading on the flow table should be correct (± 5 %) for an extended period. The instrument will come with an initial flow calibration from the factory. Initial offsets and a calibration check will be performed on-site by the Sunset Laboratory Engineer. Because the sensors work using the carrier gas heat capacity and have been exposed to air during shipment, the initial calibration may change over the course of the first week or so of operation. Thus, the flows should be re-calibrated after the system has been given sufficient time to burn in. Flow sensor re-calibration should be preformed once a year. Flow calibration measurements should be made with a NIST traceable gas flow measurement such as an electronic bubble meter, Gilibrator^{TM}, or other reputable manufacturer's flow meter. Record all data in a dated instrument log.

Materials
Flow meter
"C:\ocecpar\scinst1par.txt" file
Swageloc 1/8" fitting
"Cal Data" worksheet
Instrument log

Method

1. Turn on each of the support gas cylinders and set the secondary regulators to approximately 10-15 PSI. Flows are controlled by electronic flow controllers. The system will automatically try to control the flows to the system setpoints. Observe the flow table for each of the gases as they settle into a constant flow. *Note: The flow sensors are sensitive instruments! Keep the secondary pressures at the recommended levels and make all adjustments slowly! Extreme, rapid changes in flows or very high pressures can destroy the sensors resulting in a non-warranty repair charge!*
2. Attach the gas flow meter as a Gilibrator or FlowCal device with a 1/8" fitting on the "Back Oven Vent" port on the back of the instrument.
3. On the lower window of the software, check the "Valves" box. This will bring up the Valves screen. Use this screen to control the flows while performing the calibrations.

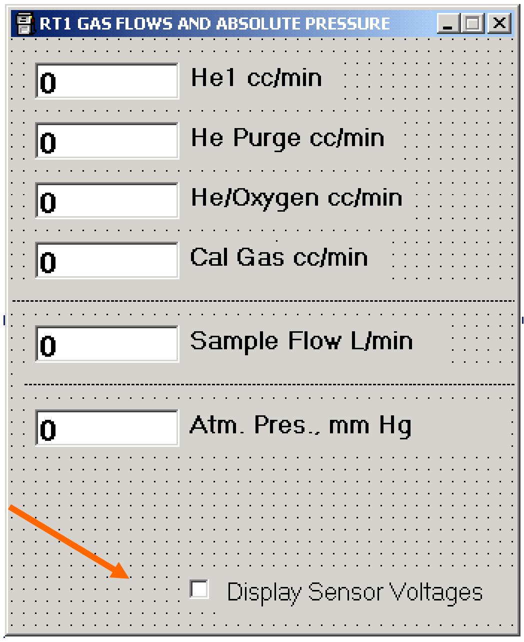




Valve F-He1 | Text1 | Text1 | Text1
Valve E-Purge | Text1 | Text1 | Text1
Valve C-HeOx | Text1 | Text1 | Text1
Valve B-Cal Gas | Text1 | Text1 | Text1

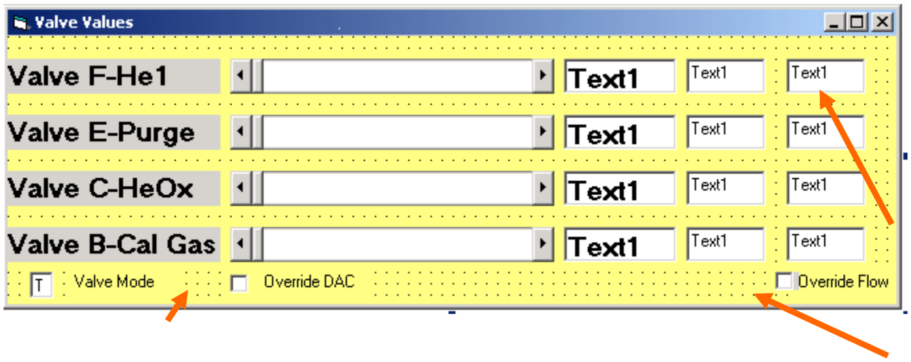
T

4. You will need to collect flow vs. Voltage output from the instrument. Pull down the bottom edge of the "Flow Table" screen and check the "Display Sensor Voltages" button. This will bring up the actual voltage readings from the data system.



0 He1 cc/min
0 He Purge cc/min
0 He/Oxygen cc/min
0 Cal Gas cc/min
0 Sample Flow L/min
0 Atm. Pres., mm Hg

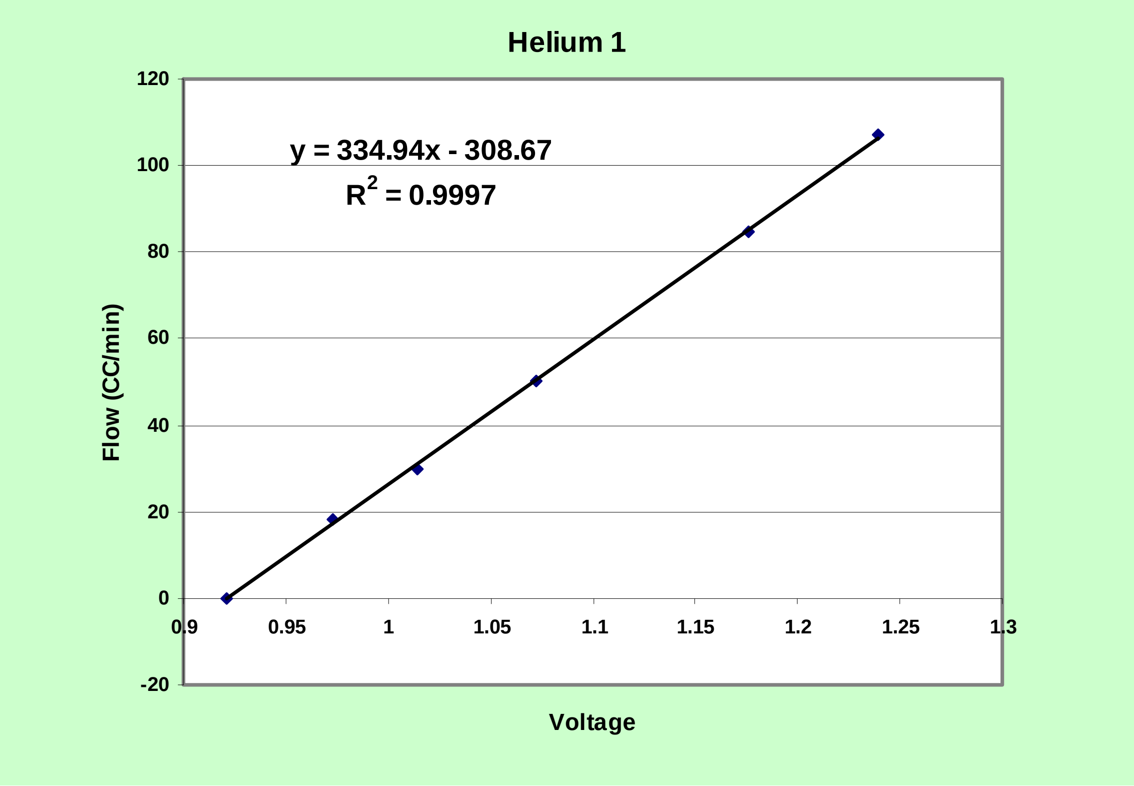
5. First get your "zero" readings. This is best done by checking the "Override DAC" box and then moving the slider bars all the way to the left. This forces the flow control valves shut and gives the most accurate zero reading. Record the readings for all four flow gases on the top section of the flow table.
6. Now for the upper limit readings, uncheck the "Override DAC" box and check the "Override flow" box. Highlight the flow in the right column for each of the flows and type in a "0". Now type in "100" for the He1 flow and wait for the computer to stabilize the flow by monitoring the Voltage on the flow table. Once it appears stabile, (+- a few millivolts), record the voltage and measure the actual flow using the flow meter on the "Back Oven Vent". Record the flow and the voltage.



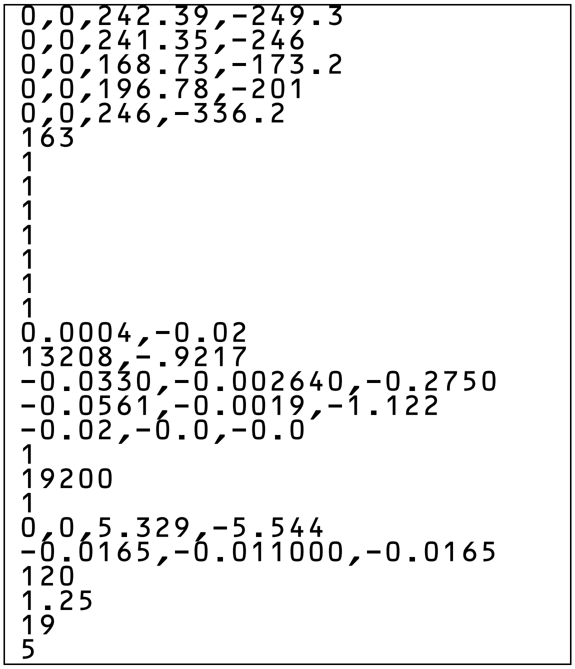
7. Now type in a “0” for the He1 flow and perform the same sequence for HePurge and HeOx recording the flow and voltage. The flow measurement is taken from the “Back Oven Vent” for these two flows as well as the He1.
8. Move the flow meter to the “Cal Gas Vent” and repeat the flow measurements for the He/CH4 cal gas.
9. Record your data in a spreadsheet similar to below. You may choose a multipoint calibration as shown by recording data over a range of flows chosen using the Valve Screen.

Helium 1			**HelPurge**			**Helium/Oxygen**			**Calibration Gas**	
Volts	Flow (cc/min)		Volts	Flow (cc/min)		Voltage	Flow (cc/min)		Voltage	Flow (cc/min)
1.239	107		1.173	86.1		1.247	77.3		1.163	70.7
1.176	84.7		1.098	61.4		1.103	43.3		0.998	25.8
1.072	50.1		1.033	38.9		1.022	25		0.955	12.9
1.014	30		0.989	26.2		0.978	13.4		0.937	6.9
0.973	18.1		0.95	12		0.945	7.04		0.913	0
0.921	0		0.917	0		0.916	0			

10. Once you have recorded the data in a spread sheet such as Excel, you should make an X/Y graph of the data and compute the slope and intercept. Typically a linear fit is sufficient to calculate an equation for the data.



11. Now you need to update the data in the instrument parameter file. Go to Explore and find the **C:\Ocecpar\scinst1par.txt file**. Save a backup copy of this file now. Double click on that so that it opens in **Notepad.** The file will look something like the figure below.



```
0,0,242.39,-249.3
0,0,241.35,-246
0,0,168.73,-173.2
0,0,196.78,-201
0,0,246,-336.2
163
1
1
1
1
1
1
1
0.0004,-0.02
13208,-.9217
-0.0330,-0.002640,-0.2750
-0.0561,-0.0019,-1.122
-0.02,-0.0,-0.0
1
19200
1
0,0,5.329,-5.544
-0.0165,-0.011000,-0.0165
120
1.25
19
5
```

```
rt name
```

12. The first line in the file are the coefficients for He1

    `0,0,242.39,-249.3`

    Use the results for the calculated line in the graph from the spreadsheet

    y = 334.94x - 308.67

    to update the file coefficients by updating the first line to read:

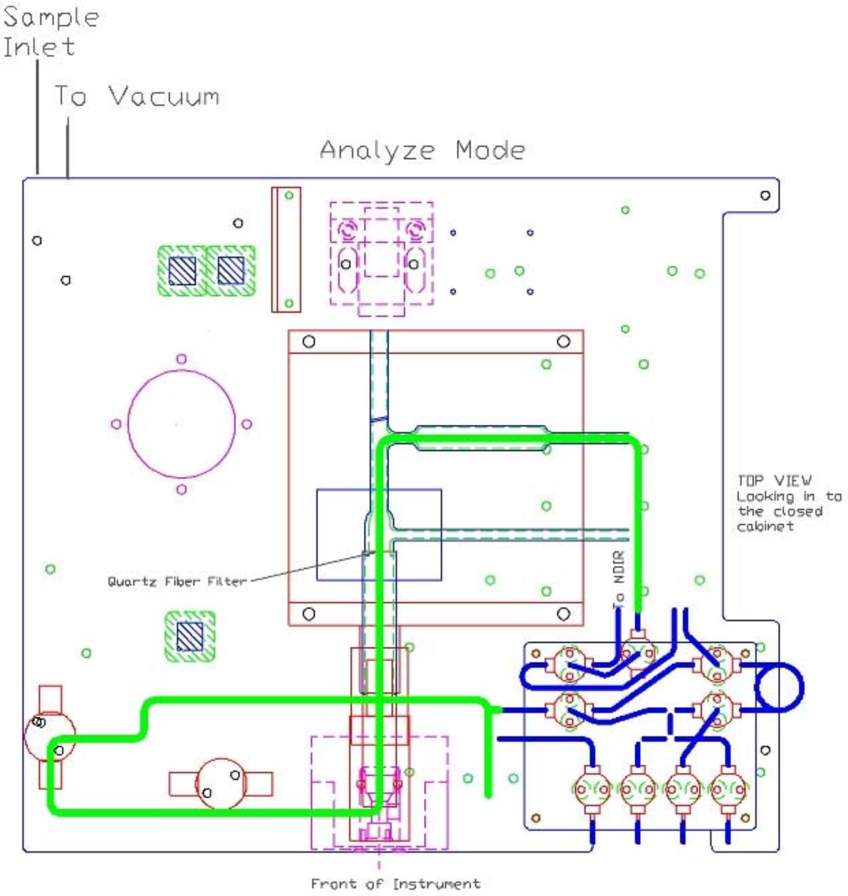
    0, 0, 334.94, -308.67

13. Update the remaining lines for the other gases as follows:

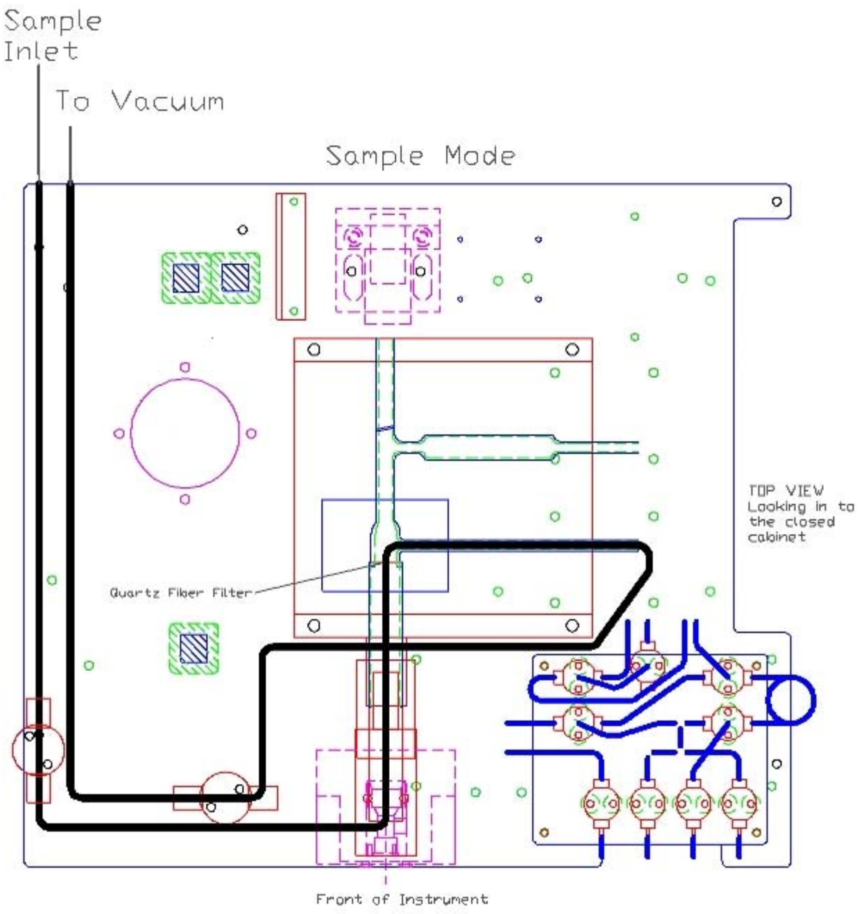
    Line 1: He1
    Line 2: HePurge
    Line 3: He/Ox
    Line 4: CalGas
    Line 22: HV flow sensor

14. Make sure that there are no extraneous commas, lines or characters in the file. Save the file under its original file name.

15. Now turn off the heated zone switch and restart the software. The new flow coefficients will be used for controlling the flows. You can spot check the flows using the Valve window to set individual flows and your flow meter to verify the settings in the same manner as you did for the original calibration. If there are no problems, turn on the heated zones and start collecting data. A flow diagram is included on the next pages for diagnostic purposes.



Analytical flow system



Sample Flow System

Standard Operating Procedure (SOP)
For the Analysis of Organic and Elemental Carbon (OC/EC) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer

January 10, 2005

Sunset Laboratory Inc.

Sunset Laboratory Inc.

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Table of Contents

List of Tables

II Scope and Applicability

This SOP describes the analytical method to determine the levels of organic and elemental carbon in particulates collected using the Sunset Laboratory semi-continuous carbon aerosol analyzer (RT-OCEC). The particulate samples are collected by the instrument using a predetermined sample schedule and analyzed by a thermal/optical method. Time resolution of 30 minutes to 8 + hours are possible.

III Summary of Method

A quartz filter is mounted in the quartz oven and samples are collected for the specified time. After the sample is collected, the system closes off the sample port, purges the analytical flowpath with helium and performs the thermal/optical analysis. The thermally removed carbon components are converted to CO_2 which is subsequently measured by non-dispersive infrared (NDIR). External sucrose solution and methane gas carbon standards are used for NDIR calibration. Correction for the pyrolytically generated carbon (char) that sometimes forms during the first stage of the analysis is based on filter absorbance measurements. The pyrolysis step is facilitated using a laser absorbance technique.

IV Working Definitions

Organic Carbon (OC) - Optically transparent carbon removed (through thermal desorption or pyrolysis) and char deposited when heating a filter sample to a preset maximum (840 °C) in a non-oxidizing (helium) carrier gas.

Elemental Carbon (EC) - Carbon (e.g., in soot particle cores) that can only be removed from the filter under an oxidizing carrier gas (He/O_2). Optically absorbing carbon removed at high temperatures (e.g. 850 °C) in a non-oxidizing carrier gas when internal (sample matrix) oxidants are present.

V Health and Safety Warnings

The Sunset Laboratory Thermal/Optical Carbon Analyzer uses high temperatures (up to 870°C) and laser radiation to perform the required steps in this analytical procedure. Under normal operation, the analyst is protected from exposure to these energy sources. However, during repair or trouble shooting, when the instrument cover is removed, the analyst must take the following precautions:

a) Before attempting any repairs, turn off the power and wait for all heated zones to cool.

b) For most repair work, unplug power to the ovens and avoid contact with any power sources in the oven cabinet.

c) Although the laser source has an interlock protection system, if the interlock is overridden, direct exposure to the laser can occur under certain conditions. Do not look directly at the laser source as permanent eye damage can occur.

d) Use caution when handling all support gas cylinders and regulators. Always have cylinders properly chained to a safety rack.

VI Procedure

a) General Instructions

See the attachment – "Installation Notes" for basic installation and operation procedures

b) Samples

The analyzer is deployed to the field site. It collects airborne particulate samples on an internally mounted filter and analyzes the sample on a semi-continuous basis. There is no option for replicates without a second sampler. Sample data are stored in raw data files. Additionally, a short result file is printed to a file at the end of each analysis. An optional output can also be transmitted to a data logger equipped with a serial input. The data should be considered irreplaceable and should be backed up on a frequent basis to some sort of permanent media such a CD-rom or tape.

c) Materials

See Table 1 for all required reagents and gases. Check the labels carefully to ensure that they are not expired and are of the proper purity/grade. Document the supplier, grade/purity and Lot No. as appropriate on the Analysis Data Form.

Table 1. Materials

Material	Use
UHP Helium (99.999%)	Carrier gas
Helium/Oxygen Mix (10% O_2; balance UHP He)	EC oxidant carrier gas
Helium/Methane (5.0% methane; UHP He balance)	External standard gas
Sucrose (99.9% reagent grade)	Analytical standard

d) Equipment

See Table 2 for all required major pieces of equipment. Check calibration of all equipment requiring calibration to ensure that it is current.

Table 2. Equipment

Equipment	Use
Forceps	Filter installation
Clean quartz filters	Work area preparation
Filter punch tool (1.6 cm diameter circle)	Preparing sample filters
Filter removal tool	Periodic replacement of filters
10 µl analytical syringe	Calibration
Volumetric Flasks, Class A.	Standard preparation
Analytical balance	Standard preparation

e) Sample Collection and Analysis Procedure

This procedure includes default instrument setup, standards preparation as well as general operation of the Sunset Laboratory RT-OCEC analyzer. It is assumed that the analyst has experience with the routine operation of the instrument.

i) OC/EC instrument startup - Setting up for data collection

(1) Check cylinders for sufficient volume and pressure.
(2) Turn ON computer be sure that the serial port cables are installed correctly and the software configured correctly.
(3) Turn on both switches on the back of the instrument.
(4) Start the RT Program by double clicking
(5) Make sure the computer and instrument CPU link up. Note the temperature boxes and the flows on the flow table. They should start changing as the instrument stabilizes after startup.
(6) Check the instrument gas flows on the table to be sure they are stable.
(7) Check the instrument pressure to be sure it is normal (0.5 to 1.5 psi; instrument dependent)
(8) Install new filters if necessary.
(9) Run a “CLEAN OVEN” procedure from the Pull down menu if a new filter has been installed.
(10) Enter a sample name.

(11) Select the proper parameter file to be used for analysis. By default it is "rtquartz.par".

(12) If you desire the raw data to go into an automatically generated file each day, the default ending of "\" is already selected. To have the data go into a file of another name, type the name of the file after the "\" already there. Be sure and end the filename with the extension "txt"(example: yourfilename.txt)

(13) Determine how the instrument will be cycled; either by sampling for a fixed time followed by the analysis; or by starting sampling times and pre-determined times and lengths from an external file.

(14) Make sure the Cycle Box is checked for continuous operation.

(15) Click on "Start"

VII Calibration and Audit Procedures

Calibration and Audit procedures are related in that each is designed to check the instrument performance. Calibration measurements are performed to set up critical instrument performance parameters while Audit measurements are more routine measurements performed to assure the instrument is operating within a desired specification. Many of the techniques and procedures are similar.

i) Test Equipment and Materials

(1) Preparation of Carbon Standard Stock Solution

(a) Weigh 10.00 ± 0.01 g of sucrose on the analytical balance and quantitatively transfer it into a 1 liter volumetric flask. Dissolve in and dilute to volume with DDi H_2O. Record in the laboratory notebook. This will serve as the general QA/QC performance standard. Concentration = 4.207 μg C/μl solution. Note the date and replace every 6 months. Pour about 20 mL of the standard into a clean glass vial (with Teflon cap liner) and place the rest in the refrigerator.

(b) For a "low-level" working standard, make a 1 to 4 dilution in a volumetric flask with DDI H_2O. This solution has 1.05 μgC/μl of solution and is used for the lowest concentration standard of a multi-point calibration. Note the date and replace every 6 months. Pour about 20 mL of the standard into a clean glass vial (with Teflon cap liner) and place the rest in the refrigerator.

(2) External Standard

The external standard is the mixed helium/methane cylinder noted in Table 1. Methane in a sample loop is automatically injected at the end of every analysis. The analytical result is normalized to the response of the methane standard to adjust for slight variations in flow rates that might occur during the day. At 760 torr and 298 K, a 5.00% methane in helium mixture contains 24.54 μg of carbon per ml of gas.

(3) Basic Performance Calibrations

The Sunset Laboratory OC/EC instrument is calibrated during the initial installation using a multipoint external standard calibration. The external standard calibration is used to determine the carbon in the external standard gas loop. The external standard carbon content is dependent on the volume of the loop (nominally 0.8 ml) and the concentration of methane in the methane/helium tank standard. Once the standard loop carbon in determined, a parameter file is set up containing (among others) three calibration parameters; 1) the measured deposit area, 2) the calibration constant which is the number of µg carbon in the loop specific to the cylinder of helium/methane mix provided at the site, and 3) the transit time which is the time required for methane generated from a sample to reach the NDIR. These parameters are often stable for many months. External standards should be run according to program requirements with results monitored on a control chart. See sections on Acceptance Criteria and Remedial Action when the external standard responses fall out of accepted range.

(a) External Standard Loop Calibration using the stock sucrose solution

(i) Punch out three new, clean 16 mm diameter filter sections of quartz filter with the circular filter punch.

(ii) Insert 2 of the filters in the oven as required for a normal analysis cycle. Place the third filter horizontally in the quartz tube insert as close to the end as possible so that it will be in close proximity to the 2 vertically mounted filters. Re-install the insert and photodetector as required for a normal analysis.

(iii) Go to the “Run” Pull-down Menu and left-click on the Clean Oven cycle to completely clean the filter punches.

(iv) Wait for the instrument to complete the clean cycle and the status window to read “Safe the put in a new Sample”

(v) Expand the lower status window to full screen and check the “QAQC Peak Performance” Box. This will set the back oven to a constant value during the calibration testing. You will be asked to verify this setting each time you run a sample.

(vi) Go to the top Start Window and un-check the “Cycle” box and set the sample time to “0”.

(vii) Go to the “Parameter File” field and select sucrose-TC.par from the PAR folder.

(viii) Using the precision syringe, measure a sample volume of from 5 - 10 µl of the standard carbon (sucrose) solution.

(ix) Remove the photodetector head and slide out the quartz insert.

(x) Carefully apply the solution on the filter suspended in the quartz insert. Re-install the quartz insert and photodetector promptly. Use caution so as not to contaminate the insert or quartz filter. Record the exact volume of the aliquot in the log book.

(xi) Go to the user interface field that is labeled “Output Raw Data file” and type a new name for the raw data file.

(xii) In the “Sample ID” field in the top “Start” window, type in the expected carbon loading.

(xiii) Start the analysis. Wait for the instrument to run through its analysis protocol and return to the Idle mode and safe to put in a new sample.

(xiv) Analyze a range of samples as required for the calibration. A typical multi-point calibration for ambient filters would include;

1. A 10 µl sample from the “low-level” working standard yielding 10.5 µg carbon.
2. A 5 µl sample from the standard carbon stock solution yielding 21.03 µg carbon.
3. A 10 µl sample from the standard carbon stock solution yielding 42.07 µg carbon.

(b) **External Standard analysis using a fix volume standard gas injection.**

(i) Check the OC/EC oven to determine if the temperature is cool enough to insert a sample. (Flashing green screen section on the computer monitor).

(ii) Expand the lower status window to full screen and check the “QAQC Peak Performance” Box. This will set the back oven to a constant value during the calibration testing. You will be asked to verify this setting each time you run a sample.

(iii) Go to the top Start Window and un-check the “Cycle” box and set the sample time to “0”.

(iv) Go to the “Parameter File” field and select cal-injection.par from the PAR folder.

(v) Go to the “Sample ID” field in the top and type in 1.0 ml cal gas sample.

(vi) Go to the lower status window and check the “Valve Values Table” checkbox.

(vii) A new window will pop up with the gas flow controls present. Check the “Override flows” box at the lower right of the panel. Highlight the bottom right number (Default = 5) for the flow rate of the Cal Gas. Change the value to 25 and wait for the new flow setting to stabilize.

(viii) Using a 1.0 ml gas tight syringe, collect a cal gas sample from the back “Cal Gas Vent” port.

(ix) Start the analysis. Wait for the Analyze mode and the temperature to stabilize. Inject the gas sample in a steady single motion in 1 – 2 seconds. Leave the syringe in the septum until the peak has finished eluting then remove the syringe and wait for the analysis to finish.

(x) Calculate the result and verify that the carbon measured is within (±) 5.0% of the expected total carbon.

(xi) Calculations:

Total Carbon (ugC) = (mls inj) x (% methane/100) x 12 x (P/RT) x 1000

Where: P/RT = pressure (atm) / (.082 x Temp (K)

VIII Data Analysis - Calculations

a) The Sunset Laboratory OC/EC Analysis Program is used to calculate the results from a sample set after the data are stored under the base file name. The OC/EC calculation program is initiated by clicking on the icon. The program then asks for the file name to perform calculations. In general, the following software parameters apply to all calculations;

b) The overall carbon response is based on a multi-point external calibration.

c) The external methane standard for every cylinder is calibrated against the external multi-point calibration.

d) The external methane standard is run at the end of every sample. This known amount is used to normalize the response factor for each sample. This essentially cancels out small drifts in detector response over time.

e) The software determines an initial NDIR response baseline prior to the desorption. The area at each point along the thermogram curve minus the baseline is multiplied against the calibration response to determine the carbon. The data are summed over the range to yield the total carbon results.

f) The automated OC/EC split point is calculated from where the laser absorbance in the oxidizing phase of the EC analysis matches the initial absorbance measured when the sample was first inserted into the oven. Carbon observed before the split point is considered organic carbon and carbon after the split is considered elemental carbon.

g) The analyst has several options in computing the results from a set of experiments. These should be exercised with caution based on the extent of the analyst's experience.

h) The analysis program can batch process all of the sample data sets in a file without further review. It is recommended that the analyst study each individual data set as it is processed to look for any anomalies.

i) During the processing, the analyst can calculate carbonate (if evolved as a single peak) by using the manual integration feature in the program. This must be performed by setting the left and right cursors on the beginning and ending points of the carbonate peak. When re-integrating, the program draws a baseline between the designated points and calculates the peak area. The program will then automatically call this area carbonate and subtract it from the initial area for organic carbon (which includes carbonate, if present). There is no option for validating the presence of carbonate (as there is with integrated sample filters) because all of the sample is consumed during the analysis.

j) If necessary, the OC/EC split point can be manually set (reassigned) by moving the cursor to the desired point. The software will calculate the split based on that point. This decision is based on the analyst's experience and information about the sample.

IX Results

a) The analysis software automatically stores the data in a spreadsheet format for compilation. The spreadsheet format is illustrated in Attachment B. The data for each sample may also be printed in graphic form with the temperature, laser absorbance, and

NDIR profiles. The net results are tabulated and a line is provided for the analyst′s signature. An example of this results output is provided in Attachment C.

Table 4. Acceptance Criteria

Parameter	Number	Limit
Single point external standards	1 per week	Calculated ± 5.0 %
Instrument blanks	1 per week	Value ± 0.3 µg C
Multipoint external standard set	1 per 100 samples	Calculated ± 5.0 %

X Remedial Action

a) External standard out of range - carefully prepare and re-run two standards. If standards are still uniformly out range then;

- i) Check gas flows
- ii) Check for leaks
- iii) Check system temperatures
- iv) Re-make stock solution. Re-run samples
- v) Perform multipoint calibration and update calibration parameter file

b) System blanks too high

- i) Check for leaks
- ii) Check system pressure
- iii) Check oxygen trap
- iv) Check gas lines to be sure no Teflon is used

c) External methane standard out of range

- i) Check carrier gas flow rates. Recalibrate if necessary
- ii) Check system pressure
- iii) Check for leaks

XI Instrument/Equipment Inspection, Testing, and Maintenance

a) Routine instrument inspection

- i) Check cylinder pressures - replace as necessary
- ii) Observe oven pressure - check for leaks if out of typical range (1.0 - 1.7 psi).
- iii) Observe standby temperatures of back oven and methanator oven prior to startup. If out of range, determine cause and initiate repair.
- iv) Check gas flows on computer output and verify that they are within required set points. If out of range, look for system leaks. Repair or adjust as necessary.

b)Testing

- i) Daily
  - (1) Check instrument for error flags showing hardware problems.
- ii) Weekly
  - (1) Run calibration check
  - (2) Replace sample filters
  - (3) Check Gases

- iii) Monthly
    - (1) Replace denuder filters
    - (2) Clean Cyclone
- iv) Semi-annual
    - (1) Re-calibrate flow sensors using NIST traceable calibration source.

c)Maintenance

- i) The instrument requires virtually no routine maintenance over extended periods of time. Breakage or failure can occasionally occur with the components described below. If breakage or failure occurs, components should be replaced as necessary with replacements from Sunset Laboratory. Sunset Laboratory has Power Point presentations available for many of the typical maintenance repair procedures.

- ii) Replacement of quartz oven - the quartz oven/MnO_2 converter almost never fails except in the case of operator breakage or development of cracks. If this occurs, the oven will have to be replaced. Begin by cooling the oven to ambient and shutting off all gas flows. Unplug all electrical power. Begin disassembly by removing the thermocouple, photodetector and top cover. Next, carefully remove all insulation from the oven area. Disconnect the heating coils and carefully unwrap them from the oven assembly. Remove the top oven supports and lift out the oven. Remove the thermocouple from the back of the instrument. Remove the desorption oven thermocouple by disconnecting the Swagelok fitting. Replace in reverse order using care in installing the oven thermocouple, heating coils and insulation. Once installed, re-start gas flows to purge with helium and initiate startup sequence in the software.
- iii) Replacement of heating coils - heating coils will occasionally burn out. When this happens, they will have to be replaced. Follow the replacement steps for the appropriate component above (Maintenance, Steps 1 and 2) until the coil can be removed. Replace with Sunset Laboratory replacement part. Assemble in reverse order.

XII References

a)NIOSH Method 5040 (1998), In *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed., 2nd Supplement, ed. Cassinelli M.E., O'Connor P.F. [Supplement to DHHS (NIOSH) Publication No. 94-113]

b)M. E. Birch, *Analyst* (1998), **123**:851-857

c)M. E. Birch, R. A. Cary (1996) *Aerosol Science and Technology*, **25**:221-241

d)Cass, et. Al.

XIII Revision History

XIV Attachments

A. Sample Temperature Parameter File

```
' NIOSH 5040.par   quartz filter analysis profile
' Parameter file for Sunset Lab
' analyzes for organic and elemental carbon
' mode <comma> time <comma> temperature
' purge for 10 sec with blower off.
'
Helium, 10, 1, .001, 95, 0
Helium, 90, 600, .20, 45, 0
Helium, 90, 840, .27, 25, 0
Helium, 37, 0, .001, 95, 16
Helium, 3, 550, .17, 50, 0
Oxygen, 35, 550, .17, 50, 0
oxygen, 45, 650, .22, 40, 0
Oxygen, 90, 870, .28, 25, 0
CalibrationOx, 110, 0, .001, 95, 16
Offline, 1, 0, .001, 95, 16
'******************
'don't put any comma's in your comments - bad things happen
'format
'Mode; time; temperature; power constant; time constant; blower mode
'power constant - .0001 to 1; think of it as a percentage
'typical .01 to .4  must be positive
'time constant (seconds) - 1 to 200  must be positive
'typical - 10 to 120
'low temperature - long time constant; low power
'high temperature - high power; short time constant
'blower speed - 0 and 3 to 16; 0 = off; 16 = full
'do not run blower at settings of 1 or 2 - too slow
```

There are three added coefficients to each line for the 62xxx software. There are notes at the bottom of the Par file describing the general limits of each coefficient.

Analysis Phase	Step Time	Step Target Temp	Power Coef.	Time Constant	Blower power
Helium	70	310	0.1	75	0
Helium	60	475	0.2	60	0
Helium	60	615	0.25	45	0

You can optimize these for each step. Included are couple of example plots to give you a typical range for the individual coefficient ranges. The operating files in Parameters are current working par files from our instrument here. Just try running the default at first and see what it looks like. We believe all of the files I sent you are "error free" in terms of the setup. You have to be careful with the changes you make. Usually save a backup of a working parameter before you change anything. The software will mostly find any typos you make and tell you the line number of the error. A couple of kinds of errors will cause the software to bail out completely but is not catastrophic as it would only happen in the calling of the par file and not a failure in the middle of a run. With a little practice, the profiles can be dialed in very precisely.

Pre-start checklist - New Installation

(1) Install Sample inlet using 3/8 inch tubing. The sequence should be:

   (a) Air Intake at 2.5 um cut Cyclone
   (b) 3/8 inch tubing to area of instrument
   (c) Denuder (note directional flow of air)
   (d) 3/8 inch tubing into Ball Valve inlet

Note: Either Copper or S.S tubing can be used. It must be extremely clean from the standpoint of organics such as manufacturing oils. S.S tubing is preferred. If there is any doubt as to cleanliness, the tubing can be cleaned with reagent grade methylene chloride and then dried. Alternately, a propane torch can used to heat the length of tubing to remove any volatile organics.

(2) Install tubing from gas cylinders.

Use clean 1/8 inch copper or S. S. tubing. NoOx tubing may be used, but the length should be kept to a minimum. DO NOT use Teflon because of the diffusion of CO2 through its walls.

(3) Install tubing to pump.

Use ¼ inch copper or plastic tubing. This does not have to be clean because it is downstream of the sampling filter. Make sure **NOT** to use thin wall tubing that might collapse under vacuum. The sequence should be:

   (a) ¼ inch tube to one end of ballast tank
   (b) ¼ inch tube containing bleed orifice and vacuum gauge at other end of ballast tank
   (c) ¼ inch tube to 120 VAC Sampling Solenoid – if used
   (d) ¼ inch tube to vacuum pump

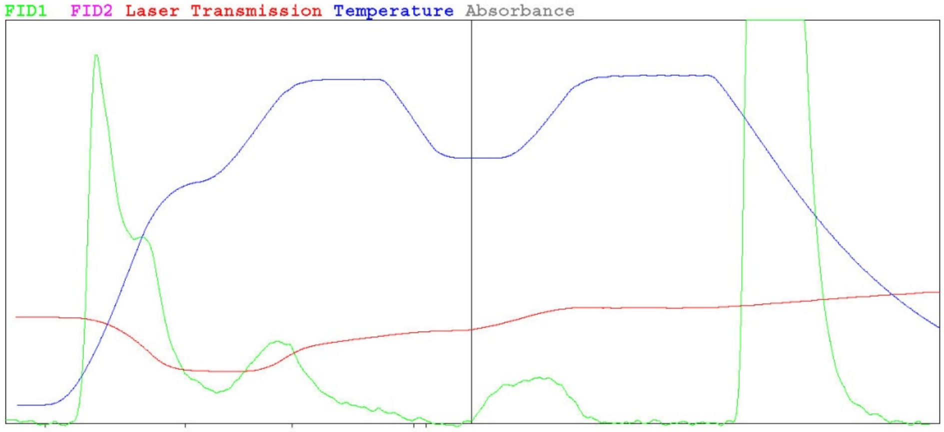
(4) Connect Control cable of Pump (or Solenoid) to 120 VAC control box. The 120 VAC Solenoid may be left out and the outlet of the ballast tank connected straight to the vacuum pump. In this case, the pump itself should be connected to the 120 VAC control box
(5) Connect the 120 VAC Power Cord to the plug on the back of the instrument
(6) Connect the CPU serial cable from the computer to the CPU Serial Port
(7) Connect the NDIR serial cable from the computer to the NDIR Serial Port

B. Sample spreadsheet data tabulated by Analysis Program.

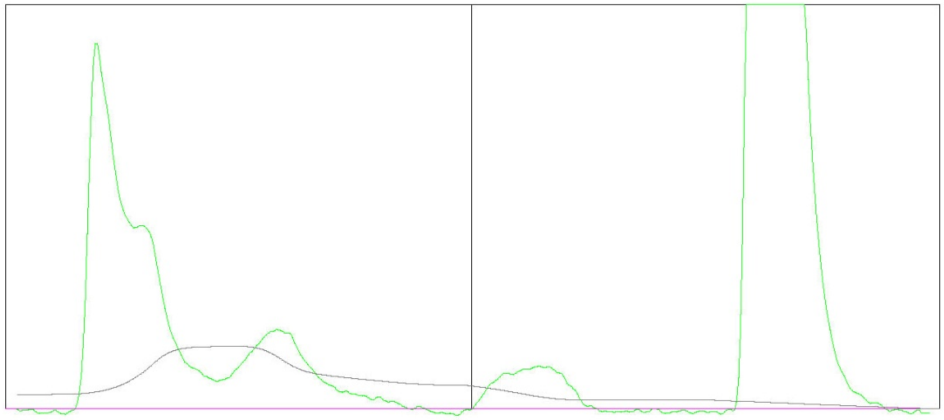
Sample ID	Thermal OC (ugC/M3)	Thermal EC (ugC/M3)	OptOC (ugC/M3)	OptEC (ugC/M3)	TC (ugC/M3)	Start Date/Time	Mid-time of Collection	Sample Volume
2 hour samples	3.175	0.354	3.151	0.379	3.529	1/7/2005 16:35	1/7/2005 17:35	974.7
2 hour samples	2.243	0.378	2.232	0.390	2.621	1/7/2005 18:47	1/7/2005 19:47	974.6
2 hour samples	2.333	0.305	2.331	0.307	2.638	1/7/2005 20:58	1/7/2005 21:58	974.3
2 hour samples	2.111	0.288	2.081	0.318	2.399	1/7/2005 23:09	1/8/2005 0:09	973.7
2 hour samples	2.216	0.332	2.176	0.372	2.548	1/8/2005 1:20	1/8/2005 2:20	973.6
2 hour samples	2.309	0.428	2.398	0.339	2.737	1/8/2005 3:31	1/8/2005 4:31	972.9
2 hour samples	2.474	0.373	2.511	0.335	2.846	1/8/2005 5:42	1/8/2005 6:42	971.9
2 hour samples	2.808	0.325	2.831	0.301	3.133	1/8/2005 7:53	1/8/2005 8:53	972.0
2 hour samples	2.422	0.340	2.490	0.271	2.761	1/8/2005 10:04	1/8/2005 11:04	970.7
2 hour samples	2.904	0.469	2.934	0.439	3.373	1/8/2005 12:15	1/8/2005 13:15	970.1

* Calculated errors are based on long-term historical data for replicates and instrument blanks (see Reference #4). Over the course of hundreds of replicate runs, the relative standard deviation is typically 5%. True instrument blanks measured by running previously run filters without re-opening the oven report an average of 0.2 µgC/cm^2 background. Thus, the reported error is obtained by multiplying the carbon yield of the sample in µgC/cm^2 by 0.05 for the typical sample and instrument variability and adding 0.2 µgC/cm^2 from the typical instrument background.

```
Sample ID: 60 min samples
Analysis Date/Time    01/12/2005  17:26:01
 Organic C =           5.46 +-0.47  ugC                   5.63 ugC / M3
 Carbonate C =         0.00 +-      ugC
 Elemental C =         0.73 +-0.24  ugC                   0.76 ugC / M3
 Total C =             6.19 +-0.61  ugC                   6.38 ugC / M3
 EC/TC ratio =        0.118

   Sample Volume (M3) =       0.97                        Punch Area, sq cm  =  1
   Calibration area Used =      32754.0                   Calibration Constant  =  18.1
   Laser correction factor =       0.88
   Split time Used = 234 seconds     Split time Calculated = 234 seconds
   Pk1=      3.76   Pk2=      1.12   Pk3=      0.57   Pk4=      0.01
                                                    FID GRAPHIC SCALE=  152
```



```
   Inital absorbance =      0.210       Absorbance at StartPyrolize =      0.350
   Absorbtion Coefficient of original elemental C =      28.7
   Absorbance plotted from 0 to 6
```



```
   OC/EC Analysis Program (c) Sunset Laboratory, Inc.              Analyst -
```

Appendix N

Sunset Labs Semi-continuous OC/EC Analyzer to EnvidasFW Data Acquisition System Configuration Guide.

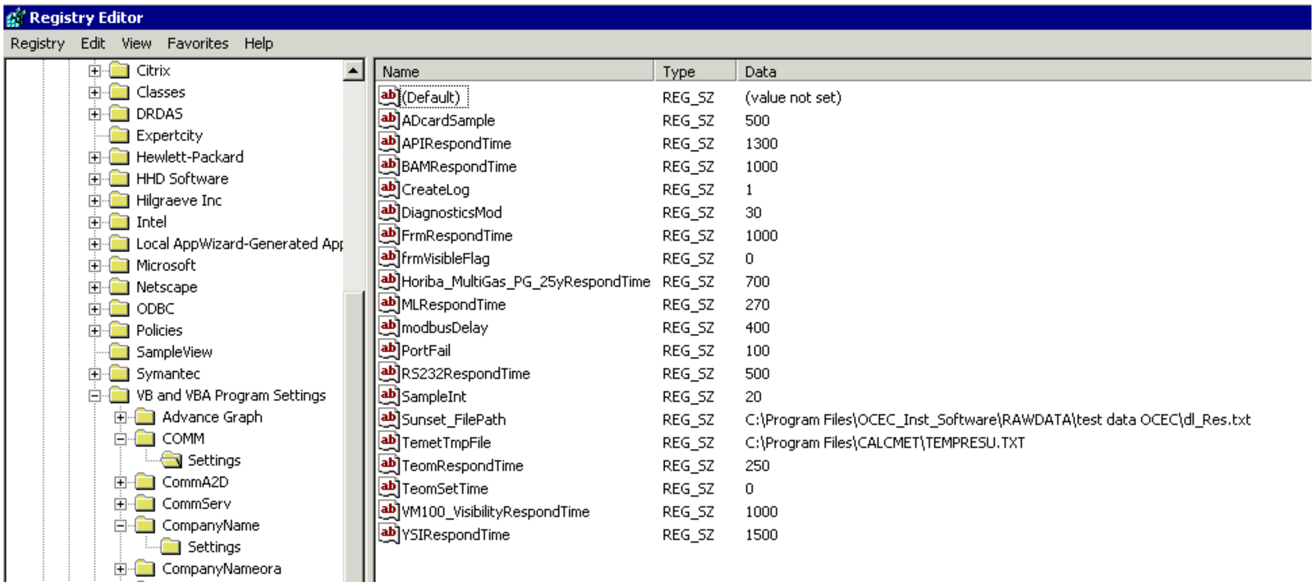
Sunset Labs Semi-continuous OC/EC Analyzer to EnvidasFW Data Acquisition System Configuration Guide

I. Review Appendix D19 in the EnvidasFW manual. A copy of this follows.

D19 – Sunset

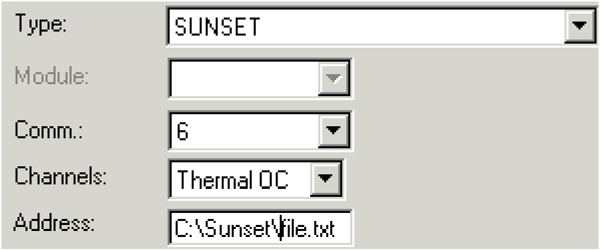
Sunset Lab's organic carbon analyzer is run by a control program on a PC. It is convenient to run this program on the same PC as the EnvidasFW. Or it may be on a separate PC connected via a network cable to the EnvidasFW. Use a Cat 5 crossover cable if the connection is between the two PCs. If a hub it used the two cables are both standard Cat5s.

If the machines are separated you must map a drive to the Sunset's PC so you can enter the location of the output file in the registry of the Comm program. The key is called Sunset_FilePath. An example is illustrated below. The path follows the default installation for the Sunset software. If you mapped the C: of a separate machine to Z; on the EnvidasFW machine the C: in the example below would be Z: The name of the output file is user defined within the Sunset software. In the example the file was entered as "dl" in the Sunset software. The Sunset software adds "_Res.txt" to the name to make the actual file name that needs to be referred to in the registry setting. If you called the file SunsetOut the file name would be SunsetOut_Res.txt



Name	Type	Data
(Default)	REG_SZ	(value not set)
ADcardSample	REG_SZ	500
APIRespondTime	REG_SZ	1300
BAMRespondTime	REG_SZ	1000
CreateLog	REG_SZ	1
DiagnosticsMod	REG_SZ	30
FrmRespondTime	REG_SZ	1000
frmVisibleFlag	REG_SZ	0
Horiba_MultiGas_PG_25yRespondTime	REG_SZ	700
MLRespondTime	REG_SZ	270
modbusDelay	REG_SZ	400
PortFail	REG_SZ	100
RS232RespondTime	REG_SZ	500
SampleInt	REG_SZ	20
Sunset_FilePath	REG_SZ	C:\Program Files\OCEC_Inst_Software\RAWDATA\test data OCEC\dl_Res.txt
TemetTmpFile	REG_SZ	C:\Program Files\CALCMET\TEMPRESU.TXT
TeomRespondTime	REG_SZ	250
TeomSetTime	REG_SZ	0
VM100_VisibilityRespondTime	REG_SZ	1000
YSIRespondTime	REG_SZ	1500

Once the registry value has been entered. You only need to select RS232 as the Channel type. The Comm setting does not matter. For convenience you can set it to an unused Com Port. Select the desired channel from the Channels Combo. The address field is not used but for clarity it is suggested that you enter the same string as set in the registry. Copy and Paste to get it exact.



Type: SUNSET
Module:
Comm.: 6
Channels: Thermal OC
Address: C:\Sunset\file.txt

The Average Type should be set to Last Value not Average. Sunset values are updated once in a 2 hour cycle. Consequently the values will be the same for two hours in a row.

Sunset values may also be collected as diagnostics. An example from the diagnostics.ini file appear below:

```
[SUNSET]
FieldCount=5
msg1="1"
name1="Thermal OC"
unit1=""
msg2="2"
name2="Thermal EC"
unit2=""
msg3="3"
name3="OptOC"
unit3=""
msg4="4"
name4="OptEC"
unit4=""
msg5="5"
name5="TC"
unit5="
```

II. Interconnection of Sunset and EnvidasFW.

We set up so the Sunset computer (Dell Laptop) was connected though a LAN cable from the laptop to the D-Link VPN router (DL-804HV) which is also connected to the EnvidasFW computer. When the connection is made you should see a balloon popup from the laptop system tray notifying a “Network Connection” has been made.

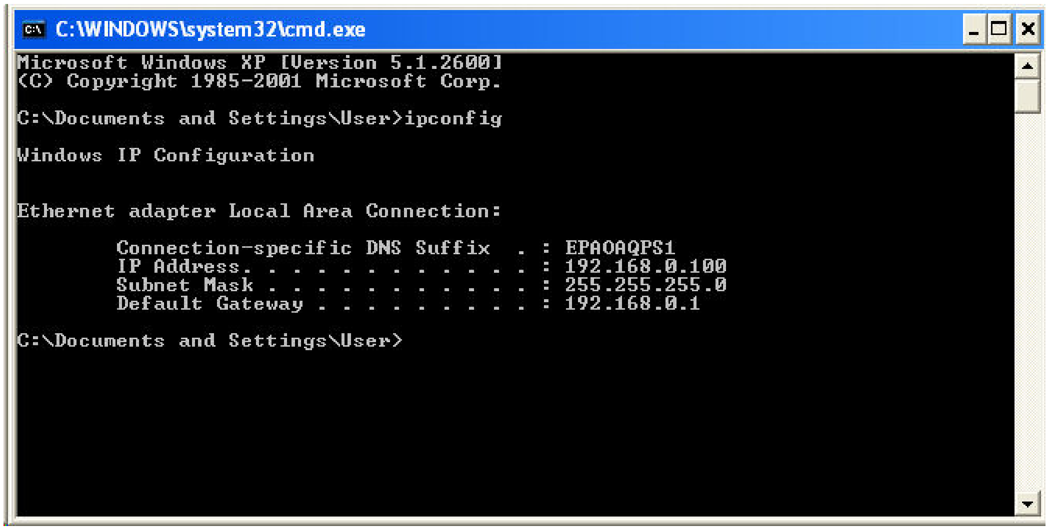
If the laptop didn’t recognize the network cable then a problem exists. Try a different cable or a different port on the router. If the laptop still didn’t recognize the network connection, something is wrong. If possible, call in a service request to your IT department.

Verify the laptop and the EnvidasFW computers can access each other by performing a “ping” from one to the other. Test the communication in both directions.

III. Testing two-way communication

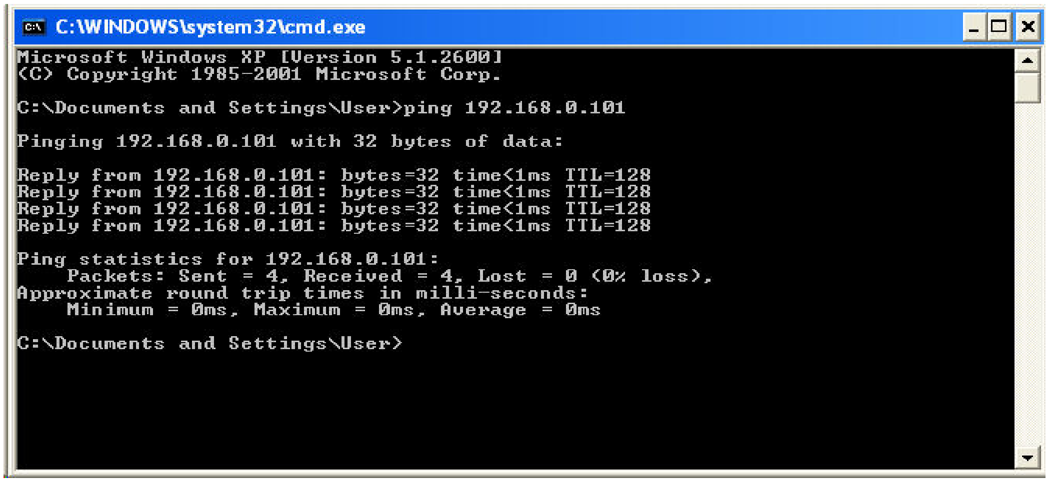
In order to ping one computer from another you need the IP addresses. If you are not sure, go to the EnvidasFW computer and minimize all EnvidasFW panels.

a) From the START menu, click RUN. In the RUN panel open “CMD”
b) When the DOS command window opens, type “ipconfig”, enter.
c) The computer will report the computer’s IP address and the Default Gateway port. As you can see the EnvidasFW IP address usually ends in “.100”. This address is the one you use when you ping from the laptop to the EnvidasFW computer. Assume the Sunset laptop has the same first three groups of numbers but with the last set one higher than the EnvidasFW address (in this case, “.101”).



```
Microsoft Windows XP [Version 5.1.2600]
(C) Copyright 1985-2001 Microsoft Corp.

C:\Documents and Settings\User>ipconfig

Windows IP Configuration


Ethernet adapter Local Area Connection:

        Connection-specific DNS Suffix  . : EPAOAQPS1
        IP Address. . . . . . . . . . . . : 192.168.0.100
        Subnet Mask . . . . . . . . . . . : 255.255.255.0
        Default Gateway . . . . . . . . . : 192.168.0.1

C:\Documents and Settings\User>
```

d) Next, verify communication from the EnvidasFW computer to the Sunset laptop.
e) From the START menu, click RUN. In the RUN panel open “CMD”
f) When the DOS command window opens, type “ping 192.168.0.101”, enter.
g) A good response is shown below.



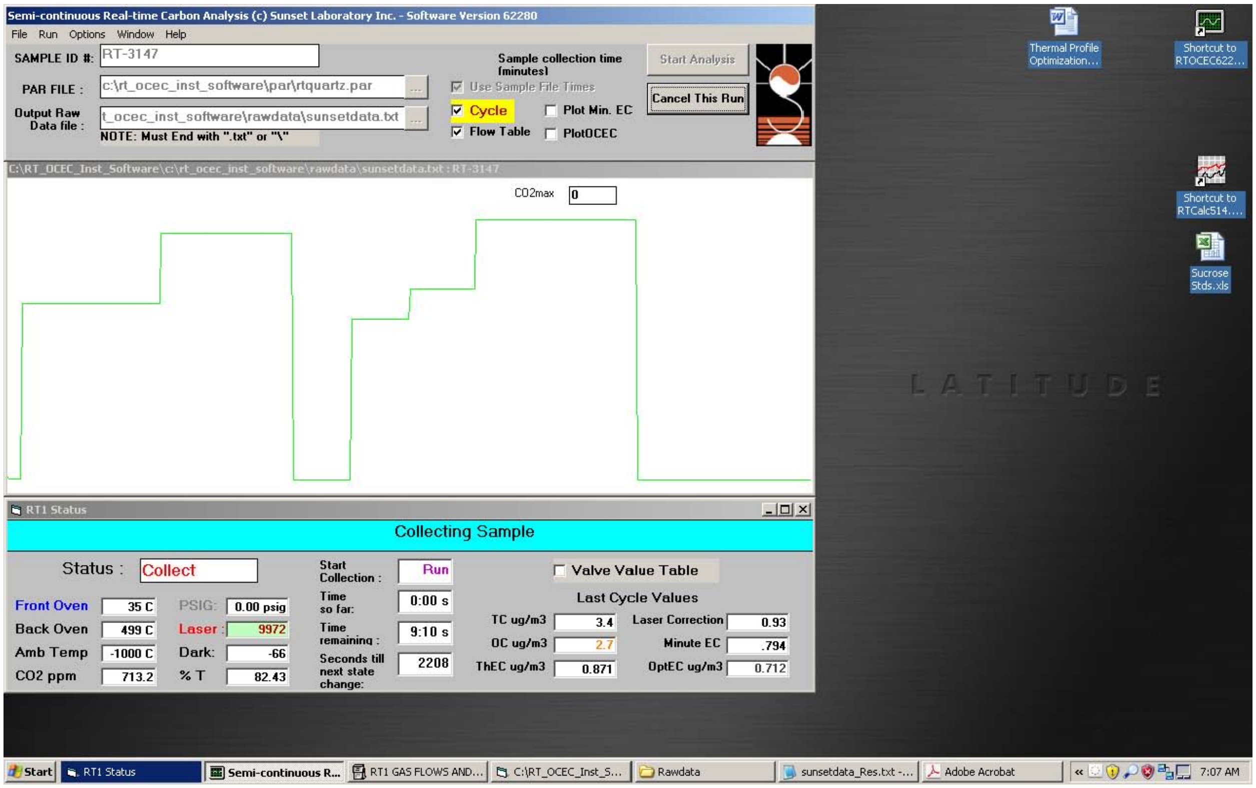
```
Microsoft Windows XP [Version 5.1.2600]
(C) Copyright 1985-2001 Microsoft Corp.

C:\Documents and Settings\User>ping 192.168.0.101

Pinging 192.168.0.101 with 32 bytes of data:

Reply from 192.168.0.101: bytes=32 time<1ms TTL=128
Reply from 192.168.0.101: bytes=32 time<1ms TTL=128
Reply from 192.168.0.101: bytes=32 time<1ms TTL=128
Reply from 192.168.0.101: bytes=32 time<1ms TTL=128

Ping statistics for 192.168.0.101:
    Packets: Sent = 4, Received = 4, Lost = 0 (0% loss),
Approximate round trip times in milli-seconds:
    Minimum = 0ms, Maximum = 0ms, Average = 0ms

C:\Documents and Settings\User>
```

e) After the successful “ping”, close the DOS Command window.
f) Next, perform the “ping” test from the Sunset laptop to the EnvidasFW computer.
g) From the START menu, click RUN. In the RUN panel open “CMD”
h) When the DOS command window opens, type “ping 192.168.0.100”, enter.
i) A good response is shown above only with the IP address of the EnvidasFW computer.

In our experience we had a successful “ping” from the Sunset laptop to the EnvidasFW computer, however not in the other direction. We determined that the laptop had the Windows Firewall set to ON which prevented communication into the laptop. If this happens in your case, go to the Windows Help program and follow directions on how to turn OFF the Firewall. (Go to: My Computer > Help > Help and support Center, then type Firewall in the search box. You must have Administration rights to turn OFF the Firewall.

IV. Prepare the Sunset laptop to write data to a specified file.

In order for the EnvidasFW program to get data from the Sunset laptop it is necessary to set the Sunset to write to one file instead of to those made using a “date code” as part of the file name. When we first began acquiring Sunset data all was well until midnight. The problem was EnvidasFW had no way to know what the new file name was. With the Sunset program loaded but in a “stopped” condition, fill in the name you want in the “Output Raw Data file” box. (Third box down on upper left)



Semi-continuous Real-time Carbon Analysis (c) Sunset Laboratory Inc. - Software Version 62280

SAMPLE ID #: RT-3147
PAR FILE : c:\rt_ocec_inst_software\par\rtquartz.par
Output Raw Data file : t_ocec_inst_software\rawdata\sunsetdata.txt
NOTE: Must End with ".txt" or "\"
Sample collection time (minutes)
☑ Use Sample File Times
☑ Cycle
☐ Plot Min. EC
☑ Flow Table
☐ PlotOCEC

C:\RT_OCEC_Inst_Software\c:\rt_ocec_inst_software\rawdata\sunsetdata.txt : RT-3147

CO2max 0

RT1 Status

Collecting Sample

Status : Collect
Start Collection : Run
☐ Valve Value Table

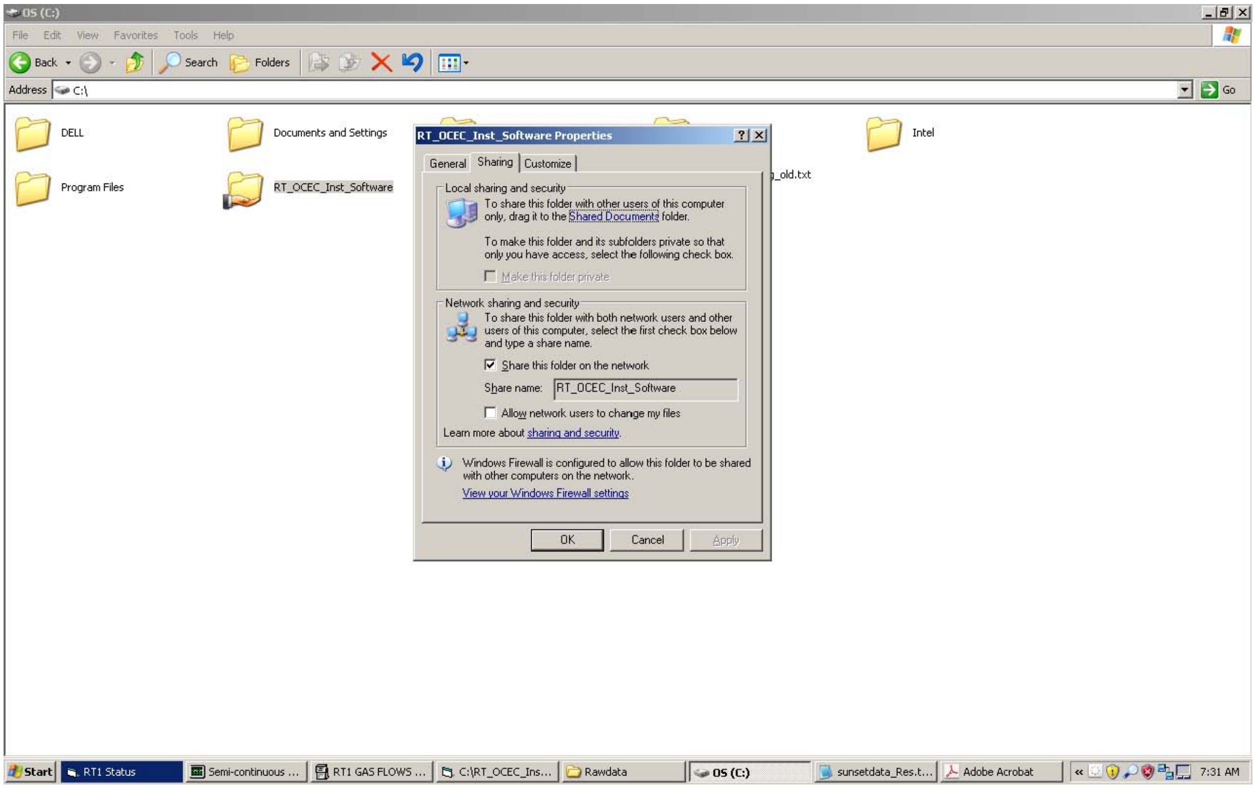
Front Oven 35 C
Back Oven 499 C
Amb Temp -1000 C
CO2 ppm 713.2
PSIG: 0.00 psig
Laser : 9972
Dark: -66
% T 82.43
Time so far: 0:00 s
Time remaining : 9:10 s
Seconds till next state change: 2208

Last Cycle Values
TC ug/m3 3.4
OC ug/m3 2.7
ThEC ug/m3 0.871
Laser Correction 0.93
Minute EC .794
OptEC ug/m3 0.712

In our case we selected “sunsetdata.txt”. Please make note of the complete path to this file for use later. (“C:\rt_ocec_inst_software\rawdata\sunsetdata.txt”

V. Prepare Sunset laptop to SHARE data file with EnvidasFW

Make the folder which will contain the data file a “Shared” folder. Minimize the Sunset program window then go to Start >My Computer > C:\ . When the folders on C:\ appear put the mouse pointer over the Sunset folder and click the RIGHT button to open a list of action choices, then select “Properties”. When the panel appears, open the Sharing tab then place a check mark in the “Share this folder on the network” box. Then type in the folder name “RT_OCEC_Inst_Software”. Note that Windows reports that Windows Firewall has been configured to allow the sharing of this folder with other computers on the network.



RT_OCEC_Inst_Software Properties

Local sharing and security

To share this folder with other users of this computer only, drag it to the Shared Documents folder.

To make this folder and its subfolders private so that only you have access, select the following check box.

☐ Make this folder private

Network sharing and security

To share this folder with both network users and other users of this computer, select the first check box below and type a share name.

☑ Share this folder on the network

Share name: RT_OCEC_Inst_Software

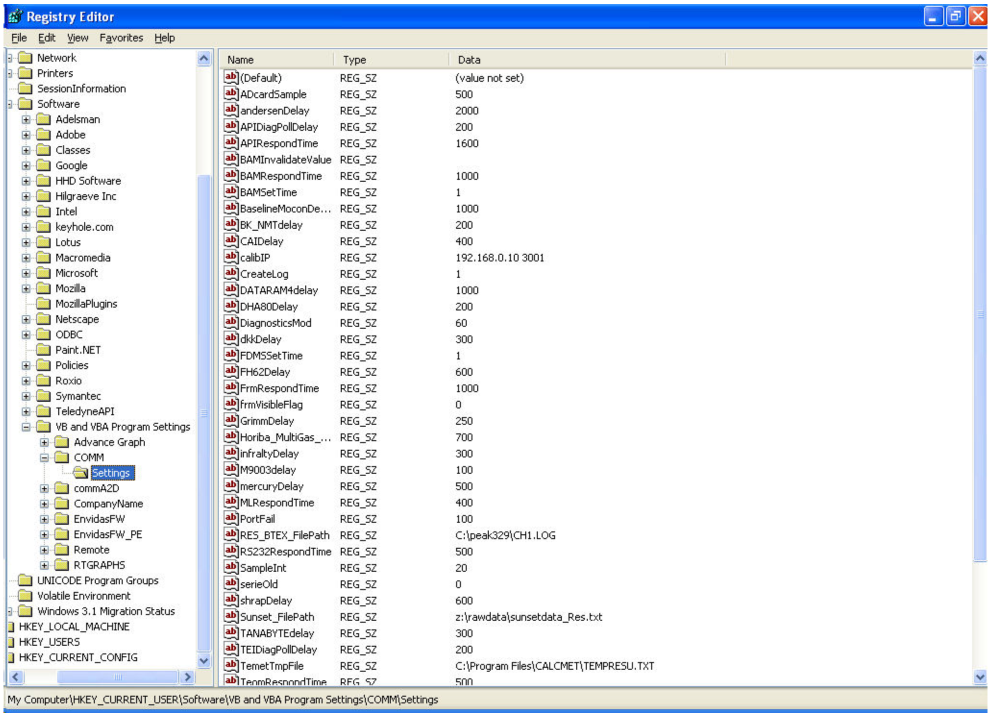
☐ Allow network users to change my files

Learn more about sharing and security.

Windows Firewall is configured to allow this folder to be shared with other computers on the network.

VI. Configure the EnvidasFW computer’s Registry.

Minimize any open EnvidasFW panels then go to “Start” > “Run”, then enter “regedit” in the box. (You must have Administrative rights to perform this action). Under “Software > VB and VBA Program Settings > COMM” look down the list until you locate “Sunset_FilePath”. Double-click on this name and an edit window will open. Type in “z:\rawdata\” and the name of the Sunset data file you selected. In our case we will enter “z:\rawdata\sunsetdata_Res.txt”. (Sunset always appends the “_Res.txt” to the name you select). When this has been done, cancel the panel.

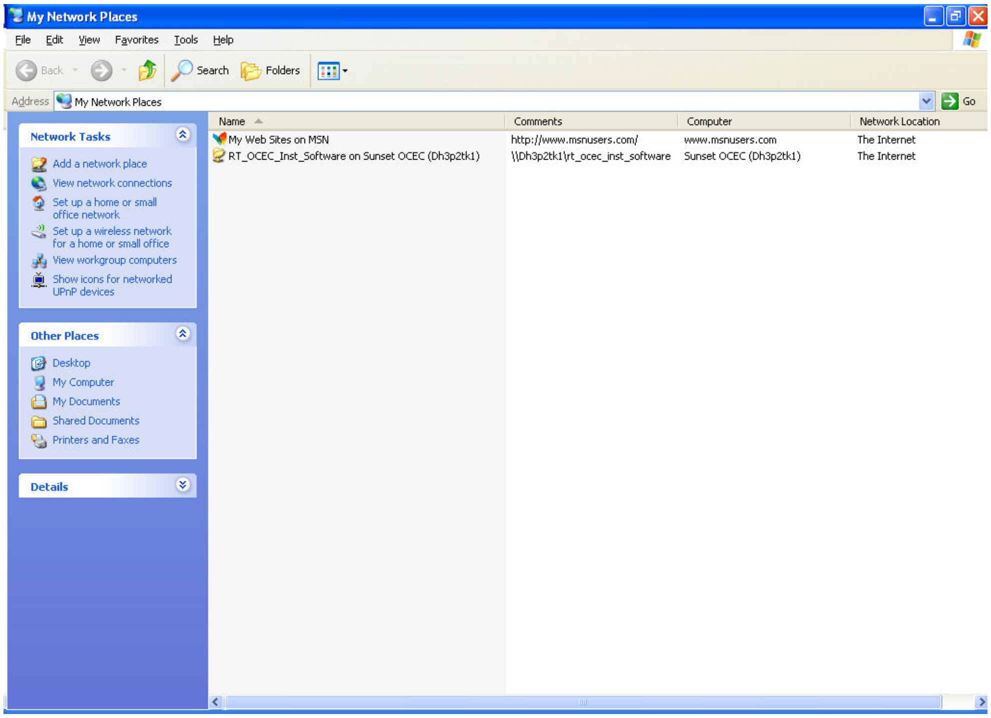


Name	Type	Data
(Default)	REG_SZ	(value not set)
ADcardSample	REG_SZ	500
andersenDelay	REG_SZ	2000
APIDiagPollDelay	REG_SZ	200
APIRespondTime	REG_SZ	1600
BAMInvalidateValue	REG_SZ	
BAMRespondTime	REG_SZ	1000
BAMSetTime	REG_SZ	1
BaselineMoconDe...	REG_SZ	1000
BK_NMTdelay	REG_SZ	200
CAIDelay	REG_SZ	400
calibIP	REG_SZ	192.168.0.10 3001
CreateLog	REG_SZ	1
DATARAM4delay	REG_SZ	1000
DHA80Delay	REG_SZ	200
DiagnosticsMod	REG_SZ	60
dkkDelay	REG_SZ	300
FDMSSetTime	REG_SZ	1
FH62Delay	REG_SZ	600
FrmRespondTime	REG_SZ	1000
frmVisibleFlag	REG_SZ	0
GrimmDelay	REG_SZ	250
Horiba_MultiGas_...	REG_SZ	700
infraltyDelay	REG_SZ	300
M9003delay	REG_SZ	100
mercuryDelay	REG_SZ	500
MLRespondTime	REG_SZ	400
PortFail	REG_SZ	100
RES_BTEX_FilePath	REG_SZ	C:\peak329\CH1.LOG
RS232RespondTime	REG_SZ	500
SampleInt	REG_SZ	20
serieOld	REG_SZ	0
shrapDelay	REG_SZ	600
Sunset_FilePath	REG_SZ	z:\rawdata\sunsetdata_Res.txt
TANABYTEdelay	REG_SZ	300
TEIDiagPollDelay	REG_SZ	200
TemetTmpFile	REG_SZ	C:\Program Files\CALCMET\TEMPRESU.TXT
TeomRespondTime	REG_SZ	500

My Computer\HKEY_CURRENT_USER\Software\VB and VBA Program Settings\COMM\Settings

VII. Map a EnvidasFW computer Network Drive to the Sunset laptop

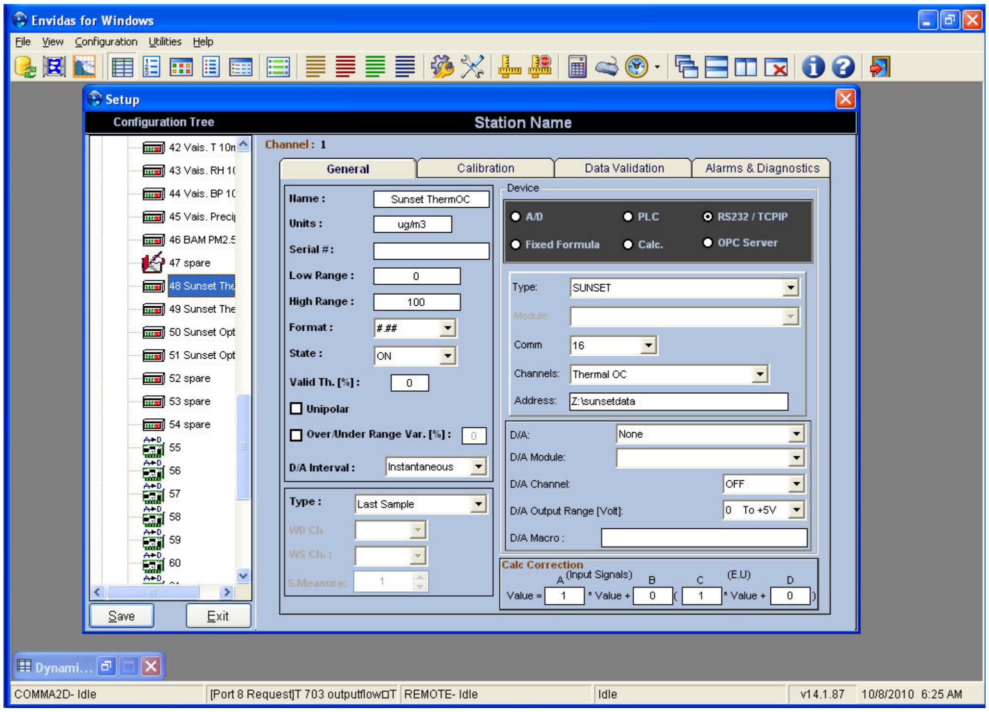
Go to “My Computer > My Network Places” and select “Add a Network Place”. Follow directions in the “Add a Network Wizard”. When requested to enter the location, type two backslashes, then the Sunset computer name (in our case it is “Dh3p2kt1”), followed by the folder name which contains the “sunsetdata_Res.txt” file. Our network place name was then “\\Dh3p2kt1\rt_ocec_Inst_software”. After the Wizard finishes, the My Network Places directory will show the new Name and Path to the Sunset laptop.



Name	Comments	Computer	Network Location
My Web Sites on MSN	http://www.msnusers.com/	www.msnusers.com	The Internet
RT_OCEC_Inst_Software on Sunset OCEC (Dh3p2tk1)	\\Dh3p2tk1\rt_ocec_inst_software	Sunset OCEC (Dh3p2tk1)	The Internet

VIII. Configure EnvidasFW for Sunset data channels.

Follow the usual set up process to add four new data channels to the configuration. These will be “RS232” type channels (in name only – since they are actually via a mapped network drive). Appendix D19 above provides guidance how to set up each channel. One discrepancy to note is that our version did not have a “Last Value” choice for the “Average Type”. Our version had “Last Sample” and this worked as expected. We also noted that the “Address” field was not as suggested in the D19 guide. In our case we used “Z:\sunsetdata” and this worked as expected. Make the “Valid Thr [%] file 0 (zero) as the Sunset data will only be available once per cycle – in our case once per two hours.



Channel : 1

Name : Sunset ThermOC
Units : ug/m3
Serial # :
Low Range : 0
High Range : 100
Format : #.##
State : ON
Valid Th. [%] : 0
☐ Unipolar
☐ Over/Under Range Var. [%] : 0
D/A Interval : Instantaneous

Type : Last Sample
WD Ch
WS Ch. :
S.Measure: 1

Device
○ A/D ○ PLC ● RS232 / TCPIP
○ Fixed Formula ○ Calc. ○ OPC Server

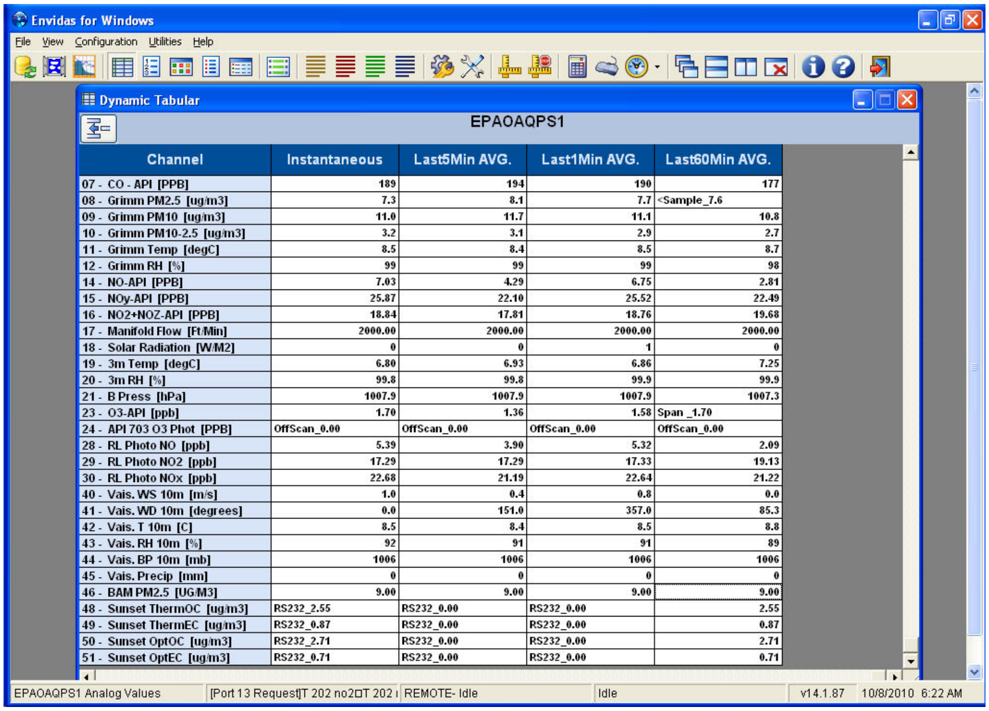
Type: SUNSET
Module:
Comm 16
Channels: Thermal OC
Address: Z:\sunsetdata

D/A: None
D/A Module:
D/A Channel: OFF
D/A Output Range [Volt]: 0 To +5V
D/A Macro :

Calc Correction
A (Input Signals) B C (E.U) D
Value = 1 * Value + 0 (1 * Value + 0)

COMMA2D- Idle | [Port 8 Request]T 703 outputflow□T | REMOTE- Idle | Idle | v14.1.87 | 10/8/2010 6:25 AM

When the Dynamic Tabular data is viewed the Sunset data channels report an RS232 error in the Instantaneous, Last 5 Min AVG., and Last 1 Min AVG. columns. However, the Last 60 Min. AVG. data appears valid.



EPAOAQPS1

Channel	Instantaneous	Last5Min AVG.	Last1Min AVG.	Last60Min AVG.
07 - CO - API [PPB]	189	194	190	177
08 - Grimm PM2.5 [ug/m3]	7.3	8.1	7.7	<Sample_7.6
09 - Grimm PM10 [ug/m3]	11.0	11.7	11.1	10.8
10 - Grimm PM10-2.5 [ug/m3]	3.2	3.1	2.9	2.7
11 - Grimm Temp [degC]	8.5	8.4	8.5	8.7
12 - Grimm RH [%]	99	99	99	98
14 - NO-API [PPB]	7.03	4.29	6.75	2.81
15 - NOy-API [PPB]	25.87	22.10	25.52	22.49
16 - NO2+NOZ-API [PPB]	18.84	17.81	18.76	19.68
17 - Manifold Flow [Ft/Min]	2000.00	2000.00	2000.00	2000.00
18 - Solar Radiation [W/M2]	0	0	1	0
19 - 3m Temp [degC]	6.80	6.93	6.86	7.25
20 - 3m RH [%]	99.8	99.8	99.9	99.9
21 - B Press [hPa]	1007.9	1007.9	1007.9	1007.3
23 - O3-API [ppb]	1.70	1.36	1.58	Span _1.70
24 - API 703 O3 Phot [PPB]	OffScan_0.00	OffScan_0.00	OffScan_0.00	OffScan_0.00
28 - RL Photo NO [ppb]	5.39	3.90	5.32	2.09
29 - RL Photo NO2 [ppb]	17.29	17.29	17.33	19.13
30 - RL Photo NOx [ppb]	22.68	21.19	22.64	21.22
40 - Vais. WS 10m [m/s]	1.0	0.4	0.8	0.0
41 - Vais. WD 10m [degrees]	0.0	151.0	357.0	85.3
42 - Vais. T 10m [C]	8.5	8.4	8.5	8.8
43 - Vais. RH 10m [%]	92	91	91	89
44 - Vais. BP 10m [mb]	1006	1006	1006	1006
45 - Vais. Precip [mm]	0	0	0	0
46 - BAM PM2.5 [UG/M3]	9.00	9.00	9.00	9.00
48 - Sunset ThermOC [ug/m3]	RS232_2.55	RS232_0.00	RS232_0.00	2.55
49 - Sunset ThermEC [ug/m3]	RS232_0.87	RS232_0.00	RS232_0.00	0.87
50 - Sunset OptOC [ug/m3]	RS232_2.71	RS232_0.00	RS232_0.00	2.71
51 - Sunset OptEC [ug/m3]	RS232_0.71	RS232_0.00	RS232_0.00	0.71

EPAOAQPS1 Analog Values | [Port 13 Request]T 202 no2□T 202 | REMOTE- Idle | Idle | v14.1.87 | 10/8/2010 6:22 AM

This completes the configuration and set up guide for the Sunset semi-continuous OCEC monitor.