

PM_{10-2.5} Speciation Pilot Monitoring Program, Sample Analysis, and Data Reporting

Quality Assurance Project Plan (QAPP) QA Level IV

FINAL

Prepared by
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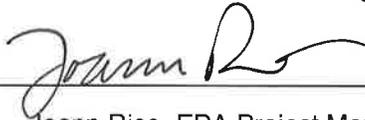
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QAPP Approval Signatures
Category IV QAPP



Joann Rice, EPA Project Manager

4-1-10

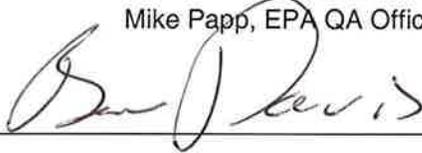
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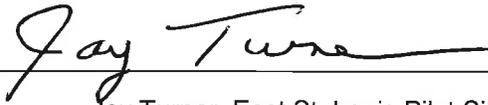
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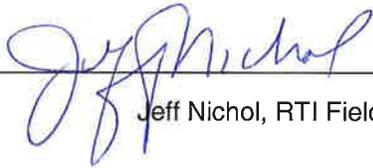
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DISTRIBUTION LIST

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1.0 Introduction

This is a level IV Quality Assurance Project Plan (QAPP) that covers an environmental data operation (EDO) to collect pilot study field data at two locations (Phoenix, AZ and East St. Louis, IL) to evaluate field sampling and analysis methods and investigate the feasibility of those methods for long-term PM_{10-2.5} speciation monitoring. A category IV QAPP includes projects involving Environmental Data Operations (EDOs) to study basic phenomena or issues, including proof of concepts, screening for particular analytical species and their physical characteristics. This work assignment is such a project and thus generally does 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, local scale monitoring; monitoring, modeling, emission inventory, assessments; and field testing of performance test methods and source monitoring procedures, evaluating formal requests to allow the use of alternative methods, or investigating the feasibility of new or modified performance test methods or source monitoring procedures. Note that the majority of the PM_{10-2.5} particulate matter fraction will be collected and 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 majority of analytical needs for this PM_{10-2.5} Speciation Pilot Study.

1.1 Project/Task Description

In 1997, the United State Environmental Protection Agency (EPA) promulgated revisions to the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM), including adding a standard for fine particulate matter (PM_{2.5}). In 2006, EPA issued a final monitoring rule for thoracic coarse particles. Coarse particles have aerodynamic diameters between 2.5µm and 10µm (PM_{10-2.5}). The promulgated monitoring requirements specified the placement of PM_{10-2.5} speciation samplers at National Core (NCore) sites. Sample collection procedures and analysis methods for PM_{10-2.5} speciation measurements must be developed prior to field deployment of the routine monitoring network. EPA has examined PM_{10-2.5} *mass measurement methods* through an extensive, multi-site field study. On February 11, 2009 EPA conducted a consultation with the CASAC Ambient Air Monitoring & Methods (AAMM) Subcommittee for external input on sampling and analysis issues for PM_{10-2.5} speciation. To address concerns of both the EPA and CASAC AAMM members, an important next step towards implementing the PM_{10-2.5} speciation monitoring program is the development and execution of a small-scale pilot monitoring study. The CASAC AAMM strongly recommended the use of dichotomous samplers over the FRM for PM_{10-2.5} speciation.

This study is important from several perspectives. First, to assess if chemical and physical characterization of PM_{10-2.5} differs when the coarse values are determined using the PM₁₀ minus PM_{2.5} method as compared to characterization of the PM_{10-2.5} fraction derived from the dichotomous sampler which contains 10% or less of the PM_{2.5} fraction. There is concern that

“mixing” of the PM_{10-2.5} fraction with the PM_{2.5} fraction on a filter from the PM₁₀ sampler gives rise to the possibility of chemical and physical changes due to the “mixing.” Two sites with significant differences in the makeup of PM will be tested over four seasons. Another important reason for conducting the pilot study is determine the training and skills required of the field operator and supporting laboratory to produce quality data with a high percentage of data capture at reasonable overall expense. A third reason for the pilot study is to provide a data base of PM_{10-2.5} chemical and physical information, supplemented by information from measurements not normally made in the PM_{2.5} chemical speciation network (e.g., protein content, water soluble organic material content, metals determination by ICP-MS) and derived from collocated instruments (TEOM sampler for continual measurements; MOUDI sampler for size-fractionation of PM₁₀). This data base will be provided to EPA personnel, atmospheric scientists, and others concerned with the science of PM air pollution and with making decisions about health effects and the possible need for lessening human exposure to the PM_{10-2.5} fraction of particulate matter.

Two monitoring sites will be operated for one year. The sites were chosen to represent different environmental concentrations and aerosol mixes. Two methods will primarily be used to collect PM_{10-2.5} samples for analysis - dichotomous samplers and paired PM₁₀ and PM_{2.5} Federal Reference Method samplers (the “difference method”). The filter samples collected at these sites will be analyzed with various laboratory analysis methods. Additional samplers and semi-continuous monitors will be operated to further characterize the coarse particulate matter and aid in the interpretation of any differences between dichotomous and difference method data. The results of this study will be used to establish routine field operating procedures and laboratory standard operating procedures (SOPs) for implementation in the PM_{10-2.5} speciation monitoring program.

A pilot site in Phoenix, AZ will be operated by the Maricopa County Air Quality Department. A pilot site in East St. Louis, IL, will be operated by personnel from the Air Quality Laboratory at Washington University in St. Louis. (Throughout this document these organizations are referred to as the “local monitoring agency”.) EPA will provide the necessary sampling equipment and semi-continuous monitors. Equipment installation will be the responsibility of the local monitoring agency, as well as continued operation, maintenance, and coordination of site audits with their QA staff or other organizations as noted below. The local monitoring agency will receive the filters from the contractor, RTI International, collect all field filter samples, and return the samples to RTI for processing and data report-out.

Twenty-four hour integrated samples (from midnight-to-midnight local standard time) will be collected at the pilot sites. Support for integrated sampler installation and operation, necessary training, initial equipment audits and flow checks, and filter preparation and laboratory sample processing/analyses will be conducted by RTI International personnel and subcontractors who regularly serve the EPA/OAQPS PM_{2.5} Chemical Speciation Network. Laboratory work areas will include: sample handling and archival laboratory (SHAL) for shipping and receiving filters, acid denuder preparation, sampling module assembly and disassembly, and data sheet handling; gravimetry; X-ray fluorescence (XRF) analysis for elements; ion analysis by ion chromatography (IC); analysis for organic, elemental, and carbonate carbon; inductively coupled plasma mass spectrometry (ICP-MS) analysis for selected metals. Additional analyses may include: analysis for semi-volatile and water-soluble organic compounds; scanning electron microscopy (SEM) analysis to characterize particles; and chemical assays for the identification and quantification of biological material, including proteins.

Each pilot site will include a semi-continuous mass monitor for PM_{10-2.5}. Installation, operation, training, and audits of the semicontinuous monitors will be responsibility of the local monitoring agency.

Data analysis and preparation of quarterly data summary reports will be carried out by Sonoma Technology, Inc. (STI) personnel under contract EP-D-09-097 in concert with personnel from the EPA.

1.2 Pilot Study Objectives

The primary pilot study objectives are to develop the target species analyte list for long-term routine speciation (what species need to be measured); evaluate and define analysis methods for long-term routine speciation monitoring and the necessary SOPs; evaluate the appropriateness of using a dichot for long-term speciation monitoring; learn about sampling and operational issues regarding the use of dichots (e.g., manual versus sequential); and to evaluate data from the study to inform the issues below.

As a secondary objective, the data from the pilot study will be used, to the extent possible, to inform and gain insight regarding the questions below and future study related to PM_{10-2.5} speciation. These questions may not be definitively answered. Particular assessments of the data (done quarterly) and the confidence in which we can draw conclusions regarding these questions will be made as the study progresses.

- What species should be routinely measured? Major soil components (Si, Al, Ti, Ca, and Fe) have been shown to be important contributors to the PM_{10-2.5} mass. Are there other elements that are important PM_{10-2.5} species to routinely measure?
- What are the PM_{10-2.5} speciation sampling artifacts that may be encountered?
- Has the issue of fine particle intrusion into coarse mode been adequately resolved with dichotomous samplers? It has improved, but is still around 10% under some conditions. Is that sufficient for speciation using dichotomous samplers?
- What are the issues with using current PM_{2.5} speciation analysis methods on PM₁₀ and PM_{10-2.5} filters? For example, can the complication of particle size effects in XRF be adequately resolved using absorption correction procedures? Does XRF provide adequate sensitivity (detection limits) to measure elements in the coarse fraction (minor flow) of the dichot for typical loadings obtained from 24-hour samples?
- Should ICP-MS be considered instead of XRF for PM_{10-2.5}? Is it an improvement over XRF and how does the sensitivity and quantitative results compare? If so, is inconsistency with PM_{2.5} and IMPROVE an issue for data use and comparability? ICP-MS is a destructive method and no filter will be available for long-term archive or subsequent analysis. ICP-MS is also relatively expensive.
- Are metal oxides a significant source of interference in the thermal-optical analysis of PM_{10-2.5} OC and EC?
- Is carbonate carbon a significant PM_{10-2.5} constituent? Are the measurement methods robust?

- To what extent can we address the collection of biological materials (e.g., pollen, etc.)? Analysis of biological material is not currently part of the PM_{2.5} speciation program and may need a different filter type in addition to additional analysis methods? If biological particles need to be characterized, what specific types of biological materials need to be measured and how will they be collected and analyzed? Could SEM be used on Teflon filters to characterize biological material?
- For nitrate sample collection on nylon filters, can an acid gas denuder be placed in the dichotomous sampler? Is an acid gas denuder necessary, or is a clean PM₁₀ head sufficient to serve as a denuder by itself due to the large surface area and acid gas interactions with it?

1.3 Pilot Monitoring Program Sample Analysis and Data Reporting

Filter-based samples and semicontinuous monitoring data for the PM_{10-2.5} pilot study will be collected by the local monitoring agency in Phoenix, AZ and by university personnel at the St. Louis – Midwest Supersite in East St. Louis, IL. All sampling equipment, including filter modules, will be provided by the EPA. Shipping containers and shipment costs will be provided by the EPA. RTI will service the sites with prepared filters, loaded into modules or cassettes, for the filter-based methods chosen for testing and comparison. This service will include any quality assurance checks such as providing filters for field blank determination. RTI will provide 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 various types of PM_{10-2.5} samples. Field forms and data processing procedures for the semicontinuous measurements will be developed. These forms will be completed by field personnel and reviewed and archived by STI. EPA Regional offices and/or the respective local monitoring agencies will provide staff and funds to conduct any quality assurance reviews and audits of the pilot study field sites, for example, on-site checks of sampler flow rate, temperature, and pressure.

Filters will be shipped from the field under cold conditions as is done for the PM_{2.5} CSN. Sample filters collected will be analyzed by RTI in accordance with the analysis methods specified in the pilot test design identified in Section 2.2. Analyses of filters for PM_{10-2.5} mass by microbalance gravimetry; elements by XRF, metals by ICP-MS; ions by IC ; and organic carbon, elemental carbon, and carbonate carbon by thermaloptical analysis will be provided through the existing CSN contract and laboratory QAPP (RTI/0212053/01QA) prepared under EPA contract EP-D-09-010. Total protein analysis and SEM of deposits on Teflon filters, and analysis for water soluble organics will be provided by RTI under EPA contract EP-D-08-047 as described in this QAPP.

For the laboratory operation performed under the CSN contract, a draft version of the data from the filter-based integrated sampling will first be reported to the pilot study data file maintained by RTI within 45 to 60 days of the sampling event and transferred to EPA/STI for interpretive analysis as the study proceeds. Continuous data from the semicontinuous mass monitors will be electronically transferred to EPA's secure AIRNowTech data system (www.airnowtech.org) for access by EPA/STI. If authorized, the data will then be uploaded to the EPA's Air Quality System (AQS) along with applicable uncertainties and method detection limits. All analytical data reported will be accompanied by information regarding quality control

of the analytical sequence (blank and control sample analysis results, etc.). Some data generated during the pilot study, such as SEM morphology and biological data, may not be generated in a format easily uploaded to AQS. The draft evaluation data for these operations will be transferred to EPA/STI for interpretive analysis within 60 to 75 days of the sampling event. If these types of samples are collected on a less frequent basis, the samples will be batched and the 60 to 75 day timeframe will be based on the last sampling event in the batch.

1.4 Standard Operating Procedures (SOPs)

The majority of the sampling and analysis techniques to be used in the PM_{10-2.5} Speciation Pilot Monitoring Program are those from the PM_{2.5} Chemical Speciation Network (CSN) program and the Federal Reference Method (FRM) gravimetric network. All these methods and SOPs are already approved by EPA. In several cases, existing SOPs and procedures approved for use in other studies and by State Agencies will be used as PM_{10-2.5} speciation pilot program SOPs.

RTI will provide SOPs for all analysis and physical characterization methods used in the pilot program and will document any new method procedures and method detection limits by preparing or revising SOPs 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. Refer to Table 4 for a list of SOPs applicable to chemical and physical characterization of PM_{10-2.5}.

For field sampling devices used to collect PM on filters, operator's manuals and available approved SOPs will initially be used to operate the field sampling devices. Site operators will be encouraged to provide input on these materials during all phases of the study. At the end of the field study, SOPs will be developed by RTI for the recommended sampling devices and analysis methods for the long-term PM_{10-2.5} speciation monitoring program. Some of the samplers to be deployed in this pilot program are filling research needs (e.g. the MOUDI and TEOM samplers) and are not expected to become part of the long-term monitoring network. The field sampling and analysis method SOPs to initially be used for this project are attached in Appendices C and D.

2.0 Quality Objectives and Criteria for Measurement Data

The quality objectives and criteria for field sample collection and laboratory measurements are discussed in Sections 2.1 and 2.2. Sampling and analysis protocols are described in this QAPP; the every 3rd day sampling and analysis schedule will result in a total of 336 Teflon\Nylon filter samples and 456 Quartz filter samples per site. Ten percent of the filter samples will be collocated. The Teflon filters will be analyzed for elements and ions and the Quartz filters will be analyzed for carbon under the CSN contract. This schedule of sample collection and analysis may be adjusted during the one-year study after periodic review of the field operations, laboratory analyses, and collected data. At the end of the study, all data will be evaluated and decisions regarding continued sampling may occur at these two sites, different sites, or additional sites across the US. The pilot study is indeed exploratory research needed to make decisions regarding the long term program in the future.

The data from this study will be used to determine estimates of certain measurement quality attributes or indicators. We do not yet have data for these attributes for PM_{10-2.5} speciation analyses and want to get estimates of this information from this study.

- Bias (the degree of agreement between a measured value and a true value): There are no FRMs for PM speciation measurements to assess bias; however, the FRM for mass will be collocated and bias between the filter-based PM_{10-2.5} mass measurements can be assessed.
- Precision (measure of agreement between two determinations of the same parameter): A small percentage (10%) of collocated filter measurements will be collected to assess precision of the analysis methods.
- Representativeness (how closely these locations represent areas of similar aerosol compositions): The two sites were chosen to represent different environmental concentrations and aerosol mixes. The site in Phoenix represents an area of high PM coarse aerosol and the site in St. Louis represents an industrialized urban area. The CASAC AAMM supported the selection of these locations to test PM_{10-2.5} methods and the monitoring agencies in these locations were willing participants.
- Completeness (amount of valid data obtained): The targeted completeness for this study is 80%.
- Comparability (comparison of measurements between locations): The data from both sites can be compared since identical samplers and measurements will be made at both locations.
- Method detection limit – MDL (the lowest concentration that can be measured with a method): The analysis methods used for PM_{2.5} speciation have MDL estimates provided in the Appendix 2 of the CSN QAPP, Revision 6, dated February 20, 2009. Those estimates will be used for this study.

2.1 Field Measurements

The following equipment will be installed and operated at each of the two sites:

- Two (2) sequential dichotomous samplers (Thermo 2025D);
- Two (2) sequential Thermo 2025 Federal Reference Method samplers of same make and model, one for PM₁₀ and the other for PM_{2.5} (for the PM_{10-2.5} “Difference Method” measurements);
- One (1) dichotomous semi-continuous mass monitor (Thermo 1405-DF FDMS TEOM);
- One (1) eight-stage (0.18, 0.32, 0.56, 1.0, 1.8 2.5, 5.6, and 10 µm) MOUDI impactor (MSP Corporation); and
- Operational acceptance limits for the PM sampling devices are presented in Table 1 below.

The field site managers will ensure that the site has 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 (one year). See Appendix A for

the 2010 three-day monitoring schedule. Continuous PM instruments will also be operated on local standard time. A maintenance schedule must be developed for field sampling equipment and verification devices. Consult the operator’s manuals and the SOPs in Appendix C of this QAPP for procedures for calibration of temperature and pressure sensors and the flow rates of sampling channels. A summary of required field operations and maintenance tasks that are more fully explained in the SOPs in Appendix D is presented in Table 2 below. Maintenance activities for the TEOM are described in the “Standard Operating Procedure for the Continuous Measurement of Particulate Matter Thermo Scientific TEOM[®] 1405-DF Dichotomous Ambient Particulate Monitor with FDMS[®] Federal Equivalent Method EQPM-0609-182 for PM_{2.5} (Number STI-905505.03-3657-SOP” by Sonoma Technology, Incorporated. The FRM and dichotomous samplers maintenance needs are in the Rupprecht & Patashnick Partisol-Plus Model 2025 PM-2.5 Sequential Air Sampler [Air Quality Surveillance Branch SOP 404, R&P Model 2025 by the California Environmental Protection Agency Air Resources Board. The maintenance requirements for the MOUDI sampler are discussed in the DRI Standard Operating Procedure: “Micro-Orifice Uniform Deposit Impactor (MOUDI) Field and Laboratory Operations Number 1-208.3, Revision 3 (TUUH.92).”

Table 1. Measurement Quality Objectives for the PM sampling devices

Requirement	Frequency	Acceptance Criteria
Clock/timer verification	Every sampling event (FRM, dichotomous) and monthly (TEOM) by site operator (MOUDI sampler uses a mechanical timer.)	1 min/month
Barometric Pressure (all PM samplers except MOUDI that has no pressure sensor)		
Single-point barometric pressure verification	Quarterly audit (FRM and dichotomous) and monthly for TEOM by the site operator	±10 mm Hg
Multi-point barometric pressure verification	1 per year or upon failure of the single-point verification	±10 mm Hg
Barometric pressure calibration	Upon failure of the multi-point verification	±10 mm Hg
Ambient and Filter Temperature (all PM samplers except MOUDI that has no temperature sensors)		
Single-point temperature verification	Quarterly audit (FRM and dichotomous) and monthly for TEOM by the site operator	±2 °C of standard
Multi-point temperature verification	1 per year or upon failure of the single-point verification	± 2 °C of standard
Temperature calibration	Upon failure of the multi-point verification	Adjust to within ± 0.1 °C of std.
Flow Rate		
External leak check	Quarterly audit by site operator (FRM, dichotomous, and MOUDI) Monthly or when the filter is replaced (TEOM)	<100 mL/min (FRM) <25 mm Hg/min (Dichotomous) <150 mL/min (TEOM) Auditory (MOUDI)

Internal leak check	Upon failure of external leak check by site operator (FRM, dichotomous, MOUDI, and TEOM)	<100 mL/min (FRM) <25 mm Hg/min (Dichotomous) <150 mL/min (TEOM) Auditory (MOUDI)
Single-point flow rate verification	Quarterly audit (FRM and dichotomous) and monthly for TEOM by the site operator	±4% of indicated flow or ±5% of design flow
Multi-point flow rate verification	1 per year or upon failure of the single-point verification	±2% of transfer standard
Flow Rate (FR) calibration	Upon failure of the multi-point verification	±4% of design flow
NIST-traceable Standards		
Field barometer	1/yr	±1mm Hg resolution; ±5mm Hg accuracy
Field thermometer	1/yr	±0.1 °C resolution; ±0.5 °C accuracy
Flow rate transfer standard	1/yr	±2% of NIST-traceable standard

Table 2. Maintenance Activities for the PM sampling devices.

Frequency	Maintenance Item
PM Samplers (FRM and dichotomous)	
Every visit by site operator	<ol style="list-style-type: none"> 1. Solar radiation shield of the sampler head should be cleaned with a wet cloth. 2. Inspect and, if necessary, empty water collector bottle. 3. Inspect the filter cassettes for contamination (wipe with a clean dry cloth). 4. Inspect the seals of the filter cassette (wipe seals with a clean dry cloth).
Every 10 sampling events or as needed by site operator.	<ol style="list-style-type: none"> 1. Solar radiation shield of the sampler head should be cleaned with a wet cloth. 2. Inspect and, if necessary, empty water collector bottle. 3. Inspect the PM₁₀ inlet and clean if necessary. 4. Inspect the O-rings on the VSCC (FRM sampler) and clean VSCC if necessary. 5. Inspect and clean the virtual impactor on the dichotomous sampler if necessary.
Quarterly (every 3 months)	<ol style="list-style-type: none"> 1. Inspect O-rings and apply a light coat of vacuum grease, if required. 2. Clean the outside of the solar radiation shield with moist Kimwipe. 3. Remove and clean PM₁₀ inlet and virtual impactor (dichotomous sampler). 4. Remove and clean the VSCC (FRM sampler). Re-grease the O-rings. 5. Inspect in-line filters and replace at least one a year. 6. Inspect the pump operation.
PM Sampler (TEOM)	
Every visit by site operator	<ol style="list-style-type: none"> 1. Inspect the TEOM filter. 2. Inspect the PM₁₀ inlet and clean if necessary. 3. Solar radiation shield of the sampler head should be cleaned with a wet cloth. 4. Inspect and, if necessary, empty water collector bottle.

Monthly or as needed by site operator.	<ol style="list-style-type: none"> 1. Replace the TEOM filter or as filter loading approaches 100%. 2. Replace the 47-mm FDMS purge filter. Replace when the TEOM filter is replaced. 3. Clean the PM10 inlet. 4. Clean the virtual impactor. 5. Inspect the O-rings on the VSCC (FRM sampler) and clean VSCC if necessary 6. Inspect O-rings and switching valves. Re-grease O-rings and clean switching valves. 7. Inspect and, if necessary, empty water collector bottle. 5. Inspect the filter cassettes for contamination (wipe with a clean dry cloth). 6. Inspect the seals of the filter cassette (wipe seals with a clean dry cloth).
Semiannual or Annual	<ol style="list-style-type: none"> 1. Replace the inline filters every 6 months. 2. Clean the coolers annually or as needed. 3. Clean the switching valves annually or as needed. 4. Replace switching valve seals and O-rings and lubricate annually or as needed. 5. Clean the air inlet system inside the mass transducer annually or as needed. 6. Replace the dryer annually. 7. Rebuild the sample pump every 18 months or as needed.
PM Sampler (MOUDI) Maintenance will be developed as we work with the sampler verification.	
Every visit by site operator	<ol style="list-style-type: none"> 1. Inspect the PM10 inlet and clean with a wet cloth if necessary. 2. Inspect and, if necessary, empty water collector bottle. 3. Inspect operation of the mechanical timer (Phoenix site).
Every 10 sampling events or as needed by site operator.	<ol style="list-style-type: none"> 1. Apply silicon grease to the double O-Rings between stage-bodies on the impaction plate assembly. 2. Inspect the PM₁₀ inlet and clean if necessary. 3. Inspect and, if necessary, empty water collector bottle.

During shipment from the laboratory to the sample location, there are no specific requirements for temperature control; however, the filters or sampling modules will remain in their protective containers and inside the transport container. Excessive heat must be avoided (e.g., do not leave in direct sunlight or a closed-up car during summer). During the sampling period, the filters will be subject to ambient temperatures. Once sampled filters are retrieved, the temperature of sampled filters must be brought to 4 °C as soon as possible and the shipment package, cooled to 4 °C, will be picked up by the courier service as soon as possible.

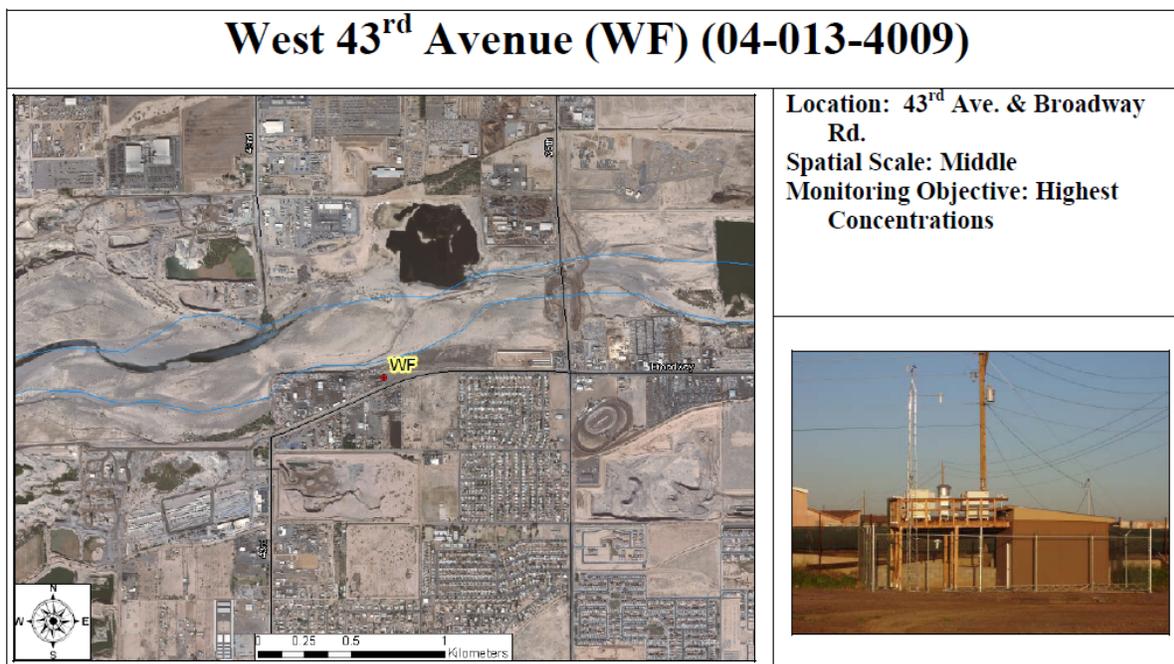
Operators of individual field sites will maintain field records. The following types of notebooks or binders are to be used by field personnel to keep documents in order and readily accessible for review if needed. Each field site operator will maintain a field notebook. The notebooks will be uniquely numbered and associated with the pilot study. Generally, all data from all routine field operations will be entered on the field data forms to be supplied by RTI. At the discretion of the local monitoring agency additional data may be downloaded electronically from the sampler's memory. The field notebook is used to record additional information about these operations, such as information regarding weather conditions and activities in the area that may influence the sample content and concentration (e.g. wind or electrical damage to equipment, construction or mowing activities in the area, welding, and traffic). Such information will also be included in the comments section of the Chain-of-Custody (COC)/Field Data Sheet (FDS) form (examples of FRM and dichotomous COC/FDS forms are provided as Table 2) so the laboratory is made aware a sample may be compromised. 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.

Information on sample shipping and receipt will be recorded. Information about sample receipt and shipment may be used by the field site operator to locate missing packages or resolve shipping issues. Documentation may include standard shipping/receiving forms and areas for free-form notes about shipment difficulties or concerns such as equipment that arrives damaged or has missing parts.

Field measurements will occur at two sites. The sites for pilot measurements are Phoenix, AZ and East St. Louis, IL. Details on the Phoenix site and the East St. Louis site are illustrated below.

The Phoenix site (Figure 1) is located at 43rd Avenue and Broadway Road in Phoenix, AZ. Day-to-day operations are managed by the Maricopa County Air Quality Department in Phoenix (AQS ID 04-013-4009).

Figure 1. Maricopa County, AZ pilot monitoring site



Site Description: Monitoring began at the site in the 2nd quarter of 2002. This site is located at a Maricopa County Department of Transportation storage lot. The site is surrounded by a combination of heavy industry and residential homes. The site has one continuous TEOM PM₁₀ monitor and a temperature inversion monitor, as well as other meteorological instruments. The main purpose of the site is to measure maximum concentration PM₁₀ and to determine the impact on ambient pollution levels of significant sources or source categories. The sources around the site include sand and gravel operations, auto and metal recycling, landfills, paved and unpaved haul roads, and cement casting.

		2006	2007	2008
PM ₁₀	Max. 24-hr PM ₁₀ Avg. (µg/m ³)	260*‡	227*‡	279*‡
	Number exceedances 24-hr PM ₁₀	18	6‡	6‡
	Annual PM ₁₀ Avg. (µg/m ³)	79.9	71.8	57.0

* Indicates an exceedance of the standard.

‡ Indicates Exceptional Events at this site. Listed value is the highest official current AQS reading.

The East St. Louis, IL PM_{10-2.5} speciation pilot site (Figure 2) is the PM Supersites location used previously for PM research. The St. Louis - Midwest Supersite is located at 13th Street and Tudor Avenue in East St. Louis, Illinois, which is about 3 km east of the City of St. Louis, Missouri, central business district. Day-to-day operations are managed by the Air Quality Laboratory at Washington University in St. Louis. The physical footprint managed by Washington University is immediately adjacent to the East St. Louis compliance monitoring site operated by Illinois EPA (AQS ID 17-163-0010).



Figure 2a. East St. Louis, IL Supersite (13th Street and Tudor Avenue)

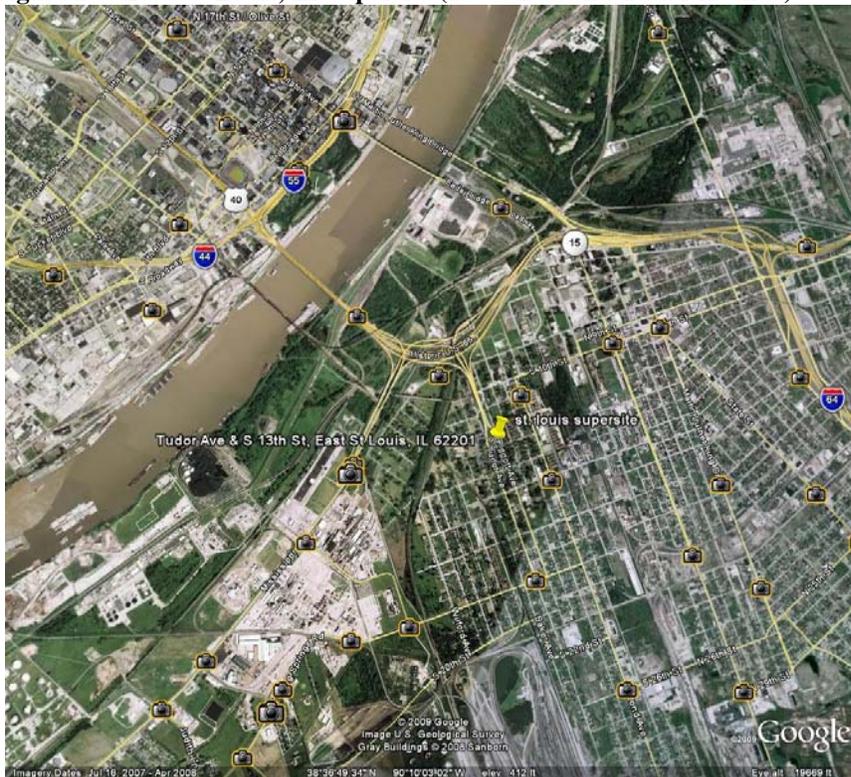


Figure 2b. East St. Louis, IL site Google Earth view

All work performed and data collected at the PM_{10-2.5} Pilot Monitoring Program site locations will be based on the following quality objectives:

- Multiple samplers will be installed at each pilot site. Samplers will be installed as close to the same height as possible and within a 1 to 4 meter separation from each other. This objective also applies to the positioning of the PM_{10-2.5} Difference Method (i.e., subtracting PM_{2.5} concentrations of a given species from its PM₁₀ concentrations) samplers.
- All routine field sampling information (start time, end time, average flow rate, temperature and pressure data, meteorological conditions, etc.) and verification QA checks will be recorded on hard-copy field data forms prepared for use with each sampler.
- All integrated sampler field data will be verified and placed in the RTI database and periodically provided to EPA/STI. The semicontinuous mass monitor data will be submitted to STI via the AirnowTech web site. RTI will be the central repository for all integrated sampler data (including raw data) and related field information. STI will maintain the combined integrated sampler data and semi-continuous data base for data assessments.
- All sampler parameters (flow rate, ambient and filter temperature, and barometric pressure) must be verified against NIST-traceable standards prior to beginning and at the completion of the study or after any sampler maintenance events. The design flow rate for the FRM samplers is 16.7 L/min. The dichotomous samplers will operate at 16.7 L/min total flow (15 L/min for PM_{2.5}, 1.67 L/min for PM_{10-2.5}) and the FDMS TEOM samplers will operate at 16.7 L/min total flow (3 L/min for PM_{2.5}, 1.67 L/min for PM_{10-2.5}, and 12 L/min bypass flow). The MOUDI multi-stage, cascade impaction sampler will be operated at 30 L/min as specified by the manufacturer.
- For this project, the completeness (the percentage of valid data compared to the total expected data) objective for all species and measurements is 80% of all attempted measurements. In addition to individual measurement completeness, the program completeness (sampling events with all attempted measurements having valid data) will be tracked because this dictates the robustness of the data set across the entire measurement strategy.

Refer to Appendices B and C of this QAPP for audit procedures, audit/verification data sheets, and routine operations for field samplers that will be used during the pilot study. The local monitoring agencies are to use NIST-traceable standards to conduct quarterly audits of the sampling equipment. This information must be made available to EPA/STI/RTI for quarterly data assessment and analysis efforts.

Table 1 above outlines the acceptance limits that operators will strive to meet to verify and calibrate the PM samplers. During normal operations and verification checks, the measured flow rate must operate within $\pm 5\%$ of the design flow rate.

Meteorological equipment is not required for the pilot monitoring sites; however, on-site meteorological measurements 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.

2.2 Sample Handling and Custody Requirements

This section describes sample handling and custody procedures that are necessary to ensure that site operators properly handle the sampling components from the time of receipt at the field office until they are released to the shipping agency for return to the analysis laboratory. Field sites will use the field data forms developed for the study; subsequent laboratory chain of custody (COC) is maintained for each sample, beginning with placement of the filters in the sampler collection modules and extending through all analytical steps to final sample archival.

Care must be taken when handling, storing, and transporting filters at all stages in their use due to the small mass of particles collected on exposed filters, the potential for sample losses due to rough handling or sample volatilization, and the potential for weight gain due to contamination or uptake of reactive gases on the filter and particulate matter surfaces. Sample handling procedures must be consistently followed in order to provide data of good quality. These procedures are discussed below and presented more fully in the sampler SOPs which are included in Appendix D and sample handling SOPs for the SHAL included in Appendix D.

Sample custody procedures are required to avoid misplacement of samples or confusion of one sample with another, and to provide documentation to assist in detection and resolution of problems. A sample is considered to be in custody if it is in one's actual physical possession or stored in a secured area restricted to authorized personnel. Each set of sampling modules and other equipment supplied by the laboratory will be accompanied by a 3-page, carbonless COC and field data sheet (FDS) form. The three pages of the COC/FDS form are color-coded (white, yellow, and pink). When a sample is prepared in the SHAL, the pink copy of the COC/FDS form is removed just prior to shipping the sample to the site location. This pink copy is maintained at the SHAL for recordkeeping and that the sample has been sent to the site location. At the site location after the sampling event and the site operator has completed field entries on the form; he/she will remove the yellow copy for their records. The white copy will be packed with the exposed sample by the site operator and sent back to the SHAL. The COC/FDS form will contain the filter identification number (if available), filter type, container (module or cassette) identification number, and date by which the sampling media must be used. Example COC/FDS forms of the FRM and dichotomous samplers are illustrated in Table 3. RTI will develop the COC and field data forms for the FRM, dichotomous, and MOUDI samplers used in this study. These forms will be sent to EPA for review prior to the beginning of sampling. The information on the custody form is ultimately entered into a sample tracking system, where an electronic record is kept.

Information recorded on these field forms is very important because it serves as a backup in case the data downloaded from the sampler become corrupted or lost. Difficulties with or suggestions for improved operation of the samplers will be recorded here and in the field

notebook. Information about significant events near the site that may affect the representativeness of the sample will also be entered into this form so the laboratory will be on alert for an unusually high concentration sample.

Upon receipt at the field office, the site operator will carry out the following documentation and handling steps:

- Enter receipt of the shipment in the operator's field notebook, noting the date and time of receipt and any air bill or other identifying numbers associated with the shipment.
- Inspect the exterior of the shipping container, note any evident damage, and record observations in the operator's field notebook.

- Open the shipping container and ensure that a COC/field data form is present for each set of sampler components sent in the shipment. Also check to be sure shipping items such as ice substitute gel packs and a min/max thermometer (if required) are present. Ensure each identifying number printed on the COC form corresponds to an enclosed sampling channel component. Do not use any sampling component whose identifying bar code number is not listed on the COC form. Notify the support laboratory about any discrepancies. **Remove the gel packs and freeze them.**

- Sign and date the custody record portion of the COC form.

- Store all components for a sampler run together in a container in an air-conditioned secure area for later transport to the site. Adopt a first-in, first-out use schedule. Sampling components will be stored and tracked so that the correct set of sampling components reaches the designated field collection site for use on the designated sampling day.

Do not interchange sampler channel components intended for use with a particular speciation sampler with components for any other sampler or site. The support laboratory has labeled each sampler channel component for use at a particular site. Should an interchange occur, the site operator must fully document the variance and inform the support laboratory so the analytical results can be associated with the correct sampler and site.

It has been noted by the support laboratory, that the interior temperatures of some shipping containers received in the laboratory were above 4°C. This problem may be due to the gel packs not being frozen long enough or at a cold enough temperature. It is recommended that gel packs be placed in a freezer and frozen for at least 3 days. This will help ensure that the filters do arrive at the support laboratory at temperatures near 4°C.

The following is a brief description of the post-sampling procedures at the field site. At the end of a sampling period, the site operator will remove the sampling modules from the sampler.

At the site, the operator must complete the following:

- Read selected data from the sampler's display screen and enter them in COC/field data form. Double-check all entries against the sampler display. Print clearly. Be certain the entries are clear on the second and third pages of the carbonless form. A site may have more than one speciation sampler and thus the operator must complete the additional field data forms supplied.

- Remove the filter cassettes or sampling modules from the sampler. Briefly examine the cassette or module for damage and ensure it is, in fact, the correct module for the sampling channel from which it was removed.
- Place the sampling modules in protective container(s); cap the acid gas denuders if they are to be returned. Place all sampling materials in the shipping/transport container containing ice substitutes, but do not seal.
- Download data from the sampler via a laptop computer to a labeled diskette. Alternatively, download to a data transfer device for later entry to a diskette or file.

Components/modules must be used at the field collection site on the sampling date specified on the COC/field data form. Unused sampling modules and denuders will remain sealed or capped and kept from exposure to ambient air, temperature extremes, or vibrations.

Upon arrival at the site to set up for a sampling event and retrieve modules or cassettes from the completed sample runs, the site operator will follow the sampler's operation manual. Once the sampling modules or cassettes are installed at the site and the sampler is programmed to begin operation, the operator will complete the appropriate sections of the COC/field data form. For data forms prepared for completed sample runs, the field operator will retain the second page of the 3-page COC/field data form and package the top copy in the shipping container. Package the sampling modules/filters/cassettes, insert the ice packs in the shipping container, make a final check to ensure all samples, ice packs, and data forms are in the container, and seal the container securely. Air bills will be pre-printed and provided with the appropriate shipping and billing information for return shipment to the laboratory. Then take the container to a drop point or arrange for pickup by the contracted overnight air shipping company.

The support laboratory's procedures for receiving the sampling components and field data, disassembling the sampling modules, and handling the filters and denuders after their distribution to the various laboratories are covered in the SOP for the SHAL in Appendix D.

Figure 3. Examples of FRM and Dichotomous COC/FDS Forms

<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;"> Assign barcode here. </div>	<h3 style="margin: 0;">PMcoarse Pilot Study COC/FDS Form for FRM Sampler</h3> <p style="margin: 5px 0;">PM Fraction (Check one): <input type="checkbox"/> FRM PM-2.5 <input type="checkbox"/> FRM PM-10</p>
PART I – SUPPORT LABORATORY (Filter Weighing and Shipping Information from Support Laboratory)	
Filter Type (check all that apply) <input type="checkbox"/> Teflon <input type="checkbox"/> Nylon <input type="checkbox"/> Quartz <input type="checkbox"/> Other	
Filter ID (Teflon only)	Filter Cassette ID
Weighing Lab (Teflon only)	Cassette Type
Analyst/Custodian	Tare Weight Date (Teflon only)
Shipment Date	Airbill Tracking No.
Sent to (Pilot Study Site)	Shipped via <input type="checkbox"/> UPS <input type="checkbox"/> Other
Date This Filter Must be Used by:	Return to:
PART II – FIELD OFFICE	
Date Received:	Received by:
Location:	
Package Condition: <input type="checkbox"/> Good <input type="checkbox"/> Reject (Why? And return to Support Lab)	
PART III – FIELD SITE (Sampling Event Information)	
AQS Site ID	Site Name
FRM Sampler Make:	Model:
Site Operator (print)	Serial No.:
Other Operators or Observers	
Sample Type	
<input type="checkbox"/> RO-Routine <input type="checkbox"/> FB-Field Blank (RO Cassette ID: _____) <input type="checkbox"/> TB-Trip Blank (RO Cassette ID: _____) <input type="checkbox"/> Other (describe) <input type="checkbox"/> Void (comment in Notes Section)	
Sampling Event Filter Data	
Sampling Date:	Retrieval Date:
Time:	
Event Filter Integrity: <input type="checkbox"/> OK <input type="checkbox"/> Reject (describe)	
Filter Exposure Data	
Elapsed Time (ET)	Filter Integrity OK? <input type="checkbox"/> Yes <input type="checkbox"/> No (describe)
Total Volume (m ³)	
Flow Rate (L/min) Q: 16.7	Avg:
Start Date/Time	CV:
Stop Date/Time	Data Download OK? <input type="checkbox"/> Yes <input type="checkbox"/> No (describe)
Ambient Temperature (°C) Max:	Min:
Filter Temperature (°C) Max:	Avg:
Barometric Pressure (mm Hg) Max:	Min:
Sampler Flags ³ :	Avg:
Field Flags:	
PART IV – FIELD FILTER SHIPPING TO SUPPORT LAB	
Shipment Date	Affiliation:
Shipped by	Shipping Destination:
Airbill No.	Shipped via: <input type="checkbox"/> Federal Express <input type="checkbox"/> Other
<i>On completion of Part II-IV, the site operator keeps one copy and sends the top (original) copy to the laboratory with the filter.</i>	
PART V – SUPPORT LABORATORY RECEIPT	
Date Received	Received by:
Integrity Flag:	
Shipment Integrity OK? <input type="checkbox"/> Yes <input type="checkbox"/> No	Max Temperature: °C Cold Pack Condition: <input type="checkbox"/> Frozen <input type="checkbox"/> Cold <input type="checkbox"/> Ambient
<i>The Support Laboratory will DATE-STAMP and attach the COC/FDS form to the receiving log-book, in which same info is recorded.</i>	
Notes:	

Assign barcode here.

PMcoarse Pilot Study COC/FDS Form for Dichotomous Sampler

PM Fraction (Check one): PM-coarse PM-fine

PART I – SUPPORT LABORATORY (Filter Weighing and Shipping Information from Support Laboratory)			
Filter Type (check all that apply)	<input type="checkbox"/> Teflon	<input type="checkbox"/> Nylon	<input type="checkbox"/> Quartz <input type="checkbox"/> Other
Filter ID (Teflon only)		Filter Cassette ID	
Weighing Lab (Teflon only)		Cassette Type	
Analyst/Custodian		Tare Weight Date (Teflon only)	
Shipment Date		Airbill Tracking No.	
Sent to (Pilot Study Site)		Shipped via	<input type="checkbox"/> UPS <input type="checkbox"/> Other
Date This Filter Must be Used by:		Return to:	

PART II – FIELD OFFICE		
Date Received:	Received by:	Location:
Package Condition: <input type="checkbox"/> Good <input type="checkbox"/> Reject (Why? And return to Support Lab)		

PART III – FIELD SITE (Sampling Event Information)			
AQS Site ID		Site Name	
FRM Sampler	Make:	Model:	Serial No.:
Site Operator (print)		Other Operators or Observers	
Sample Type			
<input type="checkbox"/> RO-Routine <input type="checkbox"/> FB-Field Blank (RO Cassette ID: _____) <input type="checkbox"/> TB-Trip Blank (RO Cassette ID: _____) <input type="checkbox"/> Other (describe) <input type="checkbox"/> Void (comment in Notes Section)			
Sampling Event Filter Data			
Sampling Date:	Retrieval Date:	Time:	
Event Filter Integrity: <input type="checkbox"/> OK <input type="checkbox"/> Reject (describe)			
Filter Exposure Data			
Elapsed Time (ET)		Filter integrity OK?	<input type="checkbox"/> Yes <input type="checkbox"/> No (describe)
Total Volume (m ³)			
Flow Rate (L/min)	Q: 1.67 (coarse); 15.0 (fine)	Avg:	CV:
Start Date/Time		Data Download OK?	<input type="checkbox"/> Yes <input type="checkbox"/> No (describe)
Stop Date/Time			
Ambient Temperature (°C)	Max:	Min:	Avg:
Filter Temperature (°C)	Max:	Min:	Avg:
Barometric Pressure (mm Hg)	Max:	Min:	Avg:
Sampler Flags ³ :		Field Flags:	

PART IV – FIELD FILTER SHIPPING TO SUPPORT LAB	
Shipment Date	Affiliation:
Shipped by	Shipping Destination:
Airbill No.	Shipped via: <input type="checkbox"/> Federal Express <input type="checkbox"/> Other

On completion of Part II-IV, the site operator keeps one copy and sends the top (original) copy to the laboratory with the filter.

PART V – SUPPORT LABORATORY RECEIPT			
Date Received		Received by:	Integrity Flag:
Shipment Integrity OK?	<input type="checkbox"/> Yes <input type="checkbox"/> No	Max Temperature: °C	Cold Pack Condition: <input type="checkbox"/> Frozen <input type="checkbox"/> Cold <input type="checkbox"/> Ambient

The Support Laboratory will DATE-STAMP and attach the COC/FDS form to the receiving log-book, in which same info is recorded.

Notes:

2.3 Laboratory Measurements

All laboratory work for the PM_{10-2.5} pilot study will be conducted according to SOPs or other documented procedures described in this QAPP. Table 3 lists the target analyte or process; briefly states the quality control and quality assurance methods used; and available SOPs, references, or guidance documents for each laboratory operation. Details of the QC and QA methods are given in the SOPs. Note that an asterisk (*) by the name of the SOP listed in Table 3 indicates that that particular SOP has been approved by EPA for use in the PM_{2.5} Chemical Speciation network and that the SOP is expected to meet the needs of this PM_{10-2.5} pilot study.

Some laboratory species measurements of the PM_{10-2.5} fraction will likely require modifications or complete changes to procedures. Additional or revised SOPs may be required after experience with analysis of PM_{10-2.5} filters during the pilot study.

Appendix D to this QAPP, “Standard Operating Procedures for Field and Laboratory Operations” includes all support laboratory SOPs that will be adopted for the pilot study. Table 4 below, lists many of the SOPs that are now available for use.

Table 3. QC/QA and SOPs for Analytical Methods for Use in PM_{10-2.5} Pilot Studies

Target Analyte or Process	Quality Control and Quality Assurance Methods	Available SOP or Guidance for SOP Preparation
SHAL support operations for monitoring sites and analytical laboratories	-Use of CSN Level 0 Validation Form -Temperature of sample shipment cooler checked -Flags & unusual field conditions noted	-RTI SOP for Sample Handling and Archiving Laboratory (SHAL). Revision 10. February 18, 2009 (*)
Mass (from Teflon filter)	- Filter lot stability test - Filter inspection and conditioning - Working standard QC weight - QC checks of microbalance	-RTI/CSN SOP for Gravimetric Analysis. Revision 9. July 8, 2008 (*)
X-Ray fluorescence for elements	- Energy calibration - Calibration verification - Ongoing calibration verification - Background determination	-RTI/CSN SOP for X-Ray Fluorescence Analysis of Deposits on Teflon Filters. Revision 5. August 19, 2009 (*)
Anions by ion chromatography	-Meet control limits for multi-concentration calibration regression parameters -Analysis of QA/QC samples, blanks, duplicates, and spiked samples per SOP	-RTI SOP for PM _{2.5} Anion Analysis. Revision 7, August 26, 2009 (*)
Cations by ion chromatography	-Meet control limits for multi-concentration calibration regression parameters -Analysis of QA/QC samples, blanks, duplicates, and spiked samples per SOP	-RTI SOP for PM _{2.5} Cation Analysis. Revision 7, August 25, 2009 (*)
Metals by ICP-MS	-Acid extraction to get total metals -Calibration standards, blanks, controls, duplicate analyses	-RTI SOP for the X-Series ICP-MS for the Analysis of Particulate Deposits on Teflon Filters. Revision 0, July 8, 2008 (*)

<p>Organic and elemental carbon (OC and EC) by thermal-optical analysis using IMPROVE_A TOT and TOR</p> <p>A subset of samples may be analyzed using the CSN TOT method</p>	<ul style="list-style-type: none"> -Instrument blanks -Calibrations -Duplicates -FID response to internal standard -Start integration and transit time -Laser transmittance 	<ul style="list-style-type: none"> -SOP for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a DRI Model 2001 Analyzer. Revision 4, February 13, 2009 (*) -RTI SOP for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer. Revision 9, February 16, 2009 (*)
<p>Carbonate by TOT and TOR</p>	<ul style="list-style-type: none"> -Special considerations for effects of acidic treatment of filter punch 	<ul style="list-style-type: none"> -Procedures contained in SOPs for OC and EC above. Revision 6, February 13, 2009 (*)
<p>Extractable or elutable organic compounds</p>	<ul style="list-style-type: none"> - Filter composites - Solvent extraction -Analysis of QA/QC samples, blanks, duplicates, and spiked samples per SOP 	<ul style="list-style-type: none"> -Procedure contained in SOP for SVOCs. July 8, 2008 (*)
<p>Water-soluble organic compounds</p>	<ul style="list-style-type: none"> -To be Developed 	<ul style="list-style-type: none"> -To be Developed
<p>Proteins and/or glucans, and endotoxins</p>	<ul style="list-style-type: none"> -To be Developed 	<ul style="list-style-type: none"> - To be Developed - Method based on Menetrez, Foarde, et al., “The Measurement of Ambient Bioaerosol Exposure”, Atmos. Environ. 41 (2007) 884-893.
<p>Bacteria, pollen, and spores by SEM microscopy of Teflon filters</p>	<ul style="list-style-type: none"> -Daily SEM instrument calibration versus copper Lα and aluminum Kα peaks prior to use. Minor variation (\pm 10 eV) requires calibration. [Applicable if analyzing for single particle composition] -Magnification calibration versus a magnification calibration stub. 	<ul style="list-style-type: none"> -RTI SOP for Sample Preparation and Analysis of PM₁₀ and PM_{2.5} Samples by Scanning Electron Microscopy. Revision 4, July 08, 2008 (*)

(*)An asterisk by the name of the SOP listed in Table 3 indicates that that particular SOP has been approved by EPA for use in the PM_{2.5} Chemical Speciation Network (CSN) and that the SOP is expected to meet the needs of this PM_{10-2.5} pilot study.

3.0 Field Sampling Process (PM_{10-2.5} Pilot Study Network Design)

Table 5 shows the proposed sampling and analysis matrix to be used in the PM_{10-2.5} pilot study. All of the analysis methods except the biological analysis and water soluble organics, are provided under the CSN contract EP-D-09-010 and the CSN laboratory QAPP applies to this project. The proposed sites for pilot measurements are Phoenix, AZ and East St. Louis, IL. These two locations should show enough variability in PM_{10-2.5} composition and sources to test the contribution of different constituents to be collected and analyzed. Sampling is expected to consist of a 1-in-3 day sampling scheme for manual methods and hourly data collection for continuous methods. Every 3rd day sampling and analysis will result in a total of 336 Teflon and Nylon filter samples and 456 Quartz filter samples per site from both the FRM and dichotomous samplers. About 10 percent of the Teflon, nylon, and quartz filter samples will be collocated for an assessment of precision. The first few months of the study will focus on identifying and resolving process issues, optimizing filter handling and the operation of the samplers as well as becoming familiar with performing some of the more sophisticated chemical and physical analyses. Sampling will be conducted over the course of at least one year to understand the temporal variability of the ambient aerosol during all the seasons, and to provide data sets large enough to evaluate the field operations and laboratory analysis methods.

Each sampling site will have two dichotomous samplers which will be used to collect samples onto Teflon/nylon filter sandwiches and quartz filter sandwiches, respectively. The Teflon/nylon filter sandwich will have the nylon filter mounted behind the Teflon filter to determine the nitrate loss from the Teflon filter. The downstream filter in the quartz-behind quartz filter sandwich will be used to estimate organic carbon artifacts. For a subset of the sampling events the dichotomous samplers will be operated with identical filter sandwiches to collect data for collocated precision estimation.

Each sampling site will have one set of Federal Reference method (FRM) samplers to be used for the difference method. The samplers (one PM₁₀ sampler and one PM_{2.5} sampler) will be approved FRMs for the measurement of PM_{10-2.5} mass determinations. Initially these samplers will be fitted with Teflon/nylon filter sandwiches to be compared with results from the dichotomous sampler measurements. Measurements will include XRF for elements, the standard suite of cations and anions, and ICP-MS analysis for selected metals. These samplers can be fitted with other filter types (e.g., polycarbonate or Teflon/nylon) during the pilot test period to maximize evaluations. Magnesium oxide acid gas denuders may be used in front of the Teflon/nylon filter pair to compare with results from the dichotomous Teflon/nylon filter (without denuder) results below to determine the need for denuders with the dichotomous samplers.

Each sampling site will have one dichotomous FDMS-TEOM (Thermo Model 14-5-DF) deployed to determine the diurnal variability in PM_{10-2.5} mass during the 24-hour integrated sampling events and to assess the SVOC contribution to the PM-coarse fraction by comparison of the TEOM data to the PM_{10-2.5} mass determined from data from the FRM difference method.

Each sampling site will have one rotating 8-stage MOUDI® to be deployed and configured with Teflon/nylon or quartz filters to assess the size distribution of organics, and possibly other species, as needed.

The measurement of mass, elements, ions, and carbon species are considered critical. Supplemental (important, but less critical) measurements of carbonate carbon, organic speciation, soluble organic compounds (WSOC), and biological analyses will also be made.

For the organics analysis, a subset of quartz fiber filters may be extracted and followed by GC-MS analysis for the quantification of all possible compounds. This will be done on a very limited basis due to the high cost for analyses. For the water soluble organic compounds (WSOC), analysis using LC-MS will identify compounds present in the coarse particle fraction.

For the biological analyses for proteins, glucans, and endotoxins (depending upon the quantity of sample required), the type of analysis may rotate among the filter samples and may only be done on a subset of filters in seasons (spring and fall) when such species are presumably highest. The total mass of the biomolecules measured in the pilot study may be attributable to a variety of sources. Protein, for example, may come from a multitude of sources, including pollens, fungal spores, insect debris, etc. The analytical laboratory needs source reference information to interpret the analysis in context. RTI will conduct a brief literature review to determine sources of biological components the laboratory might reasonably be expected to find in samples collected at each study site in each season. The collection media, polycarbonate stubs, will be used to help characterize the aerosol and identify composition, including bacteria, pollen, and spores.

Table 6 summarizes a proposed timeline schedule of activities leading up to and during a one-year sampling program at the two sites.

Table 4. PM_{10-2.5} Measurement Sampling and Analysis Matrix				
Sampler Type	Filter Type	Technique	Measurement	Comments/Notes
Two Sequential FRMs of same model for PM_{10-2.5} Difference Method 16.7 LPM Alternating Teflon/nylon (sometimes with acid gas denuders) and Quartz	Quartz/Quartz; 46.2 mm	Thermal Optical Analysis by IMPROVE_A TOR/TOT method. A subset of samples may be analyzed by CSN TOT.	OC, EC	OC and EC contribution to PM _{10-2.5} mass. Backup quartz analyzed for OC/EC only to assess artifacts. A subset of backup quartz filters will be analyzed.
		Acidification followed by OC/EC analysis using IMPROVE_A TOT/TOR method	Carbonate Carbon	Contribution of carbonate to total carbon for coarse mode aerosols.
		GC/MS (on subset of samples)	Extractable/Elutable organic compounds – only for subset of filters	Organic speciation markers present for biologicals and other PM _{10-2.5} tracers.
		LC/MS (on subset of samples)	Water soluble organic compounds	Water soluble organic aerosols contribution to PM _{10-2.5} .
	Teflon/ Nylon; 46.2 mm	Gravimetry, XRF, and Ion Chromatography	Mass, elements and Ions (NH ₄ ⁺ , Ca ²⁺ , K ⁺ , Na ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻)	Analyses of these species will be done as needed to further supplement ORD's field evaluation and compare to the dichotomous sampler. Volatile nitrate will be evaluated on backup nylon filters initially. The frequency of analysis for volatile nitrate may be decreased if indicated by the results.
		One extract for: Sigma QuantiPro BCA Quantification Kit	Total Protein	Estimate of biological material. Teflon can be used for other biological assessments as needed.
Two Thermo 2025D Sequential Dichotomous Samplers 16.7 LPM Total 15 LPM PM_{2.5}	Teflon/Nylon; 46.2 mm	Gravimetric	Mass	Mass closure and in comparison to TEOM, estimate of SVM.
		XRF	Elements	Elemental composition of PM _{10-2.5} mass.
		ICP-MS (total extractable elements) on a subset of samples	Elements	Comparison of XRF to ICP-MS. Analysis emphasizing terrestrial elements.

1.67 LPM PM_{10-2.5} One Dichot with Teflon/Nylon (undenuded) and one Dichot with Quartz		Ion Chromatography	Ions (NH ₄ ⁺ , Ca ²⁺ , K ⁺ , Na ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻)	Secondary inorganic aerosols, sea salt contribution associated with PM _{10-2.5} . Volatile PM _{10-2.5} nitrate.
	Quartz; 46.2 mm	Thermal Optical Analysis by IMPROVE_A TOR/TOT method. A subset of samples may be analyzed by CSN TOT.	OC, EC	OC and EC contribution to PM _{10-2.5} mass. Backup quartz analyzed for OC/EC only to assess artifacts. A subset of backup quartz filters will be analyzed.
		Acidification followed by OC/EC analysis using IMPROVE_A TOT/TOR method	Carbonate Carbon	Contribution of carbonate to total carbon for coarse mode aerosols.
		GC/MS (on subset of samples)	Extractable/Elutable organic compounds – only for subset of filters	Organic speciation markers present for biologicals and other PM _{10-2.5} tracers.
		LC/MS (on a subset of samples)	Water soluble organic compounds	Water soluble organic aerosols contribution to PM _{10-2.5} .
One 8 stage MOUDI	Quartz; 46.2 mm	Thermal Optical Analysis by IMPROVE_A TOR/TOT method	OC, EC	OC and EC contribution at various sizes
One Thermo 1405-DF Dichot TEOM 16.7 LPM Total 3 LPM PM_{2.5} 1.67 LPM PM_{10-2.5}	Pallflex TX40; 13 mm 30°C	TEOM	Mass	Variation of mass with time. In comparison with the dichot, how much of the mass is volatile or semi-volatile. <u>Must be operated in non-FRM mode to get SVOCs.</u>

Table 5. Projected Time Line for PM_{10-2.5} Pilot Study Activities

Proposed Time Frame	Activities
February-March 2010	Complete revisions to QAPP and Sampling Matrix. Prepare data sheets for field use.
February-March 2010	RTI checks and calibrates equipment then ships samplers to two pilot study field sites. TEOMs are shipped directly to the sites.
March-April 2010	Install samplers at the two sites
March-April 2010	RTI and/or EPA to visit sites to “audit” setup and sampler operations. Conduct operator training as needed.
April 2010	Initial “shake-down” sampling at the sites; sampling startup; submission of filters and data sheets to RTI SHAL for analysis and processing
April, May 2010	Conduct spring seasonal “quarter” of sampling
June, July, August 2010	Conduct summer seasonal “quarter” of sampling
September, October, November, 2010	Conduct fall seasonal “quarter” of sampling
December 2010, January and February 2011	Conduct winter seasonal “quarter” of sampling
March, April, May 2011	Conduct spring seasonal “quarter” of sampling (if necessary based on initial startup in 2010)
Throughout sampling	Level 0, 1 data validation and data reporting; evaluate and interpret data
June 2010	Compile and submit first quarterly summary report
September 2010	Compile and submit second quarterly summary report
December 2010	Compile and submit third quarterly summary report
June 2011	Compile and submit final quarterly summary report (tentative unless spring “quarter” is conducted in 2010)
July 2011	Compile and submit final report and recommendations

4.0 Analytical Methods

Analytical methods are listed in Section 2.2. Existing, ready-to-use SOPs for the analytical methods are included by reference in Table 4. Appendix D to this QAPP contains the SOPs used or adapted for the PM_{10-2.5} pilot study. Note that the majority of the work proposed for the PM_{10-2.5} pilot study 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.

Analytical protocols will be established to maximize data filter collection by performing nondestructive measurements in sequence when possible. For example, a Teflon filter from one sample collection event may be subjected to mass determination, XRF analysis, and/or extraction for subsequent chemical analysis. It is likely that the frequency of analyses for a specific target analyte or by a specific method may be adjusted based on data obtained during the operation of

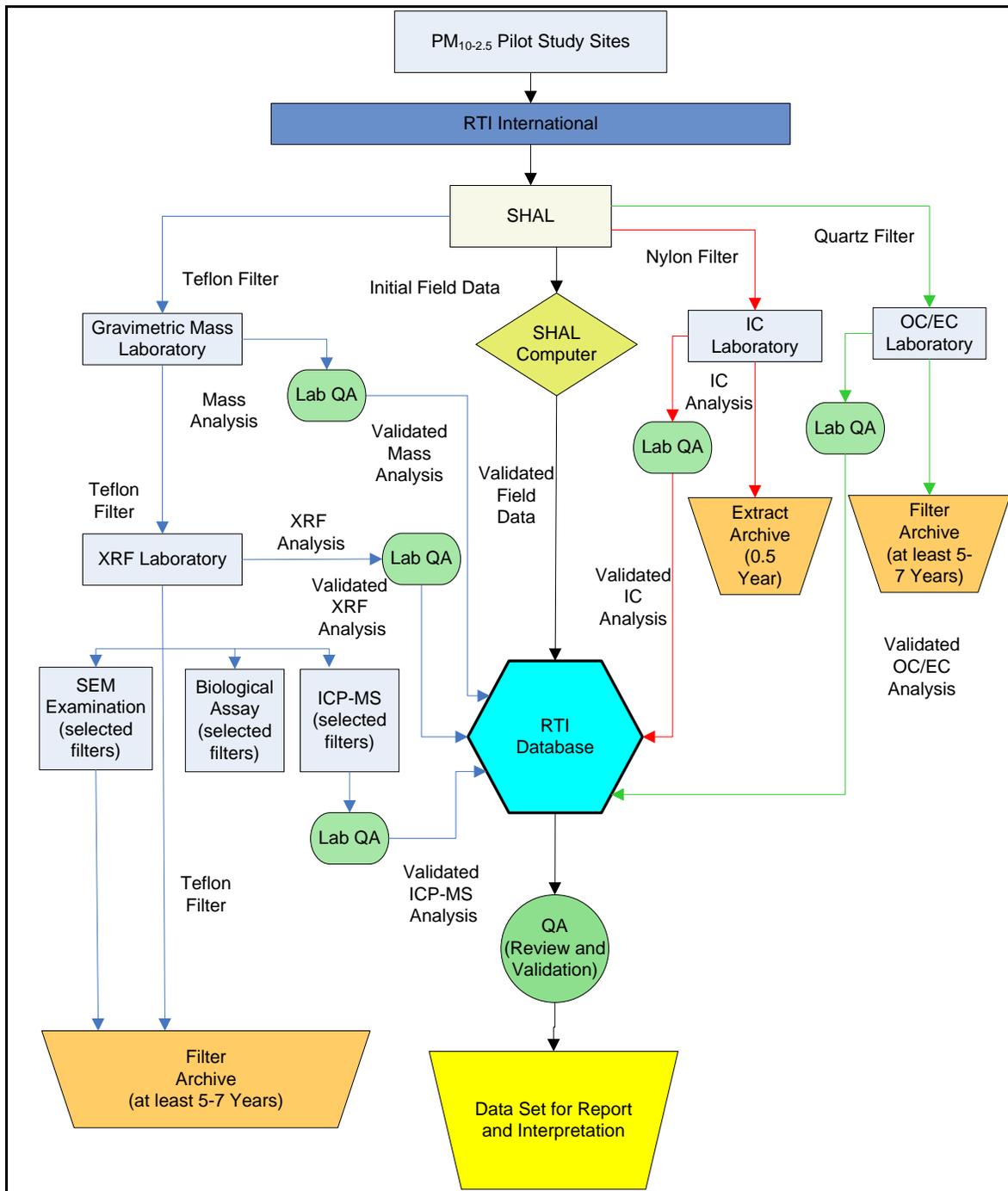
the pilot study. Adjustments in sample analysis strategy will be made in consultation with and after approval by the pilot study work assignment manager.

Figure 4 shows the proposed routing of Teflon, nylon, and quartz fiber filters through the RTI laboratories. Figure 4 also shows how the data are accumulated, reviewed and validated, and assembled into a data set for interpretation and inclusion in the final report for the PM_{10-2.5} study.

Sample processing for the FRM and dichotomous samplers starts with acquisition of the appropriate Teflon, nylon, and quartz filters. The nylon and quartz filters are cleaned, and all three types are submitted for acceptance testing. The Teflon filters are weighed, and all three types of filters are batched and shipped to the SHAL. Personnel in RTI's SHAL will be responsible for assembly/disassembly of components (including clean filters, refurbished denuders and any specialized sorbent traps or other sampling media) into sampling modules, shipment of sampling media directly to the sampling sites, receipt of samples from the sites, and distribution of filters (and other sampling media, if applicable) to the individual laboratories 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). Filters and extracts to be archived will be transferred to the archivist for entry into the archive database and storage in RTI's dedicated archive facility.

In the SHAL, filters are loaded into filter cassettes and then loaded into insulated shipping boxes and shipped to the field sites. The exposed filters are returned to the SHAL at ice pack temperature. Filters are removed from the modules and distributed to the appropriate laboratories for examination and analysis. 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. Teflon filter samples are returned to the gravimetric laboratory where they are weighed again to determine particle mass. These same filters are then sent to the XRF laboratory for elemental analysis. Selected Teflon filters may also be sent for SEM examination, ICP-MS analysis, or biological assay. Nylon filters are sent to the Ion Chromatography laboratory for ion analysis, and quartz filters are sent to the laboratory for analysis of OC and EC and carbonate carbon. Some of the quartz filters will be sent to laboratories for extraction and determination of water-soluble organic compounds and extractable or elutable organic compounds. Finally, following filter analysis, the filter samples and extract solutions will be stored in RTI's dedicated archive facility under the following conditions: (1) the remaining portions of the quartz filters from which punches were taken for OC/EC/carbonate analysis will be stored in a freezer at -15°C; (2) Teflon and unanalyzed nylon filters will be stored under refrigeration at about 4°C; (3) all filter extracts from analysis are archived under refrigeration at about 4°C. Each filter is tracked throughout the process so that every analysis result is linked to the history of the filter (from manufacturer's lot number or other identifying number), through site-specific field sampling and analysis to the end of the archiving period. All filter samples collected for the pilot study will be archived by RTI for at least 5 to 7 years and transferred to EPA for indefinite storage if needed.

Figure 4. Flowchart of Teflon, nylon, and quartz filters through RTI laboratories and data trail.



5.0 Quality Control/Quality Assurance

Elements of quality control are given in each of the SOPs provided in Appendix D. Instrument checks, by use of a transfer standard, ensure that the sampling instruments are operating within acceptable limits. Usually, if the check shows a failure, troubleshooting would occur that might lead to instrument recalibration. Refer to Section 2.1 for a summary of quality control components of the field sample collection methods and to Section 2.3 for summaries of quality control features of chemical and physical speciation of PM_{10-2.5} samples.

The chemical speciation samplers will be audited on site by the local monitoring agency with an independent transfer standard on a quarterly basis. Flow rate, temperature, and barometric pressure will be checked. For samplers with multiple flow channels, each channel and the associated sensors will be audited. The transfer standards are to be recertified or recalibrated annually. Common audit equipment can be used to check or audit samplers in this study.

The laboratory must also assess the accuracy of its analytical measurements. This will include assessment of laboratory blanks, field blanks, or trip blanks. Laboratory blanks provide an assessment of the reagents, 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 laboratory blanks against the field blanks, the amount of contamination due to field activities can be estimated. In addition, if trip blanks are utilized, one can further evaluate contamination occurring during field operations. Field blanks, loaded in sampling modules, for each type of filter may be sent from the laboratory. The field operator is to handle the field blank sampling module 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. Corrective actions may be taken if excessive contamination is found on field blanks. Trip blanks provide an estimate of measurement system contamination during transport to and from the field sites. Trip blanks may be instituted when field blank contamination is a problem or to understand the measurement uncertainty occurring during transport. 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.

Appendix B to this QAPP include detailed SOPs and audit/verification data sheets to be used by the monitoring agency in the initial setup and verification of sampling systems and in assessing and ensuring quality for the filter-based field samplers during the study.

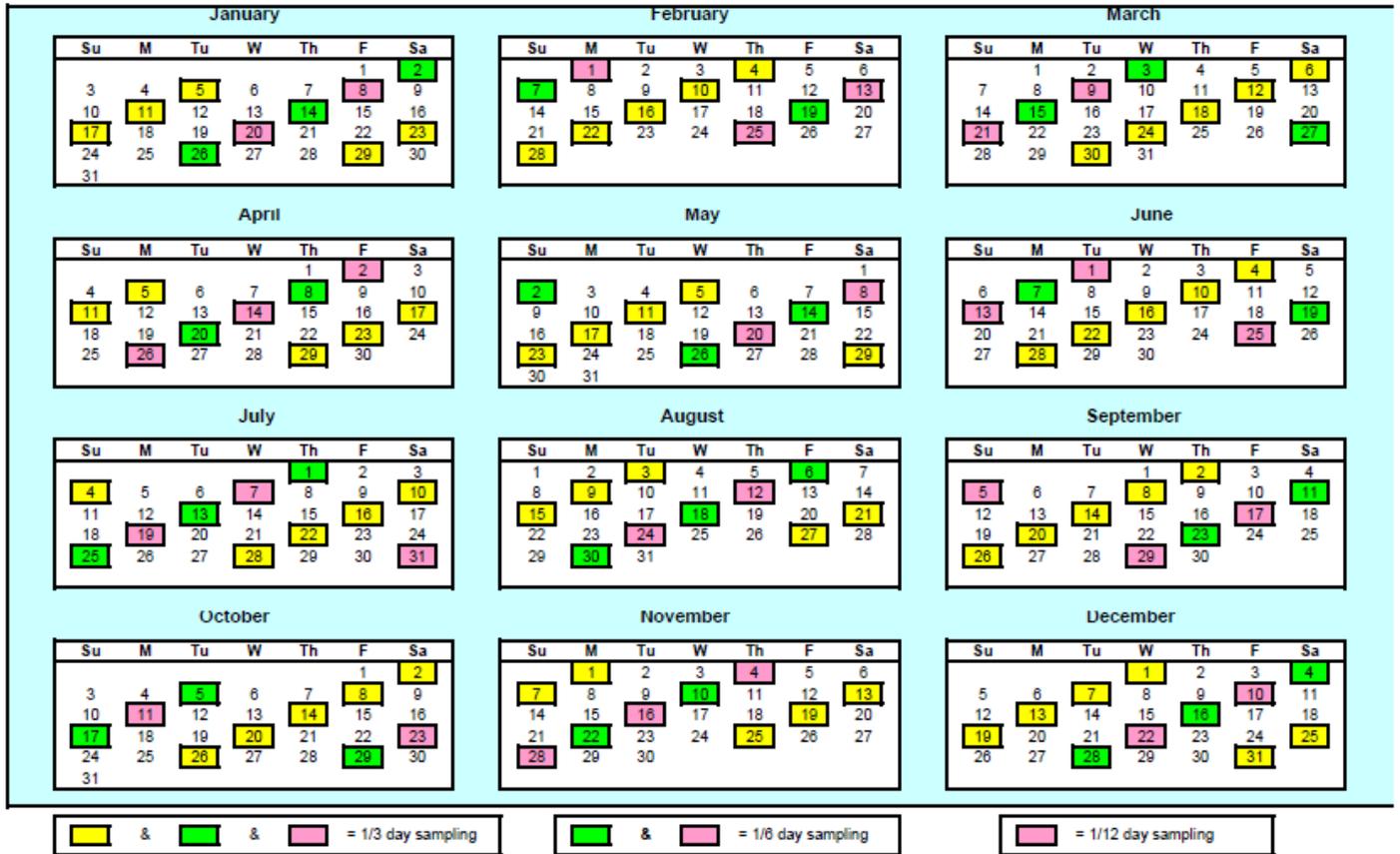
Appendix C to this QAPP refers to example SOPs for the routine operation of field samplers. Appendix D includes both existing SOPs and example SOPs to be used for routine field operations, sample handling, filter preparation, laboratory analyses, and archival of particle filter samples collected and extracts prepared.

Quality Control Requirements of Volume I of the “Quality Assurance Project Plan: Chemical Speciation of PM_{2.5} Filter Samplers” [February 20, 2009 edition RTO/0212053/01QA, EPA contract No EP-D-09-010] presents detailed information on what occurs when quality control findings indicate the need for corrective action. It includes gravimetry, ions analysis, XRF analysis, OC/EC analysis, sample handling, data processing and review, etc

Appendix A 2010 Monitoring Schedule

2010 Monitoring Schedule

3-day & 6-day Monitoring Schedule for TSP, Pb, PM-10, PM-2.5, and VOC. 12-day Monitoring Schedule for PM-2.5 Collocation.



Appendix B

Example Standard Operating Procedures for Conducting QA Audit or Verification Checks of Field Samplers

Verification/Audit SOP for TEOM Sampler

Section 10: “Maintenance and Quality Control Procedures” of the SOP provided in Appendix D of this QAPP can be used to conduct an audit or verification of the TEOM samplers.

Verification/Audit SOP for the MOUDI

Sections 5.1: “Calibration Procedures” of the example SOP provided in Appendix D can be used to verify and audit the MOUDI flow rate.

Verification/Audit SOP for Dichotomous and FRM Samplers (4/4/08 Draft Provided below)

The SOPs for conducting the QA audit or verification checks of the Sequential are listed below as “Verification/Audit of the Thermo Model 2025-D Sequential Dichot Sampler.” This SOP can also be used for the Thermo 2025 Sequential FRMs since they are from the same vendor (Thermo) and model number (2025). An example audit forms are provided in Figures 3 through 7 of this appendix.

Material needed

1. NIST-traceable standard for flow rate, temperature, and pressure
2. Two magazines (fine and coarse)
3. Four filter cassettes (two without filter and screen and two with Teflon filter and screen)
4. Flow audit adapter
5. Verification form (only enter values in the yellow cells; the blue cells are calculations)

Record date of audit, serial number of sampler (from Main Menu screen), person conducting the audit, and other information requested at the top of the verification form. Turn on standards and let equilibrate to current conditions for 1 hour. If using the BGI triCal unit, place Venturi #1 in the cell and then turn on.

Date and Clock Check Procedure

1. From the Main screen, record the Current Time and Date on Verification Form. Time is reported in Hours and Minutes (also seconds, but not required to record on form). Date is recorded in year-month-day. For example, April 5, 2008 is recorded as 08/04/05.
2. If Time and Date Values are within acceptance criteria (Time is ± 5 minutes and date is exact no error limits), continue to parameter check, filter temperature.
3. If the values are outside criteria, record error, press the “F1” key to edit. The cursor will highlight on the screen. Use the left, right, up, and down arrow keys to move around the screen. Highlight incorrect value and type in correct value using the number keys.

4. Press the “Enter” key to return to the Main screen.
5. Verify values are correct on Main screen; continue to parameter check, leak check.

Temperature check (filter and ambient)

Filter Temperature Procedure

1. From the Main Menu screen, press the “Menu” key to proceed to the list of menus. Use the down arrow to highlight the Service Mode. Press the “Enter” key. Select yes by pressing the “F4” key. Press the “F1” key to open the Audit Menu screen.
2. Remove the sampling magazines (fine and coarse).
3. In each magazine, place two filter cassettes. One cassette will have a Teflon filter for leak check and flow rate check and the other cassette will have no filter or screen. Place the cassette with no filter or screen on top.
4. Install each audit magazine in the left side of both the front and rear filter exchange mechanism and two clean empty storage magazines on the right side.
5. Press the “F4” key to advance any filter in the filter chamber. Also this will advance the filter cassette with no filter or screen.
6. Remove the PM₁₀ inlet and place in a safe place.
7. Unscrew the lock nut at the base of the downtube/sampler connection.
8. With a slight turning motion and pulling straight up on the downtube, remove the downtube.
9. Unlatch and open the sampler’s top cover. Pull straight up to remove the virtual impactor.
10. Place the standard temperature probe within 1” of the filter temperature probe in the fine side (front opening).
11. Allow probes to stabilize.
12. Record the filter temperature from the sampler screen for Filter Temperature 1 (fine) and the standard on the Verification form.
13. Place the standard temperature probe within 1” of the filter temperature probe in the coarse side (back opening).
14. Allow probes to stabilize.
15. Record the filter temperature from the sampler screen for Filter Temperature 2 (coarse) and the standard on the Verification form.
16. The acceptance criterion is ± 2 °C for temperature. If the value is within acceptance criteria, proceed to the next parameter, ambient temperature. If the value is outside the acceptance criteria, refer to calibration procedure in the Instruction Manual after completing ambient temperature, barometric pressure, leak check, and flow rate verification or audit.
17. Remove the standard temperature probe. Replace the virtual impactor (Be sure to position the nozzle housing so that it faces the front of the sampler.). Close and latch the sampler’s top cover. Insert the downtube and tighten the lock nut. Press the “F4” key to advance the filter cassette with no filter or screen to the storage magazine. The cassette with a Teflon filter must be in the sample chamber for the leak check and flow rate check.

Ambient Temperature Procedure

1. From the Main Menu screen, press the “Menu” key to proceed to the list of menus. Use the down arrow to highlight the Service Mode. Press the “Enter” key. Select yes by pressing the “F4” key. Press the “F1” key to open the Audit Menu screen.
2. Place the standard temperature probe in the second row of fins on the ambient temperature protection shield and allow the temperature to stabilize.
3. Record the ambient temperature from the sampler screen and the standard on the Verification form.
4. The acceptance criterion is ± 2 °C for temperature. If the value is within acceptance criteria, proceed to the next parameter, barometric pressure. If the value is outside the acceptance criteria, refer to calibration procedure in the Instruction Manual after completing barometric pressure, leak

check, and flow rate verification or audit. If a temperature calibration is performed, repeat verification of the flow rate.

Barometric Pressure Check Procedure

1. From the Main Menu screen, press the “Menu” key to proceed to the list of menus. Use the down arrow to highlight the Service Mode. Press the “Enter” key. Select yes by pressing the “F4” key.
2. Record the barometric pressure from the sampler screen and the standard on the Verification form.
3. The acceptance criterion is ± 10 mm Hg for pressure. If the value is within acceptance criteria, proceed to the next parameter, leak check. If the value is outside the acceptance criteria, refer to calibration procedure in the Instruction Manual after completing leak check and flow rate verification or audit.

Leak Check Procedure

1. From the Main Menu screen, press the “Menu” key to proceed to the list of menus. Use the down arrow to highlight the Service Mode. Press the “Enter” key. Select yes by pressing the “F4” key.
2. Confirm that an audit filter cassette with a Teflon filter is in the sample compartment.
3. Remove the PM₁₀ inlet and place the flow audit adapter (closed position) on downtube.
4. Press the “F5” key for leak check. Press the “F2” key to start the leak check and then press the “F1” to confirm (yes).
5. The sampler will begin the leak Check.
6. After test completed, record leak value on the Verification form. Acceptance criterion is less than 25 mm Hg drop.
6. If leak check passes, continue to flow rate check.
7. If leak check fails, check flow audit adapter and try a new audit filter for leak issues. If no leak detected, refer to Service Manual for troubleshooting steps. Recheck leak check. If leak failure continues, notify Thermo for next steps and discontinue the verification or audit for flow rate. If recheck of leak check passes, continue to next parameter, flow rate check.
8. After determining if the leak check passes or fails, release the pressure in the system by slowly turning the valve on the flow audit adapter until completely open.

Flow Rate Check Procedure

1. Only conduct a flow rate verification or audit after a successful leak check.
2. Using the BGI triCal unit, turn the power off and then back on after equilibrated to current conditions for 1 hour. Leave Venturi #1 (6 to 30 L/min) in measuring cell of the triCal unit during the power off and on step.
3. From the Main Menu screen, press the “Menu” key to proceed to the list of menus. Use the down arrow to highlight the Service Mode. Press the “Enter” key. Select yes by pressing the “F4” key.
4. Review the screen. The flow rate for coarse should read near 1.67 L/min and the flow rate for fine should read near 15.0 L/min. If the flow rates are not within 10% of expected, troubleshooting will be carried out.
5. Press the “F2” key to turn on valve for fine pump and “F3” for the coarse valve. Now press the “F1” key to turn on pumps.
6. Record the flow rates for coarse and fine compartments from the sampler screen on the Verification form for the total flow check.
7. Record the flow rate for the standard on the Verification form.
8. The acceptance criterion is ± 10 % for flow rate.
9. Press the “F3” key to turn off the valve to the coarse compartment. After a few minutes, the flow rate for the coarse compartment will reduce to near zero L/min.
10. Record the flow rate for the fine compartment and standard on the Verification form.
11. The acceptance criterion is ± 10 % for flow rate.

12. Disconnect the sample tubing to the triCal unit and remove Venturi #1 from the triCal unit and replace with Venturi #2 (1.2 to 6 L/min). Let calibrate (standardize).
13. Press the “F2” key to turn off the flow to the fine compartment and press the “F3” key to turn on the flow to the coarse compartment. After a few minutes, the flow rate for the fine compartment will reduce to near zero L/min.
14. Reconnect the sample tubing to the triCal unit and let system equilibrate.
15. Record the flow rates for coarse compartment and standard on the Verification form.
16. The acceptance criterion is $\pm 10\%$ for flow rate. If all parameters are within acceptance criteria, the site operator can place next runs sample in the sampling compartment. The audit filters can be removed from the storage magazines and stored until next verification/audit. If any of the flow rates were outside the acceptance criteria, refer to calibration procedure in the Instruction Manual after completing temperature and pressure verification or audit.
17. Press the “F3” key and “F2” key to turn off valves to coarse compartment and the pump.
18. Press the “F1” key to turn off pump.
18. Remove the flow audit adapter and replace the PM₁₀ inlet.
19. Press the “Menu” key to return to the list of menus. Use the down arrow to highlight the Exit Service Mode. Press the “Enter” key to return sampler to sample mode.

DRAFT

Project: PEP QAPP
 Appendix: E
 Revision No.: 1
 Date: 1/15/2009
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Performance Evaluation Program PEP Sampler Audit Worksheet	U.S. Environmental Protection Agency
Location: <input style="width: 100%;" type="text"/>	
AQS Site ID: <input style="width: 200px;" type="text"/>	Date: <input style="width: 100px;" type="text"/>
Latitude (if known): <input style="width: 150px;" type="text"/>	Longitude (if known): <input style="width: 150px;" type="text"/>
Audit Information	
Auditor(s): <input style="width: 300px;" type="text"/>	Affiliation: <input style="width: 200px;" type="text"/>
Site Operator: <input style="width: 300px;" type="text"/>	Affiliation: <input style="width: 200px;" type="text"/>
Phone No.: <input style="width: 300px;" type="text"/>	
Sampler Model: <input style="width: 200px;" type="text"/>	Sampler S/N: <input style="width: 100px;" type="text"/>
Last Calibration Date (if known): <input style="width: 150px;" type="text"/>	Collocated? Yes (X): <input style="width: 50px;" type="text"/>
	No (X): <input style="width: 50px;" type="text"/>
Reference Std Model: <input style="width: 200px;" type="text"/>	Reference Standard S/N: <input style="width: 100px;" type="text"/>
Calibration Date: <input style="width: 150px;" type="text"/>	
Significant Findings:	

Figure 3. Appendix B. Example FRM Audit Form

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Location:					
AQS Site ID:		Date:			
Clock Test:					
<i>If Local Time is under daylight savings, convert Ref Std to Local Standard Time. Daylight Saving Time begins for most of the United States at 2:00 a.m. on the first Sunday of April. Time reverts to standard time at 2:00 a.m. on the last Sunday of October.</i>					
Audit	Time (hh:mm)		Difference Minutes	5 minutes or less?	
	Ref Std	PQ200		Pass	Fail
	Recalibrated				
Date					
Leak Test					
	Initial Audit	After Correction	Change < 5 cmH ₂ O for 2-min interval		
Start cm H ₂ O			Difference	Pass	Fail
Stop cm H ₂ O			Initial:		
			After Correction:		
Flow Test			Calibration		
For the reference standard, enter "UR" for under range and "OR" for over range flow readings.					
	L/min		% Difference	Less than 4%?	
Ref Std	PQ200	Pass		Fail	
Retest after Calibration					
	L/min		% Difference	Less than 4%?	
Ref Std	PQ200	Pass		Fail	

Figure 4. AppendixB. Example FRM Audit Form (continued)

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Location:					
AQS Site ID:		Date:			
Reference Standard vs Design Flow					
Channel 1	L/min	Ref Std	PQ200	% Difference	Less than 4%?
					Pass Fail
Retest after Calibration					
Channel 1	L/min	Ref Std	PQ200	% Difference	Less than 4%?
					Pass Fail
Ambient Temperature Test					
	Degrees C	Ref Std	PQ200	Difference	Less than 2 degrees?
					Pass Fail
Retest After Recalibration					
Filter Temperature Test					
	Degrees C	Ref Std	PQ200	Difference	Less than 2 degrees?
					Pass Fail
Retest After Recalibration					
Pressure Test					
	mm Hg	Ref Std	PQ200	Difference	Less than 10 mm?
					Pass Fail
Retest after recalibration					

Figure 5. Appendix B. Example FRM Audit Form (continued)

Verification/Audit Form for Sequential Dichot						Page 1
Audit Information						
Auditor(s)				Date		
Sampler Model				Sampler S/N		
Last Calibration Date				Collocated?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
Reference Std Model				Reference Standard S/N		
Calibration Date						
Clock Test:						
<i>If Local Time is under daylight savings, convert Ref Std to Local Standard Time. Daylight Saving Time begins for most of the United States at 2:00 a.m. on the first Sunday of April. Time reverts to standard time at 2:00 a.m. on the last Sunday of October</i>						
Audit Recalibrated Date	Time (hh:mm)			Difference Minutes	5 minutes or less?	
	Ref Std				Pass	Fail
	Sampler					
Filter Temperature Test						
Fine (Filter 2) Coarse (Filter 1) Retest After Recalibration	Degrees C			Difference	Less than 2 degrees?	
	Ref Std				Pass	Fail
	Sampler					
Ambient Temperature Test						
Retest After Recalibration	Degrees C			Difference	Less than 2 degrees?	
	Ref Std				Pass	Fail
	Sampler					
Pressure Test						
Retest after recalibration	mm Hg			Difference	Less than 10 mm Hg?	
	Ref Std				Pass	Fail
	Sampler					

Figure 6. Appendix B. Example Sequential Dichotomous Sampler Audit Form

Verification/Audit Form for Sequential Dichot							Page 2
Sampler Model			Sampler S/N				
Leak Test							
	Initial Audit mm Hg/min		After Correction mm Hg/min		25 mm Hg/min or higher fails		
					Initial	After	Pass
Flow Test							
Calibration							
For the reference standard, enter "UR" for under range and "OR" for over range flow readings.							
	L/min				% Difference	Less than 10%?	
	Ref Std		Sampler			Pass	Fail
Total (add coarse and fine for sampler)				16.67 L/min			
Fine				15.0 L/min			
Coarse				1.67 L/min			
Retest after Calibration							
	L/min				% Difference	Less than 10%?	
	Ref Std		Sampler			Pass	Fail
Total				16.67 L/min			
Fine				15.0 L/min			
Coarse				1.67 L/min			
Reference Standard vs Design Flow							
	L/min				% Difference	Less than 10%?	
	Ref Std		Sampler			Pass	Fail
Total			16.67	16.67 L/min			
Fine			15.00	15.0 L/min			
Coarse			1.670	1.67 L/min			
Retest after Calibration							
	L/min				% Difference	Less than 10%?	
	Ref Std		Sampler			Pass	Fail
Total			16.67	16.67 L/min			
Fine			15.00	15.0 L/min			
Coarse			1.67	1.67 L/min			

Overall Status:

Satisfactory if all parameters pass the acceptance criteria. Do not use the sampler if any parameter fails the verification/audit.

Figure 7. Appendix B. Example Sequential Dichotomous Sampler Audit Form (continued)

Appendix C

Example Standard Operating Procedures for Routine Operation of the Field Samplers

There are many SOPs already written for performing routine sample runs using the FRM, Dichotomous, and TEOM samplers. Some were prepared by State agencies for use in their monitoring programs.

SOP for PM_{10-2.5} Federal Reference Method (FRM) Sampler Pair

The PM_{10-2.5} FRM pair is a set of identical FRM samplers of the same vendor/model and operated in the same manner. The only difference between the samplers is that the PM_{2.5} separator has been removed from one of the samplers. The Quality Assurance Guidance Document 2.12; "Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods" can be used as guidance for the operation of both the PM_{2.5} and PM₁₀ FRM samplers. The latest edition of this guidance document is located at:

<http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf>

An SOP for field operation of the R&P Partisol-Plus Model 2025 Sequential Air Sampler, approved by the California Environmental Protection Agency Air Resources Board, is also available. This SOP will be appropriate for training and field operation of the Thermo Environmental Partisol-Plus Model 2025 PM_{2.5} sequential sampler, the Partisol-Plus Model 2025 PM₁₀ sequential sampler, and (with some modification) the Partisol-Plus Model 2025 sequential dichotomous sampler. The title of the SOP is "Rupprecht & Patashnick Partisol-Plus Model 2025 PM-2.5 Sequential Air Sampler" [Air Quality Surveillance Branch SOP 404, R&P Model 2025, First Edition, January 2003 (39 pages)]. This draft SOP has been added to Appendix D of this QAPP.

SOP for the Dichotomous (Dichot) Sampler

An SOP for the operation of dichot samplers has not yet been developed; however, the vendor provides a hard copy of an extensive operator's manual, user's guide, and service manual with each dichot sampler. Each site will have at least one copy of these documents and they will initially be used for the operation of samplers for the pilot study. Additional electronic copies of these documents can be obtained from the vendor at:

http://www.thermo.com/com/cda/resources/resources_detail/1,2166,200503,00.html

In addition to the manual, an SOP developed by California Air Resources Board (CARB) entitled "Rupprecht & Patashnick Partisol-Plus Model 2025 PM-2.5 Sequential Air Sampler" [Air Quality Surveillance Branch SOP 404, R&P Model 2025, First Edition, January 2003 (39 pages)] will be used.

SOP for the FDMS PM_{10-2.5} TEOM and the Micro-Orifice Uniform Deposit Impactor (MOUDI)

Draft SOPs for the operation of the Thermo 1405-DF FDMS TEOM and MOUDI are provided in Appendix D of this QAPP.

A draft SOP developed for EPA by STI (Contract EP-D-09-097) will be used in the PM_{10-2.5} pilot study with the Thermo 1405-DF FDMS TEOM and is entitled:

“Standard Operating Procedure for the Continuous Measurement of Particulate Matter Thermo Scientific TEOM® 1405-DF Dichotomous Ambient Particulate Monitor with FDMS® Federal Equivalent Method EQPM-0609-182 for PM_{2.5}.” 9/1/2009. Number STI-905505.03-3657-SOP. Sonoma Technology, Inc.

An SOP that was used for the EPA Supersites project is also appropriate for use in the PM_{10-2.5} pilot study for the MOUDI sampler and is entitled:

DRI Standard Operating Procedure: “Micro-Orifice Uniform Deposit Impactor (MOUDI) Field and Laboratory Operations.” 10/21/1992. Number 1-208.3, Revision 3 (TUUH.92)

The original research paper describing the MOUDI is also available for consultation. Virgil A. Marple, Kennet L. Rubow, and Steven M. Behm “A Microorifice Uniform Deposit Impactor (MOUDI): Description, Calibration, and Use.” *Aerosol Science and Technology* 14: 434-446 (1991).

Appendix D

Standard Operating Procedures for Field and Laboratory Operations

There are many SOPs for conducting laboratory operations and support responsibilities. All SOPs currently used by RTI International Laboratories for the various PM processes and analyses listed in Section 2, are maintained in secure files at RTI and are generally available through the EPA AMTIC Web Site. Many of the SOPs used for PM_{2.5} speciation analysis will be used for both PM_{2.5} and PM₁₀ in this pilot study. The relevant SOPs are included in this appendix. A listing of the SOPs in this appendix are given below:

1. Draft SOP for the Continuous Measurement of Particulate Matter (TEOM)
2. Rupprecht & Patashnick Partisol-Plus Model 2025 PM-2.5 Sequential Air Sampler [Air Quality Surveillance Branch SOP 404, R&P Model 2025, First Edition, January 2003]
3. Example SOP for Routine Operation of the Micro-Orifice Uniform Deposit Impactor (MOUDI)
4. Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters
5. Sample Handling and Archive Laboratory (SHAL)
6. Coating Annular Denuders with Magnesium Oxide
7. Shipping Filters to and from an Off-Site Laboratory
8. Cleaning Nylon Filters Used for the Collection of PM_{2.5} Material
9. Long-Term Archiving of PM Filters and Extracts
10. PM Gravimetric Analysis
11. PM_{2.5} Anion Analysis
12. PM_{2.5} Cation Analysis
13. X-ray Fluorescence (XRF) Analysis of Particulate Matter Deposits on Teflon Filters
14. Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermo/Optical-Transmittance Carbon Analyzer
15. DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A
16. Analysis of Semi-volatile Organic Compounds by GC/MS
17. X-Series Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the Analysis of Particulate Deposits on Teflon Filters
18. Analysis of PM₁₀ and PM_{2.5} Samples by Scanning Electron Microscopy (SEM)
19. Database Operations
20. Biological Identification and Assay (**To be developed**)
21. Determination of water-soluble organic material (**To be developed**)

Standard Operating Procedure for the Continuous Measurement of Particulate Matter

**Thermo Scientific TEOM[®] 1405-DF
Dichotomous Ambient Particulate Monitor with FDMS[®]
Federal Equivalent Method EQPM-0609-182 for PM_{2.5}**

STI-905505.03-3657-SOP

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1. ABOUT THIS STANDARD OPERATING PROCEDURE

On June 17, 2009, the U.S. Environmental Protection Agency (EPA) designated four new equivalent methods for measuring concentrations of PM_{2.5} in ambient air (see 74 FR 28696). The four designations were for instruments manufactured by Thermo Scientific, Inc. Two of the four new PM_{2.5} equivalent methods, referenced here, are automated methods that employ conditioned filter sample collection and direct mass measurements with an inertial micro-balance (Tapered Element Oscillating Microbalance, or TEOM[®]) in near real time. Both of these methods use the Filter Dynamic Measurement System (FDMS[®]) to estimate and adjust for the volatile component of the mass. These two methods (monitors) are very similar, with the main difference being that one analyzer (TEOM[®] 1400a with Series 8500C FDMS[®] [1400a/FDMS]; EQPM-0609-181) achieves particle size separation by a cyclonic method and measures only PM_{2.5}, and the other method (TEOM[®] 1405-DF with FDMS[®] [1405-DF]; EQPM-0609-182) achieves particle separation by a virtual impactor that separates the particles into fine (PM_{2.5}) and coarse (PM_{10-2.5}) fractions. (The equivalency designation for the 1405-DF applies only to the fine fraction.) After particle separation, the processing of the PM_{2.5} sample air stream is identical between the two instruments; thus, even though this standard operating procedure (SOP) focuses on the 1405-DF specifically, the operating procedure principles can be applied to the 1400a/FDMS analyzer as well. The user interface, however, is quite different between the two analyzers, so the step-by-step procedures that utilize the 1405-DF user interface are not directly applicable to the 1400a/FDMS.

This SOP is based upon the Thermo Scientific, Inc. TEOM[®] 1405-DF Operating Guide (42-0100815 Revision A.003, Feb. 15, 2008), the TEOM[®] 1405-DF Quick Start Guide (42-010814 Revision A.002), and SOPs submitted by users of TEOM[®] samplers equipped with an FDMS[®]. It is meant to be used in conjunction with the 1405-DF Operating Guide, which offers additional details not specifically covered in this SOP. Because this is an SOP on operating a Federal Equivalent Method (FEM) PM_{2.5} sampler, the focus of this document will be the operation of the fine particle stream portion of the 1405-DF; however, the operation of the dichotomous sampling of fine and coarse particulate matter is integrated into the discussion.

Users from different regions of the United States, with expertise in one or more areas involving installation, programming, operating, quality checking or maintaining TEOM[®] with FDMS[®] particulate matter monitors and/or quality assuring, validating, or reporting data generated by these instruments, have contributed to the development of this SOP. Some of the diagrams and stepwise procedures from the Operating Guide and submitted SOPs are reproduced in this SOP, and the cooperation of Thermo Scientific and other contributors in development of this model SOP is gratefully acknowledged.

Sections 2 through 8 of this SOP offer synopses of some background topics. Hands-on users will find the most useful portions of the SOP to be **Section 9** “Installation Procedures” and **Section 10** “Maintenance and Quality Control Procedures”. Installation usually occurs once (or perhaps infrequently under re-location) and includes receiving, site and enclosure selection, and the actual putting in place of the system components, followed by system configuration, initial checks, and startup. Maintenance and Quality Control (QC) includes periodic maintenance (e.g.,

filter changes, cleaning) and recurring QC procedures that ensure compliance with Federal Equivalent Method (FEM) criteria and regulatory standards. **Table 10-1** provides a maintenance schedule, lists the QC protocols, and gives cross references to SOP sections containing the procedures.

Factors to consider when using external data loggers are discussed in **Section 9.7.2**, and data validation procedures are covered in **Section 11**.

The SOP attempts to identify common pitfalls and emphasizes details of operating procedures that may help avoid operator missteps and frustration. These discussions are presented so that the rationale underlying the procedures is understood. Agencies may wish to exclude this level of detail from their SOPs. Portions of this SOP may be excerpted, edited, or eliminated as deemed appropriate. For example, since installation is often a one-time-only procedure, it may be judged as unnecessary in the SOP covering routine procedures. Checklists and forms referred to in the text are provided in the Appendices as examples that may be used in whole or in part.

2. SCOPE AND APPLICABILITY

The purpose of this SOP is to provide a set of uniform protocols for installation, operation, maintenance, calibration, and quality control (QC) and quality assurance (QA) of the TEOM[®] 1405-DF Ambient Particulate Monitor with FDMS[®] configured to meet EPA FEM EQPM-0609-182 for PM_{2.5} mass. It is intended to be a "Model SOP" that incorporates best practices on the method, and its use is not required to meet the standards set forth under EQPM-0609-182. These best practices are being made available for incorporation by monitoring agencies, and for Regional offices to consider, when approving an SOP. It is acknowledged that there will always be cases where agencies' needs or guidance on writing SOPs is different from what is in the model.

To meet the federal equivalent method (FEM) requirements for measurement of PM_{2.5} mass as described in the Federal Register (74 FR 28696), the TEOM[®] 1405-DF with FDMS[®] must be

- Configured for dual filter sampling of fine (PM_{2.5}) and coarse (PM_{10-2.5}) particles using the US EPA PM₁₀ inlet and a virtual impactor;
- Operated with a total flow rate of 16.67 lpm, a fine sample flow rate of 3 lpm, and a coarse sample flow rate of 1.67 lpm;
- Equipped with firmware version 1.50 or later. (Firmware version 1.50 has a goal date for release of September 15, 2009.) The firmware update is expected to add a parameter labeled "FEM PM_{2.5} Concentration". This parameter will apply an algorithm to the PM_{2.5} concentration data to generate data that will meet FEM requirements to fit to the FRM PM_{2.5} data.
- Operated with or without external enclosures; and
- Operated in accordance with the Thermo Scientific TEOM[®] 1405-DF Dichotomous Ambient Particulate Monitor Instruction Manual. (An updated manual is scheduled to be released by Thermo Scientific in mid-September 2009.)

3. SUMMARY OF THE METHOD

The TEOM[®] 1405-DF with FDMS[®] is a dichotomous sampler providing near real time measurements of fine (PM_{2.5}) and coarse (PM_{10-2.5}) particulate matter in ambient air. The system draws ambient air first through a PM₁₀ size selective inlet at 16.67 lpm, and then through a virtual impactor that partitions the coarse and fine fractions into separate air streams at 1.67 and 15.0 lpm, respectively. The PM_{2.5} air stream is then split isokinetically into sample (3.0 lpm) and by-pass (12.0 lpm) streams to reduce the sample flow rate and air volume. The fine sample and coarse sample air streams flow in parallel through the FDMS[®] module (described below) and a pair of sample collection filters, one for the coarse particle measurement and one for the fine particle measurement. The 1405-DF maintains each sample air stream at a constant volumetric flow rate, corrected for local temperature and barometric pressure. Each sample collection filter is attached to an inertial mass transducer, or microbalance, TEOM[®] that is weighed continuously. The tapered element oscillates at its natural frequency (like the tines of a tuning fork), determined by the physical characteristics of the tapered tube and the mass on its free end. Any mass added to the filter causes a proportional decrease in oscillation frequency, while loss of mass causes a proportional increase. An electronic control circuit senses the oscillation frequency and, through positive feedback, modifies energy input to the system to modulate any increase or decrease in frequency that is presumed due to changes in mass accumulation on the filter. A precision electronic counter measures the oscillation frequency using a 10-second sampling period. An automatic gain control circuit maintains the oscillation at a constant amplitude.

The FDMS[®] facilitates the measurement of both nonvolatile and volatile PM components. Since the 1405-DF is a dichotomous sampler, the FDMS[®] utilizes parallel and identical components to condition the sample stream of each size fraction concurrently, but independently. **Figure 3-1** is a schematic representation of the 1405-DF system from the air inlet through the tapered element. **Figure 3-2** details the flow path for the PM_{2.5} sample air stream through the 1405 FDMS. (The sample air stream for the coarse fraction follows an identical and parallel path once it leaves the virtual impactor.)

After the 16.7 lpm inlet flow is sequentially split to attain the 1.67 and 3.0 lpm sample flows, the sample stream for each fraction is passed through a diffusion dryer containing Nafion[®] tubing specially designed to minimize particle loss. The dryer lowers the sample stream relative humidity (RH), minimizing positive artifact associated with water sorption onto the collection filter and making possible mass transducer operation at 5 °C above the peak air monitoring station temperature (usually 30°C). An integrated humidity sensor, downstream of the dryer, measures the humidity of each sample stream to determine the drying efficiency. The dryers use re-circulated air that has passed through the sample collection filter so that the dryers do not require any bottled air or a dedicated “zero” air system.

When the sample air exits the dryer it enters a switching valve that, every 6 minutes, alternately directs the air stream either to the sample collection filter (the base cycle) or to an alternate flow path (the reference cycle). The reference flow path includes a standard FRM-style 47-mm filter cassette with a TX-40 filter (Teflon-coated borosilicate) maintained at 4°C. The low

temperature causes volatile PM components to condense on the filter, resulting in an air stream free of both non-volatile and volatile PM components. (The 47-mm filter itself can also be used for time-integrated chemical analysis.) This clean, reference air is routed to the mass collection filter, and the mass measured on the collection filter during this cycle is termed the “Reference mass concentration” (Ref MC). The Ref MC provides an estimate of the volatile PM losses that occur during sampling of ambient particle-laden air, and any loss of mass from the sample collection filter during the Ref MC cycle is quantified and added back to the PM concentration measured during the “Base mass concentration” cycle. The Base MC cycle, operated at 30°C, yields the Base mass concentration of the ambient air sample. Based upon the change in the filters’ sample mass (adjusted for volatile component losses) and the sampled air volume, a one-hour running average of the PM mass concentration is updated every six minutes for each PM size fraction.

In summary, the Base MC is equal to the PM concentration of the conditioned particle-laden sample stream (which is usually a positive number); the Ref MC is equal to the PM concentration of the particle-free sample stream, after passing through a purge filter (which can result in a negative value if mass volatilizes from the filter); and the mass concentration is equal to the Ref MC subtracted from the Base MC. Note that this means that the sampler is measuring particle-laden air for five 6-minute periods per hour (or half of the time) and filtered air for five alternating 6-minute sample periods each hour.

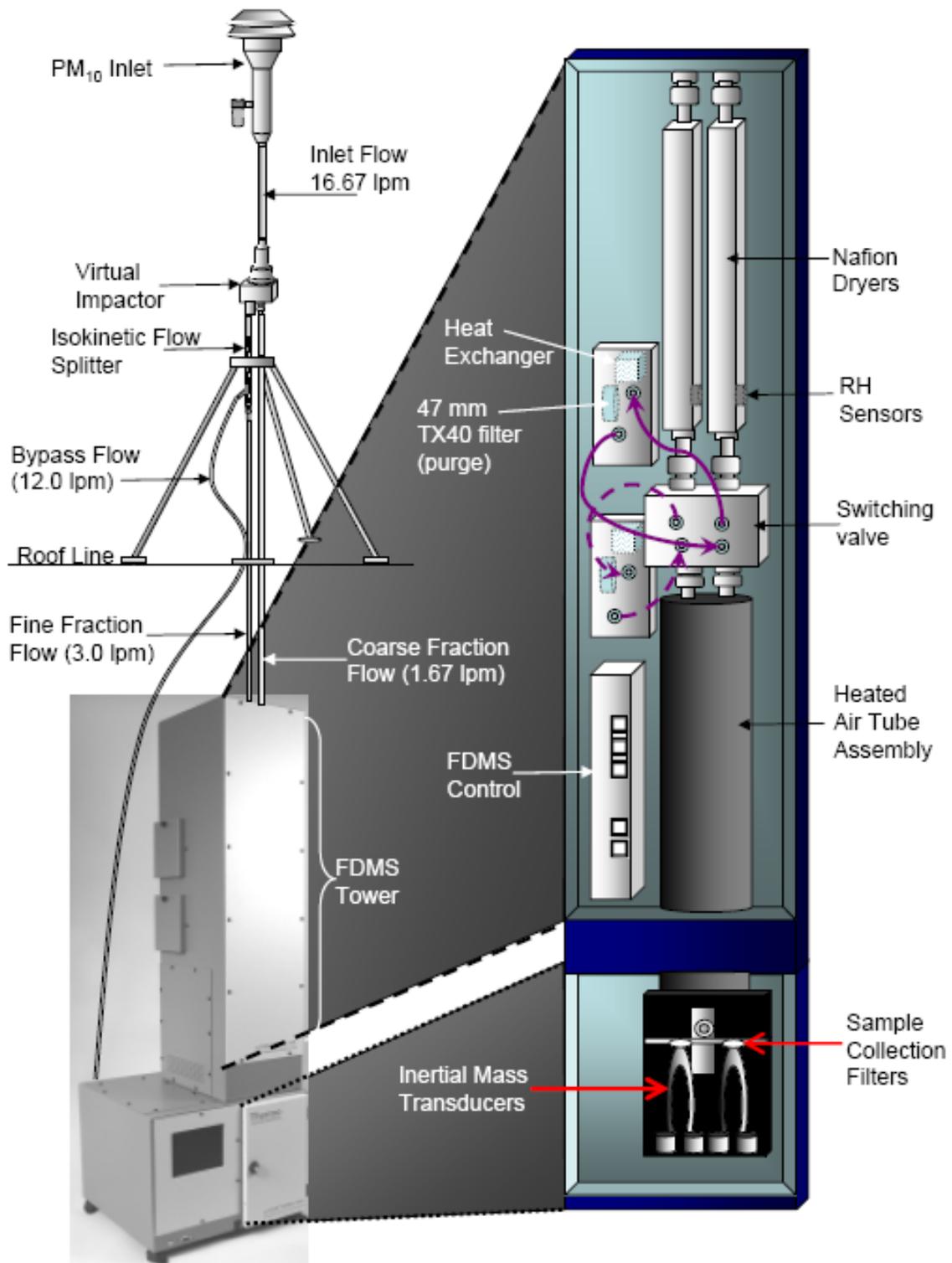


Figure 3-1. Schematic representation of the 1405-DF ambient PM_{2.5} monitoring system.

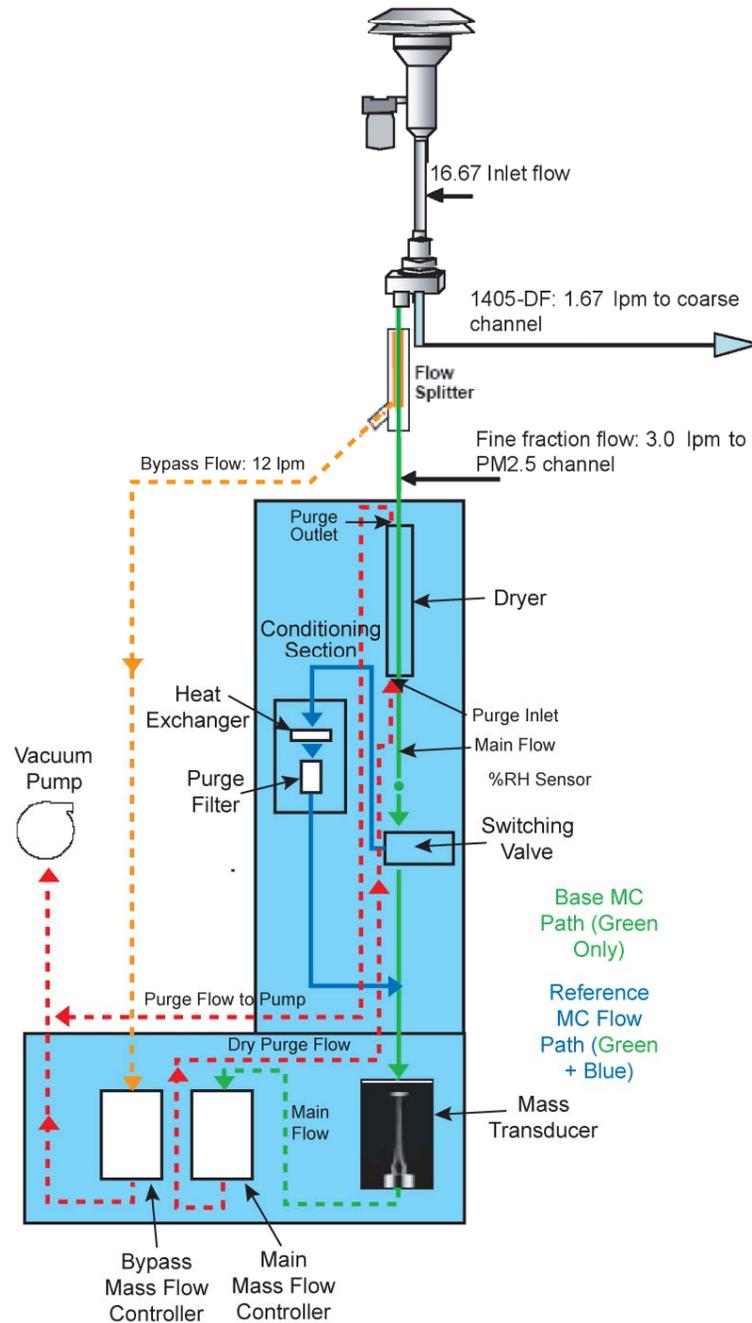


Figure 3-2. Schematic representation of the Base MC and Reference MC flow paths for the PM_{2.5} sample air stream. A parallel system operates simultaneously for the PM-Coarse sample air stream in the 1405-DF. (Original schematic courtesy of Puget Sound Clean Air Agency.)

4. DEFINITIONS

Technical terms in this SOP are defined as they are introduced so that their meaning is made clear in context. This section explains some general terminology.

Two terms used throughout this SOP are “verification” and “validation”. These terms have similar, but distinctly different, meanings. *Verification* refers to the review of interim work steps to ensure they are acceptable and to determine whether the system is consistent, adheres to standards, uses reliable techniques, and performs the selected functions in the correct manner. Verification steps are performed during the process of data collection and include such things as checklists and comparisons to standards. A leak check is an example of a verification procedure used with the 1405-DF. *Validation* involves determining if the system complies with the requirements and performs functions for which it is intended and meets the organization’s goals and user needs. It is a determination of correctness of the data and is usually performed only periodically (e.g., quarterly) or at the end of the project.

Similarly, the terms “quality control” (QC) and “quality assurance” (QA) are often used interchangeably, but in fact have important distinctions. QC refers to the operational techniques and activities used to fulfill the requirements for quality. QC is what the field technician practices when conducting maintenance and verification procedures on the 1405-DF. Routine QC procedures, such as flow checks, are referred to herein as QC checks or QC procedures. QA refers to the planned or systematic activities used to provide confidence that the requirements for quality are fulfilled. An independent audit is an example of a QA activity.

The term “audit” is often used in a generic way to mean check, inspect, examine, or assess, and many SOPs use the term audit to refer to QC procedures, such as flow checks or leak checks, that are carried out by field technicians during the course of normal operations and maintenance. Within the TEOM[®] 1405-DF with FDMS[®] user interface, the term audit is used to indicate a procedure that tests but does not alter a value.

The term “calibration” refers to the act of adjusting an instrument after comparison with a standard. When referring to the instrument software, the term “calibration” is used to indicate a procedure that would alter instrument output. A “calibration check” involves only the checking of an instrument against a standard and involves no adjustment of the instrument.

5. HEALTH AND SAFETY WARNINGS

Safety precautions should be heeded during the setup and operation of the TEOM[®] 1405-DF with FDMS[®]. General safety rules regarding electricity and power tools should be observed. High voltages may be present in all instrument enclosures. Disconnect the power cord from the power source while servicing the instrument. Working at above-ground elevations and on ladders is frequently required, and precautions should be taken to avoid falls and personal injury.

6. INTERFERENCES

The TEOM[®] 1405-DF with FDMS[®] is a robust instrument that has minimal potential interferences. Poor siting, inadequate electrical power or bad grounding, poor control of the sample air RH in humid environments, and significant vibrations are known sources of interference.

Interferences arising from improper siting can be avoided by exercising care during site selection (Section 9.3). Electrical connections should be thoroughly checked during installation and the ground potential should be measured as part of the installation procedure.

Proper control of the *RH* in the sample stream is integral to proper sampler operation. RH issues should be addressed by carefully monitoring and maintaining shelter temperature and instrument sample air dew point(s) to avoid introducing condensation into the sample train (Sections 9.4 and 9.5.1).

Proper *dryer* operation is integral to accurate sampler operation. Dryers should be replaced on a routine basis not to exceed the manufacturers' recommended interval of one year. Areas in which high humidity is common should monitor dryer efficiency; dryers may need to be replaced on a more frequent basis. The dryer efficiency can be estimated by monitoring the dew point of the sample stream which is labeled in the instrument screens and downloads as TEOM A Dryer Dew Point for the fine fraction and TEOM[®] B Dryer Dew Point for the coarse fraction. (Section 10.3.4).

Great care should be taken to maintain a *stable temperature* in the instrument shelter (Section 9.4). Ideally the temperature fluctuation should be less than 2°C over an hour. The temperature should also be maintained as close as possible to 5°C less than the operating temperature of the sample stream (which is generally 30 °C). (Sections 9.4, 9.5.1, 9.5.5, and 10.3.4).

Historical data have shown that it is crucial to avoid a *12-minute cycle on the air conditioning system* of the shelter. Experience has shown that a 12-minute cycle can lead to upwardly biased data, sometimes referred to as "aliasing." The use of a relatively large air conditioning unit in a relatively small enclosure has produced this 12-minute cycle and the "minimum reset time" for the compressor in the heating, ventilation, and air conditioning system may require adjustment to avoid this problem (Section 9.4).

Best practices dictate the use of additional insulation, such as pipe insulation, on all exposed tubing. Air conditioning vents should be directed away from the instrument so that the air flow over the instrument is diffused (Section 9.4).

Vibrations can affect any microbalance; therefore, care should be taken when placing the instrument in the shelter. Placing the instrument on an isolated bench may be beneficial to reduce excessive bench vibrations from other instruments. The TEOM[®] 1405-DF with FDMS[®] pump or any other pumps located in the shelter should be isolated from the instrument as far as is

practicable. Tubing to the TEOM[®] pump may need to be replaced with larger diameter tubing or pipe to avoid an excessive pressure drop due to the longer line length. It may be useful to dampen pump vibrations by placing pumps on foam pads if such placement can be accomplished without creating a fire hazard. Also, consideration should be given to the roof mounting of the sample lines; if the rigid connectors are used and the roof surface flexes during technician service activities then excessive vibrations may be transferred to the transducer resulting in erratic readings. A short flexible section of conductive rubber tubing (Thermo p/n 30-002274) can be used to mitigate the roof movement by allowing a 1-1.5" gap in the rigid tubing. Alternatively, an expanded and reinforced work surface can be added to the roof to minimize roof movement (Sections 9.4, 9.5.1, and 9.5.10).

7. PERSONNEL QUALIFICATIONS

While no special qualifications or training are necessary to operate the TEOM[®] 1405-DF with FDMS[®], a basic understanding of the principles governing ambient air sampling is assumed. The QA procedures detailed herein require an understanding of the TEOM[®] 1405-DF with FDMS[®] flow system and proper operation of calibration reference devices.

EPA Quality Assurance Guidance Document 2.12 (U.S. Environmental Protection Agency, 1998) covers specifics of field personnel qualifications and provides the following general guidelines. All field operations personnel should be familiar with environmental field measurement techniques. Those who service the PM sampler in the field must be very conscientious and attentive to detail in order to report complete and high-quality PM_{2.5} data. Persons qualified to perform PM_{2.5} field operations should be able to

- operate the PM_{2.5} sampler;
- calibrate, audit, and troubleshoot the PM_{2.5} sampler; and
- use common methods to determine temperature, pressure, and flow rate.

8. EQUIPMENT AND SUPPLIES

The equipment and supplies needed vary with the particular tasks associated with installing and operating the TEOM[®] 1405-DF with FDMS[®]. **Table 8-1** lists the 1405-DF standard hardware (supplied by Thermo Scientific), required diagnostic tools, and a suggested inventory of routine parts and supplies. (Additional tools and supplies required for installation are not listed here, but are listed in Table 9-2.) Conductive rubber tube connectors p/n 30-002274, not normally supplied) should be ordered and installed (see Sections 9.5.1 and 9.5.10). Rubber tube connectors allow removal and servicing of FDMS[®] tower components without having to disturb the rooftop inlet hardware.

Table 8-1. Standard 1405-DF System hardware, diagnostic tools, routine supplies, and spare parts.

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Category	Components	Part number	Use Schedule
Standard System Hardware	1405-DF TEOM [®] unit	NA	NA
	Temperature/humidity sensor and cable, 10 m	NA	NA
	3/8" green tubing for bypass flow, 10 m	NA	NA
	3/8" green tubing to pump, 5 m (16.5 ft)	NA	NA
	5 Sample tubing extensions, 1.0 m (40")	NA	NA
	1 Sample tubing extension, 0.79 m (31")	NA	NA
	Filter exchange tool	NA	NA
	Flow splitter	NA	NA
	PM-10 inlet	NA	NA
	Sample inlet tube	NA	NA
	Virtual impactor	NA	NA
	Water trap filter assembly	NA	NA
	Flow audit adapter/leak check kit	NA	NA
	Cooler cleaning kit (2 Y-adapters, orifice)	NA	NA
	Vacuum pump	NA	NA
	2 Operating Manuals (one hard copy, one on CD)	NA	NA
Diagnostic Tools	Flow calibrator(s)	NA	NA
	Temperature transfer standard	NA	NA
	Pressure transfer standard	NA	NA
	Digital Multi-meter	NA	NA
	KO calibration verification kit	59-002019	Yearly
	Hand Tools (screwdrivers, wrenches, small sizes, etc.)	NA	NA
Consumables	TEOM [®] Filters	57-007225-0020	Every 30 days or as needed
	FDMS Filters (47-mm TX 40)	10-002387-0025	Every 30 days or as needed
Spare Parts	Pump rebuild kit	32-008672	18 months
	Pump (120VAC)	10-001403	As needed

Table 8-1. Standard 1405-DF System hardware, diagnostic tools, routine supplies, and spare parts.

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Category	Components	Part number	Use Schedule
Spare Parts (continued)	In-line Filter Elements	50 cc: 32-010745 172 cc: 32-010755	6 months
	V-seal, TEOM [®] Filter Housing	22-009863	As needed
	O-rings, Inlet Receiver	22-00485-1112	As needed
	O-Rings, Virtual Impactor	22-000485-1152 22-000485-1155 22-000485-1026 22-000485-1020	As needed
	O-Rings, PM ₁₀ Head	Lg: 22-000485-1036 Sm: 22-002853-3026	As needed
	Nafion Dryer	56-009872	Annually
	Valve Seals	22-010280	As needed
	Chiller V-ring	22-002680	As needed
	Chiller Filter Holder O-ring	22-000485-1035	As needed
	Chiller Assembly	56-009871	As needed
	Touch Screen Assembly	56-010414	As needed
	Mass Flow Controller Assembly-DF	55-010022	As needed
	Fuse, Input Module (2 required)		As needed
	Fuse, Power Distribution Board		As needed
Cleaning Supplies	Valve cleaning brush (provided with instrument)	30-009091	As needed
	Ammonia-based cleaner	NA	Monthly
	Silicon grease	NA	Monthly
	Soap, alcohol or Freon solution	NA	Monthly
	Small soft-bristle brush	NA	Monthly
	Cotton swabs	NA	Monthly
	Paper towels, soft cloth	NA	Monthly
	D.I. Water	NA	Monthly
	Hand cleaner	NA	Monthly

9. INSTALLATION PROCEDURES

The installation process for the 1405-DF involves many steps and requires considerable attention to detail. The User's Manual provided by Thermo Scientific offers a comprehensive step-by-step procedure with many supporting pictures. That manual should be the primary reference for installation. This SOP lists the main steps and highlights some tasks that may require extra care when executing.

The major tasks associated with installation include:

- Unpacking and inspecting the TEOM[®] 1405-DF with FDMS[®] components
- Acceptance testing
- Site selection to meet 40 CFR Part 58 siting requirements
- Enclosure selection to provide the TEOM[®] 1405-DF with FDMS[®] with an environment within its operating specifications
- A series of sequential steps to install the TEOM[®] 1405-DF with FDMS[®] main unit and its supporting peripheral hardware
- Configuration of the instrument operating system to ensure that
 - The 1405-DF meets the requirements set forth in the FEM EQPM-0609-182 designation
 - The 1405-DF is set up to be compatible with the local agency data acquisition protocols

9.1 UNPACKING AND INSPECTION

A physical inspection of the TEOM[®] 1405-DF with FDMS[®] system should be made upon receipt of the system from Thermo Scientific, Inc. Visible damage to the shipping container should be reported to the carrier. System components should be verified against the packing list and any missing or damaged components should be reported immediately to the manufacturer.

9.2 ACCEPTANCE TESTING

As with any equipment, basic acceptance tests should be conducted. Some suggested tests include:

- Test pump vacuum
- Leak test of the system
- Test ambient temperature and pressure sensors
- Perform diagnostics test on the cooler to confirm proper operation
- Verify the mass transducer Calibration Constant (K0)

- Verify the F0 value by performing the mass balance test without a filter in place
- Compare operation of new sampler to an existing monitor (when practical)
- Compare operation of sampler in laboratory setting to field setting
- Operate the system for several days with a HEPA filter in place to test instrument stability

Like most air quality instruments, the 1405-DF is factory tested and calibrated prior to shipment to the user. The acceptance testing should verify proper operation of the monitor after shipping and before use in the field. The user must be careful to evaluate any discrepancies found before making adjustments to the system because historically, instruments have been adjusted incorrectly to compensate for a perceived error. Testing procedures will vary by agency, but users have reported that it is generally valuable to set up the instrument in a controlled environment such as a laboratory or workshop to test the instrument before deployment to a field site so that instrument problems can be evaluated separately from problems associated with instrument siting. It may be useful to operate the system with a zero-filter (0.2 micron) in place, to determine the stability of the instrument.

Users may also want to fully verify the operation of the mass transducer by purchasing a mass calibration kit (p/n 59-002107) and performing the mass verification procedure described on page 5-64 in the User's Manual (Rev. A.003). The instrument software provides a "Wizard" to guide the user through the procedure. The calibration constant is based on the mechanical properties of the mass transducer and therefore, should not change materially over the life of the instrument. In addition to verifying the Calibration Constant, labeled "K0" in the instrument software and calibration certificate, the value labeled F0 should be verified. During the K0 constant test the F0 value is displayed; the F0 value showed before a filter is installed should match the F0 value published on the calibration certificate received from the factory with the sampler. The F0 value should remain within ± 0.1 of the published value. If the F0 value changes, it is indicative of a physical problem with the mass transducer, and the manufacturer should be contacted for corrective action options.

9.3 SITE SELECTION

Site selection is important for ensuring the uniform collection of relevant (suitable to its intended purpose) and comparable ambient PM_{2.5} data, and specific site criteria must be satisfied for the 1405-DF to meet the PM_{2.5} FEM regulatory requirements. The design criteria for fine particulate matter (PM_{2.5}), including general monitoring requirements, spatial scales, and special site requirements are given in 40 CFR Part 58, App D, Section 4.7 (U.S. Environmental Protection Agency, 2008a).

Extensive details on all aspects of site criteria are given in 40 CFR Part 58, Appendix E (U.S. Environmental Protection Agency, 2006a). When siting an ambient PM_{2.5} monitor such as the 1405-DF, of particular concern is the inlet height, inlet radius clearance, proximity to

potential sources of particulate matter, and spacing from roadways and trees. **Table 9-1** gives the basic requirements applicable to each of these criteria.

Table 9-1. EPA PM_{2.5} site selection specifications, applicable to the 1405-DF, include inlet height, inlet radius clearance, proximity to potential particulate matter sources, and distance from roadways.

Siting Parameter	Situation	Specification	Comments
Inlet height	General	2-15 m AGL ^a	This height interval is considered the “breathing zone”
	On rooftop	2 m above roof surface	Matches inlet specifications for FRM samplers
	Co-located samplers	All inlets optimally at same sample height	Sample heights must meet general height specifications and be at least within 1 vertical meter of each other
	Inlet tube length	Maximum 16 ft (4.9 m)	If inlet is the highest point, then lightning rods are strongly recommended
Inlet radius clearance	General	Minimum 1 m radius clearance	Includes other sampler inlets or objects that may influence airflow
	Adjacent FEM or FRM	Minimum 1 m separation between inlets	
	Co-located	From 1 to 4 m between inlets	
	Near SSI Hi-Vol	Minimum 3 m between TEOM [®] with FDMS and Hi-Vol inlets	
	Near small obstructions	Minimum 2 m	Small obstructions include fences, walls
	Near large obstructions	Distance of 2x height of obstruction	Large obstructions: buildings, sound walls, billboards, etc.
	Overhanging trees	Minimum 20 m from tree drip line	
Arc of unrestricted air flow	Unrestricted 270 degree arc	Prevailing direction of high concentrations must be in the arc	
Nearby particulate sources	General	As far away as possible from blowers or vents	Note: filtered air can contaminate a sample as well as dirty air
Distance from roadways	Less than 3,000 VPD ^b	Minimum 5 m from nearest traffic lane	
	Elevated roadway (>25 m high)	Minimum 25 m away	
	Unpaved roads	As far away as possible	
	Other unpaved areas	As far away as possible	Unpaved sites with vegetative ground cover are acceptable

^a Above ground level

^b Vehicles per day

9.4 ENCLOSURE SELECTION

The 1405-DF may be housed in a walk-in shelter, a mobile trailer, or in specially made environmentally controlled mini-enclosures available from Thermo Scientific (p/n 34-010969-0120.) The enclosure must satisfy the 1405-DF operating temperature range of 8-25°C. (Thermo Scientific is testing the operation of the instrument under a warmer upper limit for the shelter temperature, but the results are not yet available. The results must be reviewed by EPA before a change can be implemented.) To achieve the best results, locate the 1405-DF in an environment with relatively slow temperature fluctuations. Avoid sampling locations with direct exposure to sunlight or that are near a heating or air-conditioning outlet.

As noted in Section 6 (Interferences), care must be exercised to carefully regulate the enclosure temperature to avoid sampler malfunction and/or data bias. Ideally, the enclosure temperature should fluctuate less than 2°C over an hour. The enclosure temperature should also be maintained as close as possible to 5°C less than the operating temperature of the sample stream which is generally 30°C. When possible, the air conditioning system cycle time should be regulated to avoid a 12-minute cycle because this cycle has been observed to cause excessive noise that can overwhelm the sample data.

In addition, the shelter temperature should be regulated based upon the dew point of the ambient air to keep condensation from overwhelming the trap, potentially resulting in improper operation of the sampler or damage to the instrument.

Avoid areas subject to vibration. Since the tapered element microbalance is a harmonic oscillator, external vibrations can perturb the element itself or add uncertainty to the frequency measurements.

9.5 1405-DF INSTALLATION STEPS

The Thermo Scientific TEOM[®] 1405-DF with FDMS[®] Operating Guide (Rev. A.003, Section 2) provides detailed installation procedures. The Operating Guide provides many helpful photos of an actual installation and offers “Installation Considerations” (page 2-2) on key features that must be heeded. A separate outdoor shelter is available from Thermo Scientific, and the Operating Guide provides a separate set of instructions applicable to this deployment option.

This SOP identifies the main installation tasks sequentially and draws attention to those parts of the tasks that are integral to a sound installation. Some special precautions are listed below (Section 9.5.1). Once the installation is complete, the TEOM[®] sample collection filters and the 47-mm purge filters must be installed, and an initial setup and configuration check of the 1405-DF is required (Section 9.6).

The installation procedure involves the following major steps.

1. Determine the exact location for the 1405-DF and make roof modifications
2. Install the pump and cut the tubing to length

3. Install the supplemental water trap, if used
4. Assemble the flow splitter
5. Assemble the tripod
6. Install the virtual impactor and sample flow tubing
7. Install the PM₁₀ inlet
8. Install and connect remaining tubing
9. Install the temperature/relative humidity sensor
10. Check inlet tube grounding
11. Connect power
12. Connect data logger cabling (if used)

The left hand side of Figure 3-1 depicts the 1405-DF system components as they would appear in a typical walk-in installation, with the tripod and inlets located on the roof and the 1405-DF placed on a bench or table. An alternative installation, not shown, places the 1405-DF in the Thermo Scientific environmentally controlled stand-alone outside enclosure. This is described in detail in the manual (Rev. A.003, Section 2, pp 19-26.)

9.5.1 Special Precautions

Some forethought prior to the installation of the system components can prevent subsequent problems; particular consideration should be given to the elements listed below. The 1405-DF is designed to be bench mounted, and it is not practical to install it in a rack because of the height of the FDMS[®] tower.

- Ensure proper inlet alignment and perpendicularity. This is important to avoid transverse stress on the sample tube connectors, which can cause leaks. The sample lines for the PM_{2.5} and PM-Coarse channels should proceed in a straight, vertical line from the PM₁₀ inlet and virtual impactor to the inlet of the unit. *The roof penetration for the sample lines must be drilled 1 3/4" on center directly above the sample lines on the top of the instrument.* The flexible by-pass tubing and the signal cable for the temperature/humidity sensor can be routed thorough an existing side port or a port can be drilled in the roof or wall of the shelter.
- Consider the proper clearance needed on the roof to accommodate the tripod when positioning the instrument on the bench. The legs can be adjusted to different lengths (and angles) to best position the tripod on the roof.
- Make certain the front door to the sampler has adequate room to be fully opened for TEOM[®] filter changes. The operator will generally have the best view to make TEOM[®] filter changes if the instrument is placed at the front lip of the bench.
- Provide adequate access to the back and FDMS[®] side of the instrument for maintenance, repairs, and FDMS[®]-filter changes.

- The height of the instrument (50") may require that a drop-down in the bench surface be constructed to accommodate installation.
- Provide clearance for FDMS[®] dryer and valve servicing. A short section of flexible conductive rubber tube, such as that used for Thermo Scientific 8500 FDMS systems, (p/n 30-002274) can be used as a junction in the sample tube between the top of the 1405-DF FDMS[®] tower and the ceiling of the shelter. Removing this short section allows the dryers to be removed without having to remove the rooftop inlet assembly. If this option is used, the gap in the rigid tubing should be about 1 to 1.5"; a longer gap may cause the tubing to collapse during leak checks resulting in a false test failure.
- Provide proper grounding. Poor electrical grounds in any particulate matter sampler can affect concentration values, and proper grounding of the inlet tube is needed to avoid static charge buildup that can lead to errors. The substantial inlet system has a potentially high capacitance, so adequate grounding needs to extend from the size separator inlets, through the sample inlet tubing to the 1405-DF chassis to earth ground. Generally, the design of the instrument and a proper electrical ground will accomplish this but it is best to measure the difference in the potential between the inlet tube and the 1405-DF chassis to confirm the resistance is less than a few ohms.
- Use a tubing cutter to cut the tubing to lengths. Do not allow fragments to fall into the tubes; make sure all cuts are perpendicular to the tube.
- Do not operate the instrument until the ambient temperature/humidity sensor is installed. With no ambient temperature/humidity sensor, the mass flow controllers will attempt to control the sample flow as if the ambient temperature is absolute zero.
- Route the tubing to avoid any HVAC system vents. Reports of condensation problems have been linked to carelessly routed tubing, particularly for the by-pass flow. Inadvertent heating of the sample inlet lines above the FDMS[®] tower could volatilize some PM components before the PM components are measured.
- Provide roof support or harmonic isolation during maintenance. Sampler maintenance will require operators to work on the roof, potentially causing the roof to flex, causing sample tubes to move, and causing disturbance of the mass transducer. Methods to avoid this outcome include installation of a roof platform and/or installation of a section of conductive rubber tubing (p/n 30-002274) in the sample lines to absorb the shock of the roof movement. In addition, areas that receive snow fall may need to plan to avoid extreme temperature gradients or harmonic disturbance. Snow piled along the sample tubes has been reported to cause a steep temperature gradient in the sample flow paths, preventing proper conditioning of the sample stream. It may be necessary to isolate the sample tubes by using a roof flange such as a length of PVC pipe. Also, care should be taken during snow removal from the roof; the tubing may be damaged or the mass transducer disturbed if the inlet is hit by a shovel or other snow removal equipment.

9.5.2 Tools Needed for Installation

Table 9-2 lists the basic tools and supplies that are needed for installing the TEOM[®] 1405-DF with FDMS[®]. Any given installation may require additional tools and supplies as dictated by the situation.

Table 9-2. Tools and supplies for installation of the TEOM[®] 1405-DF with FDMS[®].

Tools and Supplies	Remarks
Drill and drill bits	Half-inch, variable speed drill; 3/8" drill bit for holes to route flexible by-pass tubing and to accommodate cable from relative humidity and temperature sensor; 9/16" bit to accommodate 1/2" sample tubes, and a hole-saw if a PVC pipe is going to be used as a roof flange. Holes for PM _{2.5} and PM-Coarse sample tubes must be drilled 1 3/4" on center directly above sample inlet junction on top of instrument. Depending on roof type, a drill bit extension may be needed.
Hand tools	Screwdriver set, socket set, nut drivers, plumb bob, tape measure, straight edge measure, metal file
All weather caulking	To waterproof the roof flange and feet of the support tripod
Firing strips	To secure sampler position on the bench
Wood screws, lag screws	To secure tripod feet to roof and water trap to the wall
Level	For checking the horizontal level of the TEOM [®] with FDMS [®] and vertical level of the inlet
Tubing cutters	To cut the stainless steel tubes and by-pass tubing
Universal Power Cord	To provide power to the instrument
Bulkhead fittings if PVC pipe used as roof flange	To provide a waterproof seal (1/2" Swagelok male to male bulkhead fitting)
3/8" strain-relief fitting if PVC pipe used as roof flange	To provide a waterproof seal
Analog signal cable	2-conductor cable for analog signals
Ethernet Patch Cable	If data are to be collected through a network connection
Ethernet Cross-over cable	If data are to be collected by a stand-alone computer
25-pin Phoenix Contact male I/O connector if external data logger to be used	The TEOM [®] 1405-DF with FDMS has 8 analog outputs, four analog inputs and two digital contact closures available, or alternatively it can interface to a computer or the data can be downloaded to a USB jump drive
Pipe Insulation	To avoid condensation formation for samplers installed in humid areas

9.5.3 Determine the Exact Location of the 1405-DF and Make Roof Modifications

Refer to the 1405-DF Manual for additional details. Roof modifications for roof tops that are under warranty may need to be performed by a licensed contractor.

- Determine the exact location of the 1405-DF inside the shelter.
 - Ensure adequate access to the instrument, especially the rear and the left side housing the 47-mm purge filters
 - Check that there is adequate room for the tripod legs on the roof
 - Ensure inlet perpendicularity with the 1405-DF inlets at the top of the FDMS[®] tower
- Drill the holes for the sample tubes and roof flange.
 - Once the 1405-DF is in position, a plumb bob may be used to mark the center point of the roof penetration.
 - Once the center point of the roof penetration has been identified on the inside ceiling, use a small diameter drill bit with an extension to drill upwards through the ceiling until it penetrates the exterior roof. That point will mark the center of the roof penetration to be drilled from the rooftop downward.
 - Some users may prefer to install a short section of 4" PVC pipe to use as a roof flange (see 1405-DF Manual (Rev. A.003) for example). This approach allows a little extra leeway, because once the 4" hole is cut in the roof, the 1405-DF may be shifted slightly to accommodate accurate positioning of the stainless steel inlet tubes.
 - *The holes for sample tubes must be drilled 1 3/4" on center directly above the sample tube inlets on top of the FDMS[®] tower.*
- During drilling, protect the 1405-DF from falling debris.
- The flexible by-pass tubing and the signal cable for the temperature humidity sensor can be routed thorough an existing side port, or a port can be drilled in the roof or wall of the shelter. The diameter of the by-pass tubing is 3/8" and the diameter of the cable is approximately the same.

9.5.4 Install the Pump

Refer to the 1405-DF Manual for complete details.

- Determine where the pump will be installed. It is generally installed on the floor below the bench on which the instrument is to be located. It may be placed on a piece of closed-cell foam to dampen vibration, but care must be taken not to create a fire hazard. The pump should be less than 5 meters from the instrument or the provided tubing should be replaced with either rigid pipe or larger diameter tubing to prevent an increased pressure drop.
- Measure and cut the green conductive tubing and install as specified in the manual. All tubing cuts must be perpendicular (square) and smooth to avoid leaks at connections.

9.5.5 Select a Location for the Supplemental Water Trap and Mount It (If Used)

The coalescing filter on the rear of the 1405-DF acts as a water trap. Thermo Scientific has also been supplying an additional water trap with coiled tubing, but this is not required for the 1405. Refer to the 1405-DF Operating Guide for complete details on installing the supplemental water trap.

If the supplemental water trap is used:

- Select a location near the 1405-DF to mount the supplemental water trap assembly. Anticipate the route of the by-pass flow line from the flow splitter on the roof, and
 - Install the trap so there will not be a portion of the by-pass tubing lower than the trap which would result in water in the line instead of the trap.
 - Avoid routing the tubing past HVAC exhausts or vents that would alter the temperature of the air.
- Be aware that the filter element will load from the inside and therefore may appear clean even when heavily loaded. Because this is a redundant filter, depending on local conditions, the element may be removed so that the supplemental system is a simple water trap.

9.5.6 Assemble the Flow Splitter

Refer to the 1405-DF Manual for additional assembly details.

- For the flow splitter to correctly split the entering 15.0 lpm flow into the bypass (12.0 lpm) and fine fraction sample (3.0 lpm) flows, it is essential that the top of the inner sample tube (carrying the fine fraction flow) be positioned 6 inches ($\pm 1/4$ inch) from the top of the flow splitter (**Figure 9-1**).

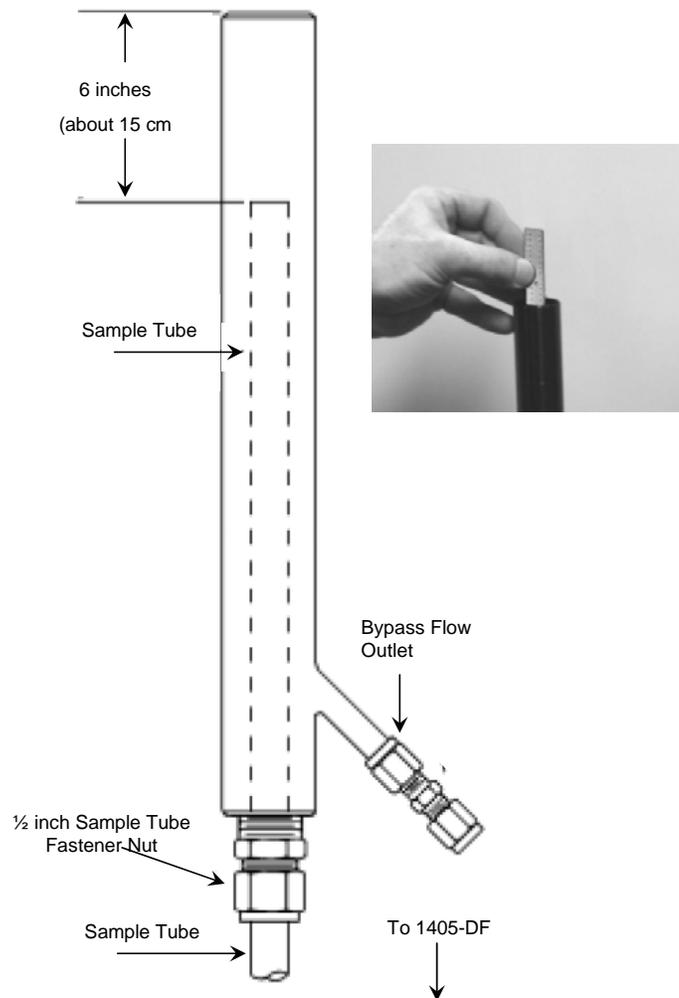


Figure 9-1. Schematic of the isokinetic flow splitter showing the position of the sample tube inside the splitter (left), which is positioned using a straight edge measure (right).

9.5.7 Assemble the Tripod

If the inlet is to be installed on the rooftop of a building, then the optional tripod should be used to support the hardware. Refer to the 1405-DF Manual for complete tripod assembly details.

The assembled flow splitter is inserted into the apex of the tripod, and the tripod is set on the roof above the roof opening leading to the 1405-DF. It is important to adjust the height and position of the tripod legs so that the sample tube extending downward from the flow splitter is vertical (plumb). At this stage only an approximate leveling adjustment is needed.

9.5.8 Install the Virtual Impactor and Sample Flow Tubing

Refer to the 1405-DF Manual for assembly details.

- When making connections, be sure fittings are fully seated to prevent leaks.
 - The flow splitter must be fully inserted into the sleeve of the impactor.
 - The sample tube for the PM-Coarse must be fully inserted into impactor before tightening the Swage nut. Note that the ½" tube for the coarse sample installs *through* the compression fitting on the base of the virtual impactor. This fitting has been drilled out to allow the tube to provide a flush outlet from the virtual impactor without any gap or protrusion that might be possible with a standard compression fitting. A common mistake is to insert the tube as if a stop exists in the fitting.
- The PM_{2.5} and PM-Coarse sample tubes should be parallel, and at equal level at the bottom.

9.5.9 Install the PM₁₀ Inlet

Install the sample inlet tube on top of the virtual impactor and set the PM₁₀ inlet on top of the sample inlet tube.

- The PM₁₀ inlet should ideally be 2 m (but must be between 1.8 and 2.1 m) above the roof.
- Adjust the tripod legs to meet the height requirements and true the sample inlet tubes.

9.5.10 Install and Connect Remaining Tubing

- Measure and cut the stainless steel tubing extensions required to connect the sample inlet ports on the top of the FDMS[®] tower to the fine and coarse sample tubes extending downward from the tripod.
- It is worth the extra effort to install rubber tubing connectors (p/n 30-002274) between the top of the FDMS[®] tower and the ceiling.
 - Install a short section of stainless steel inlet tubing extending up a few inches from the ½" Swagelok fittings on the top of the FDMS[®] tower, and install the rubber tubing connectors between the tubing stub and the rest of the inlet tubing leading to the roof. This enables dryer and valve removal during future servicing of the FDMS[®] unit without having to disturb the inlet hardware infrastructure. The gap in rigid tubing should not exceed 1.5 inches to avoid deforming during leak tests. The tubing must be periodically replaced to avoid leaks due to cracking. The tubing must be conductive; standard elastic tubing can not be substituted due to static build-up.
 - Make final adjustments to the tripod, lowering or raising as needed to complete the tubing connections, and secure the tripod to the roof.
- Connect the by-pass tubing to the by-pass fitting on the flow splitter, and connect the other end of the bypass tubing either to the coalescing filter mounted on the back of the

1405-DF, or, if the supplemental water trap is being used, connect it to the water trap. In the latter case, additional tubing will be needed to connect the water trap to the coalescing filter on the back of the 1405-DF.

- To avoid condensation in the sample tubing, Thermo Scientific strongly recommends that the user insulate the sample tube extension with pipe insulation when operating the instrument in areas of high humidity.

9.5.11 Install the Temperature/Relative Humidity Sensor

Refer to the 1405-DF Operating Guide for complete details.

- Mount the sensor on the flow splitter with the provided U-bolt.
- Identify the best route for the cable from the temperature/RH sensor to the back of the 1405-DF. Additional drilling may be required to provide a port through the roof or PVC fittings.
- Caulk the cable entry port to prevent leaks.

9.5.12 Check Inlet Tube Grounding

A solid station ground (earth ground) must be available for the 1405-DF chassis ground, and the inlet tube must be adequately grounded to the 1405-DF chassis. Any buildup of static charges from an ungrounded inlet tube can cause errors in the 1405-DF measurements, so this ground is important, especially in areas with electromagnetic fields (e.g., near high voltage power lines or radio frequency antennas). Measure the resistance between the bottom of the inlet tubes and the chassis ground terminals on the power plug of the 1405-DF. The resistance should be a few ohms or less.

9.5.13 Connect Power

- The TEOM[®] 1405-DF unit accepts all voltage inputs between 85 and 240 volts AC.
- SAFETY FIRST:
 - Use an appropriate, code-approved, grounded electrical outlet. Contact a qualified electrician if there is doubt as to whether the power service for the instrument is adequate.
 - The connection should be easily accessible.
 - DO NOT attempt to bypass the grounding requirements. It is needed for safety and to prevent buildup of static charges.

Even a momentary power interruption will cause the monitor to perform a stability self-check during which the monitor will not collect data. To avoid this data loss, some users connect the TEOM[®] 1405-DF with FDMS[®] power cord to an uninterruptable power supply

(UPS). If used, both the pump and the control unit should be plugged into the UPS to protect the mass flow controllers in the system. The control unit continuously monitors the flow rates and attempts to maintain the target flow rates by adjusting the valve in the flow controllers. If the control unit is on and the pump is off because only the power to the controller is maintained during the interruption, the controller will repeatedly send control voltage to attempt to fully open the valve, possibly leading to valve failure during an extended power failure. Some users may opt to install a power conditioning system in line, such as a “spike protector.”

9.5.14 Connect Data Logger

If an external data logger is used to capture 1405-DF data (expected), the data logging connections may be made at this time or anytime after the unit is operational. The available connectors on the back of the unit are Ethernet (RJ45), USB, and a 25-pin female I/O supporting analog out, analog in, and digital out (requires 25-pin male connector). A 9-pin RS232 connector and a USB port are available on the front of the instrument. Each user must identify the approach most compatible with their system and configure their data acquisition system and the 1405-DF appropriately. Communications and data downloads are discussed in Section 10 “1405-DF Communications”.

9.6 INITIAL SETUP AND CONFIGURATION CHECK

Once the system hardware components are in place, the following steps will get the TEOM[®] 1405-DF up and running:

- Power on the 1405-DF, the vacuum pump, and allow 1-hr warm-up
- Review touch screen functions and screen displays (new users)
- Review/adjust the configuration parameters
 - Set Flow Control to Actual conditions
 - Review/adjust PM_{2.5}, PM-Coarse, and Bypass flow rates
 - Confirm K0 constant
 - Confirm Temperature settings
 - Confirm Mass Calculation Variables’ settings
 - Set the clock
- Perform verifications/calibrations
 - Leak check
 - Ambient Temperature Calibration
 - Barometric Pressure Calibration
 - Flow calibration

- Load filters (2 TEOM[®] and 2 FDMS[®])
- Select the Data Storage options desired
- Setup the password function, if desired

9.6.1 Power On and Warm Up

Power on the 1405-DF and the vacuum pump and allow the 1405-DF to warm up. A title screen will show briefly, followed by the TEOM[®] Data screen, from which all other touch-screens may be accessed (**Figure 9-2**). In this SOP, unless otherwise explicitly stated, the path to access different screens or parameters is given as “Screen > Button > Button...”.

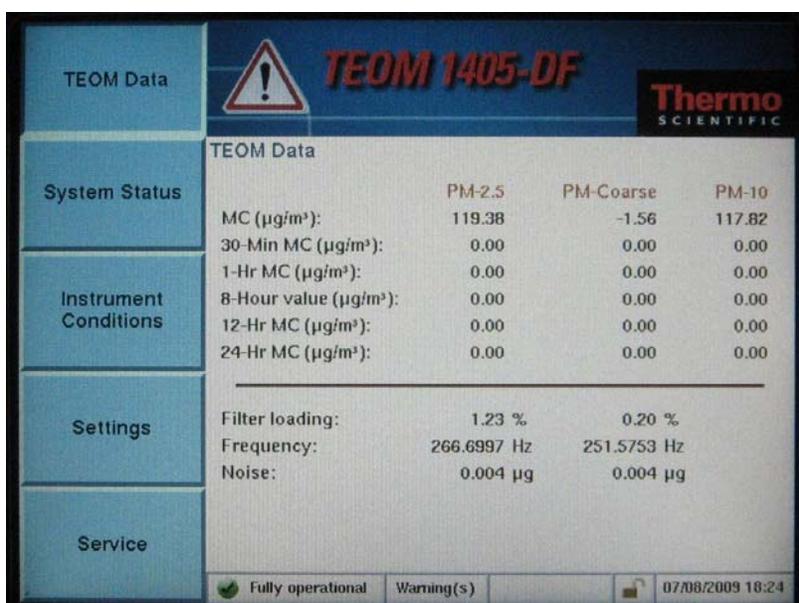


Figure 9-2. The Data Screen. Note the buttons on the left, which provide access to all available 1405-DF operating information.

9.6.2 Review Screen Displays and Touch Screen Functions

The touch screen display interface is used any time a technician interacts with the 1405-DF. Many screens launch Wizards (especially in the Service menu) to guide the operator through the necessary procedures. The instrument warm-up period offers a good opportunity for new users to become familiar with this interactive display. Select each one of the main menu buttons, and, in turn, explore the underlying layers of screens that can be accessed. Most of the screens, and parameters therein, will be intuitively understood by most users, but full explanations are offered in the 1405-DF Operating Guide. The bottom of each screen has a status bar that displays the current operating information about the instrument, including the current time and date, the current status (“Normal”, or “Warning(s)”), and whether the unit is in “lock mode” (requiring a password for access).

User provided set points are entered or changed using a number keypad (**Figure 9-3**), which will automatically appear any time the instrument needs data input from the user.

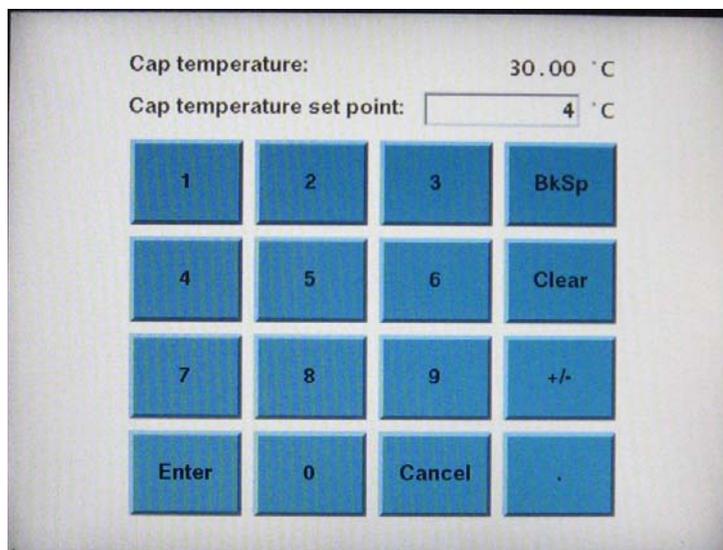


Figure 9-3. The data entry keypad for user-entered settings. The example illustrates adjusting the Cap temperature set point.

Aside from the TEOM Data screen, four other main screens are available:

- System Status Screen. Provides basic operating information and access to the list of the current active status warnings.
- Instrument Conditions Screen. Accesses several temperature and flow settings and the current ambient air conditions for the instrument.
- Settings Screen. Provides access to system, data, and advanced settings for the instrument
- Service Screen. Provides access to maintenance and verification Wizards and procedures, as well as advanced troubleshooting and service tools.

9.6.3 Review/Adjust Configuration Parameters

The setup parameters required to meet FEM EQPM-0609-182 must be checked and adjusted if necessary. Other instrument parameters should be confirmed. The default parameter settings in the instrument as received from Thermo Scientific should be correct, but they must be verified.

Set the Flow Control to Actual Conditions

The instrument must use the ambient temperature and pressure, as measured by the instruments sensors, to control and report the volumetric flow rate.

- Select the Instrument Conditions screen
- Select the Flows button to display the Flows screen
- Select the Flow Control Button to select the Flow Control screen
 - Press the Active button and the Actual button.
 - Press the OK button.

Review/Adjust the Flow Rates

- Select the Instrument Conditions screen
- Select the Flows button to display the Flows screen.
- Select the Flow Rates button to confirm, or adjust if necessary, the desired flow rates:
 - PM_{2.5} (3.0 lpm)
 - PM-Coarse (1.67 lpm)
 - Bypass flow (12.0 lpm)

Confirm K0 Constant for Each Microbalance

- Select the Settings screen
- Select the Advanced button
- Select Mass Transducer K0 Constants button
 - Confirm the current K0 settings of the PM_{2.5} and PM-Coarse TEOMs. The numbers programmed into the unit *must* match the K0 constants on the label near the mass transducer (under the insulation.) One can also locate the original calibration constants (“Average K0”) on the “Instrument Checkout Record” or the “Final Test Record” documents that are shipped from the factory with the instrument.

Confirm Temperature Settings

All parameters which are not listed specifically in FEM EQPM-0609-182 should be left at the default settings listed below.

- Instrument Conditions > Instrument Temperatures:
 - Cap: 30°C
 - Case: 30°C
 - PM_{2.5} Air Tube: 30°C
 - PM-Coarse Air Tube: 30°C

- Instrument Conditions > FDMS Module
 - PM-2.5 Cooler Temp : 4°C*
 - PM-Coarse Cooler Temp : 4°C*

* A second chiller temperature set point, 10°C, is under review, and if approved may prove useful to users in humid locations. A warmer chiller set point, adjusted seasonally, may prevent entrained condensation problems.

Confirm Mass Calculation Variables

- Settings > Advanced > Mass Calculation Variables
 - System wait time: 1800 seconds
 - XX-Hour value: 8 hours
 - Frequency Wait Time: 60 seconds

Set the Clock

The 1405-DF clock should be permanently set for standard time, and should never be reset to daylight savings time. If desired, the date format can be changed.

- Select the Settings screen
- Select the System button
 - Select the Set Time button and set the current date and time
 - Select the Date Format button to select the desired format, “Month/Day/Year” or “Day/Month/Year”. (Note: the 1405-DF must be restarted to have this change take effect.)

9.6.4 Perform Initial Verifications and Calibrations

Before routine sampling is begun, the system must be checked for leaks, the ambient temperature and barometric pressure sensors must be calibrated, and a flow calibration performed. Since the volumetric flow calibration depends upon accurate temperature and pressure inputs, perform the ambient air temperature and pressure calibration before executing the flow calibration procedure.

Conduct a Leak Check

Always use the 1405-DF Leak Check Wizard (Service > Verification > Leak Check) to conduct a leak check. In addition to providing step-by-step instructions, the Leak Check Wizard automatically disables the switching valve during a leak check. *Performing a leak check without the Wizard can damage the switching valve.* The Leak Check Wizard step-by-step instructions are also provided in Section 3 of the 1405-DF Operating Guide. The leak check should be conducted while the sample flows are routed through the two paths—the reference cycle and the

base cycle. Firmware version 1.50 (expected for release in late 2009) is expected to automatically direct the user through the process to leak check both cycles.

The Leak Check Wizard compares the measured difference between the unit's "zero" flow with the vacuum disconnected and flow through the instrument with the inlet blocked (which should match or be near to the "zero" flow value). A leak check/flow adapter is required (**Figure 9-4**).



Figure 9-4. Leak check/flow adapter.

Leak check tolerances may vary by agency. Thermo Scientific recommends a tolerance of ± 0.15 lpm for the PM_{2.5} and PM-Coarse leak checks and ± 0.60 lpm for the Bypass leak check. The Wizards are set to give failure warnings based on those recommendations.

To conduct a leak check

- Select the Service screen;
- Select the Verification button; and
- Select the Leak Check button and follow the instructions on the Leak Check Wizard.
 - Remove TEOM[®] filters from the system
 - NOTE: After the leak check adapter is installed in the inlet and closed, the 1405-DF pauses for 1 minute to allow the flows to stabilize. The next step in the Wizard advises the user to slowly open the leak check valve to restore flows to the system. This should be done right away—if the user waits too long the leak check may fail, even if it was within tolerances. Note, however, the valve should be opened slowly to avoid a sudden change in system pressure.

- NOTE: The only component of the inlet system that is removed for the leak check is the PM₁₀ inlet.

There are numerous places between the top of the inlet and the TEOM® microbalance where leaks could occur. A leak that persists must be located and corrected. The most common cause for a leak is a failure of the press-to-seal connectors. In case of a leak test failure, first check these, and adjust or replace if necessary. If the failure persists, the best method to isolate a leak in any sampler is to cap the flow at about the mid-point and then determine which section of the sampler is leaking. Ideally, the sections would be reduced by half again until the leak is located. The steps below provide guidance to isolate leaks in the 1405-DF. **Figure 9-5** shows the flow paths of the fine (A) and coarse (B) streams and is a visual guide to “section” the system during a leak check. The steps to isolate a leak follow.

1. If, when performing the leak check, the Wizard shows a failure, note which channel fails; follow the isolation process for that channel.
2. Remove the virtual impactor and cap from the separate lines of flow when prompted by the Leak Check Wizard. If only one channel failed the leak check, only the result for that channel need be reviewed. For example, if the Wizard indicated a leak in the Coarse flow channel, cap off only the Coarse flow line and run the check again using the Wizard. The Wizard will indicate an unsuccessful result for each path (because the others are not capped); review only the result for the Coarse flow path and disregard the results for the fine and bypass paths.
3. If the Wizard result still indicates a failure, move to the next connection point—the top of the FDMS® tower or inside the tower below the dryer assembly. **CAUTION!! It is critical not to draw a vacuum in the dryer because the dryer will suffer irreparable damage.** Disconnect the dryer assembly from the top of the switching valve and cap off the flow at the top of the switching valve. Review the result. If the Wizard indicates a pass, the dryer may have a leak and need replacing. If the test fails, continue to the next connection point.
4. Isolate the switching valve from the chiller/conditioner by disconnecting the Teflon lines to the chiller on the associated channel. “Loop” the two elbows on the front of the switching valve by connecting them together using the solid Teflon tube that normally connects the top port on the chiller assembly to the switching valve (**Figure 9-6**). Run the Leak Check Wizard again; if the Wizard indicates a pass, check the seating of the purge filter and seals and return to Step 3. If the test fails, go to the next connection point—the top of the air tube assembly.

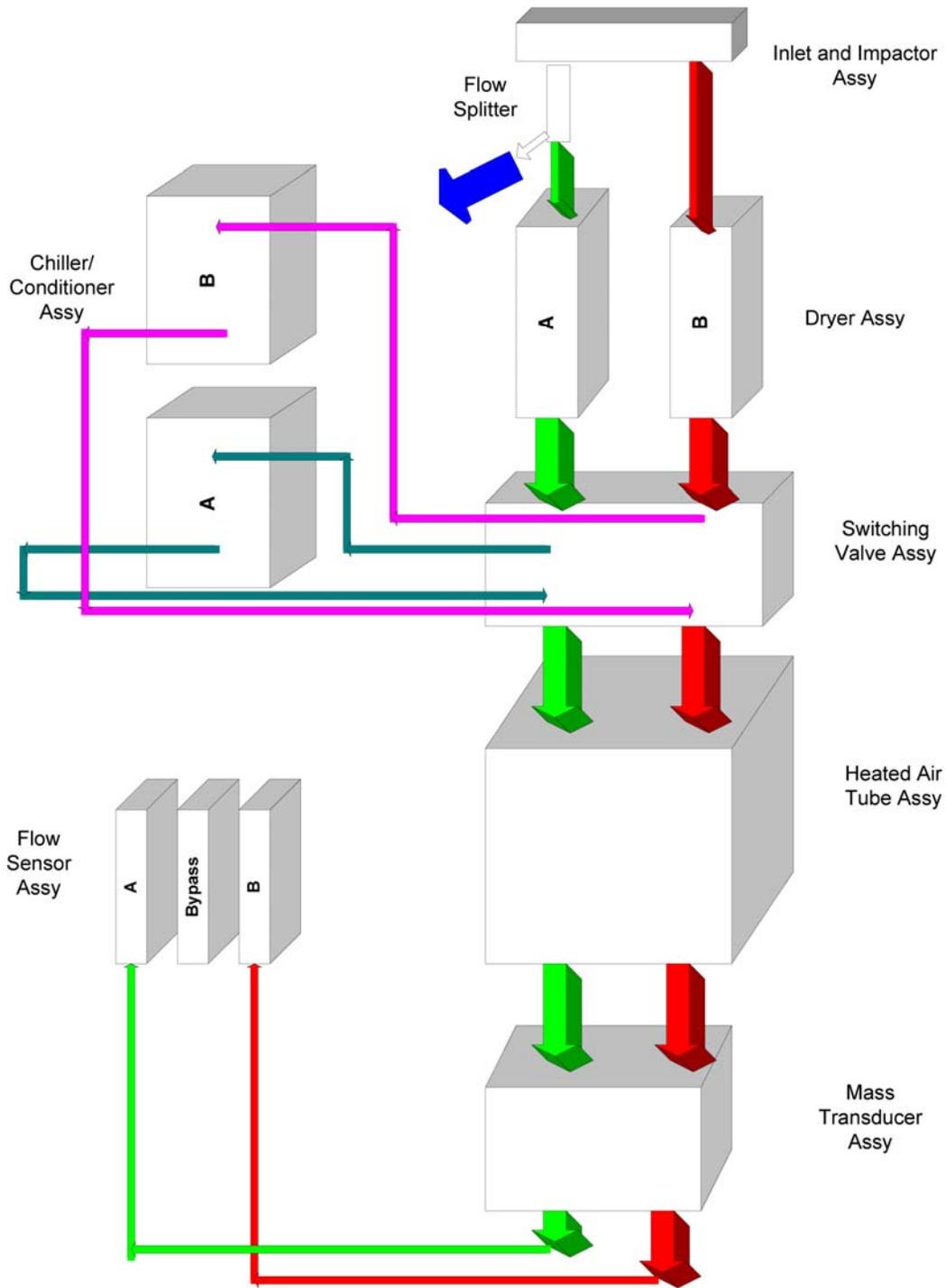


Figure 9-5. Flow paths of the fine (A) and coarse (B) streams.

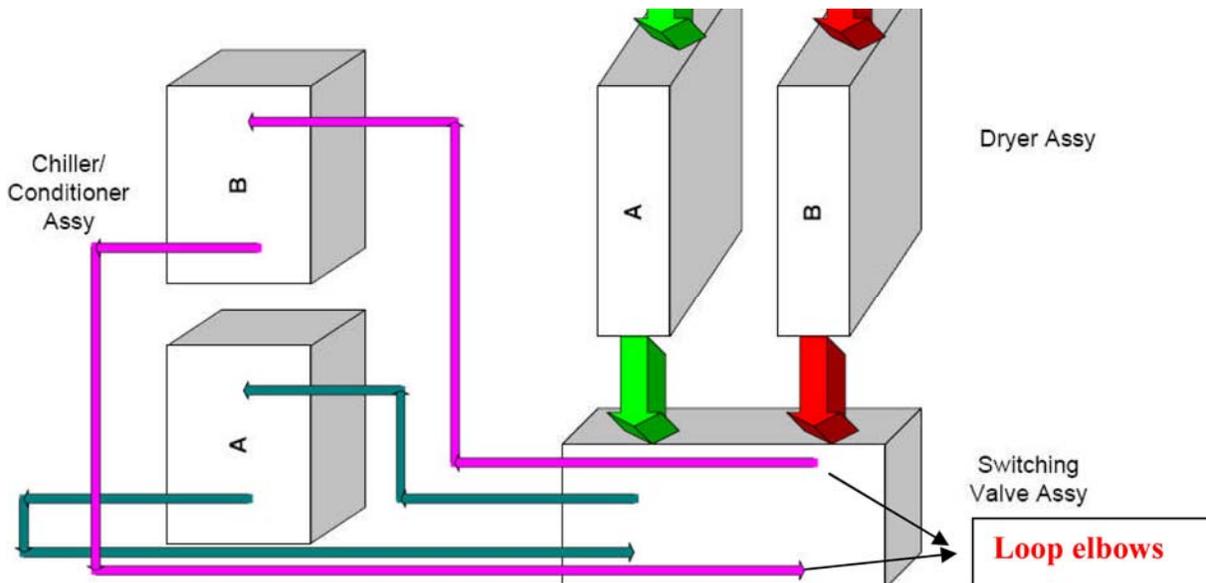


Figure 9-6. Isolate the chiller by “looping the elbows”.

5. Remove the switching valve from the top air tube assembly and run the Leak Check Wizard again. If the result shows that the leak check passes, the leak is in the switching valve. Clean the switching valve, inspect the seals in the block, and replace as needed. If the result shows a test failure, move to the next connection point—the bottom of the mass transducer assembly.
6. Disconnect the rubber tubing from the underside of the mass transducer and cap off end or pinch the tube to form a seal. If the result indicates that the leak check passes, the leak may be in the air tube assembly or in air tube assembly connection to the top of the mass transducer assembly; inspect the tubing. If the result indicates a test failure, move to the next step.
7. Check the in-line filter bowl on the back of the unit for a proper seal; verify that the O-ring is not cracked or missing. If the in-line filter is in good order, replace the flow controller assembly.
8. If the leak can not be isolated after following the steps above, contact Thermo Scientific for technical support.

Calibrate the Ambient Temperature Sensor

A temperature sensor, annually referenced to within $\pm 0.5^\circ \text{C}$ of a National Institute of Standards and Technology (NIST) thermometer, is required to calibrate the 1405-DF ambient temperature sensor. See Section 10.1.15 of this SOP (or Section 5 of the 1405-Df Operating Guide) for calibration instructions.

Calibrate the Barometric Pressure Sensor

A barometric pressure sensor, annually referenced to within ± 5 mm Hg of a NIST pressure sensor, is required to calibrate the 1405-DF barometric pressure sensor. See Section 10.1.16 of this SOP (or Section 5 of the 1405-DF Operating Guide) for calibration instructions.

Perform a Flow Calibration

Because the installation of the 1405-DF is new, all flows should be calibrated. This activity involves a three-point check of the PM_{2.5}, PM-Coarse, and Bypass flows and adjustment of the flow rate for any flow path that deviates from the target rate by more than 2%. The 1405-DF provides a Flow Calibration Wizard to guide the user through the necessary steps. It provides pictures as well as textual descriptions of the steps. The Wizard is entered via the touch screen Service > Calibration > Flow Calibration. See SOP section 10.3.5 and Section 5 of the 1405-DF Operating Guide for a complete listing of the flow calibration instructions as given in the Wizard. A NIST-traceable flow transfer standard capable of measuring flow rates between 1.3 lpm and 16.7 lpm is required.

To conduct a flow calibration,

- select the Service screen;
- select the Calibration button;
- select the Flow Calibration button; and
- follow the instructions in the Flow Calibration Wizard to calibrate the flow rate for each of the three flow fractions independently. This process requires that a 3-point calibration be conducted for each flow fraction.

9.6.5 Load the TEOM[®] (Sample Collection) and FDMS[®] (Purge) Filters

Two TEOM[®] sample filter cartridges and two FDMS[®] purge filters must be loaded into the TEOM[®] 1405-DF with FDMS[®] for sampling. It is important to have equilibrated spare TEOM[®] sample filters available to avoid data interruptions; therefore, spare filters should be installed (and replaced upon use) on the equilibration posts next to the sample filters in the transducer assembly. Thermo Scientific requires that the sample filter only be handled with the special filter loading tool provided with the instrument.

The 1405-DF has a Filter Replacement Wizard, with pictures and instructions. It is strongly recommended that this Wizard be used until the user is fully competent in the technique. Traditionally, filter seating errors have been common problems associated with TEOM[®] use, and using the Filter Replacement Wizard can help detect filter seating problems. An option, “Advanced User Mode”, can be selected in the first screen of the Wizard to allow the user to bypass the Wizard entirely. If this option is chosen, the instrument will be put into Setup mode and will be stopped. When the filters have been replaced, the Wizard will remind the user to check the frequencies and exit the Wizard. (**Important:** If the Advanced Users Mode is

selected, the Wizard DOES NOT automatically verify the frequency. Users MUST ensure that the frequency is stable in order to ensure valid data. Inspect the oscillating frequency change rate on the TEOM[®] Data screen; the last two digits of the reading will fluctuate [due to noise] but the other digits should remain steady. Fluctuation observed in more than the last two digits may indicate that the TEOM[®] filter is loose or defective. Re-seat the filter and check the frequency again. If the frequency continues to show fluctuation in more than the last two digits, replace the filter again. This process may need to be repeated until the frequency stabilizes. Note that if the “Advanced User Mode” is selected, it remains the default setting [highlighted blue]).

The 1405-DF sample collection filters for the PM_{2.5} and PM-Coarse flows need to be changed periodically before filter loading can affect the flow, or at least every 30 days. Always change the PM_{2.5} and PM-Coarse filters at the same time. Also, the 47-mm FDMS[®] purge filters *must* be changed when the TEOM[®] filters are changed. Wipe away any condensation that has accumulated on the FDMS[®] housing before installing the replacement filter.

The filter loading percentage value (TEOM[®] Data screen) indicates the percentage of the TEOM[®] filter’s total capacity that has been used. Because this value is determined by the pressure drop of the main sample flow line, the instrument always shows a non-zero value even if no TEOM[®] filter is mounted in the mass transducer. New TEOM[®] filters generally exhibit filter loading percentages of 15% to 30% at a flow rate of 3 lpm, and less at lower flow rates. Because this value is an indication of a pressure drop, the loading does not progress in a linear fashion. Operators are cautioned to become familiar with the loading pattern based on local conditions, to avoid data loss due to filter overloading. Special diligence is required to monitor the PM-Coarse flow because a small absolute change will result in a large percentage change in the low flow rate. The filter may require changing well below the indicated filter loading of 100% to maintain the proper flow rate.

Some agencies collect the used FDMS[®] filters for post-sampling analysis. If so, special filter handling procedures must be implemented, such as those used for FRM filters. The filters should only be handled with forceps or clean cotton gloves, and may need to be pre-loaded into cassettes and transported with protective covers to ensure that the filters are not contaminated.

Figure 9-7 (left) shows a close-up view of the filter element being placed on the top of the tapered element, and Figure 9-7 (right) schematically illustrates the loading steps, and unloading steps, of the sample filter cartridge in the instrument. Important considerations during the filter handling process include

- Do not touch the filter with anything except the filter tool provided. Keep the tool clean.
- The tapered element is somewhat fragile. The sleeve on the bottom of the filter cartridge needs to be placed straight down on the tapered element; do not try to twist or tilt the filter or the element may break, necessitating a major repair.
- After the filter is placed on the element, use the installation tool to press straight down on the filter to fully seat it.
- The pump should be running when the filter is installed; this will help seat it properly.

- When the filter loading is complete, confirm that the sample frequency remains steady.
- Minimize the amount of time the transducer door is open to avoid large shifts in temperatures in the sample path which will increase re-equilibration times.

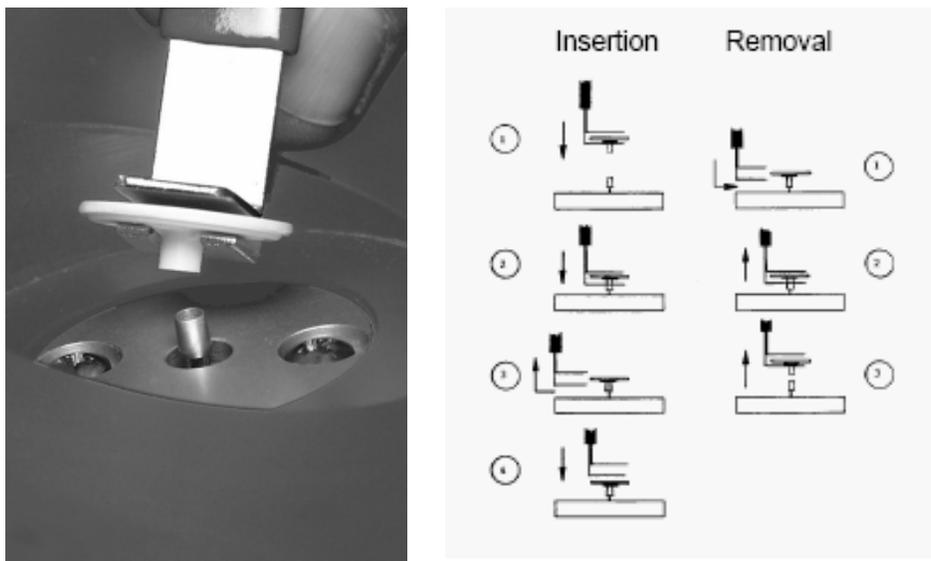


Figure 9-7. A close up of the filter element being placed on top of the tapered element (left) and steps in the filter insertion and removal process (right).

To Install a TEOM® Filter

Ensure that the filter exchange tool is clean and free of any contamination that might be transferred to the TEOM® filter.

- Select the Service button to display the Service screen
- Select the Maintenance button to display the Maintenance screen
 - Select the Replace TEOM® Filters button to start the TEOM® Filter Replacement Wizard.
 - Place two TEOM® filters on the TEOM® filter holders in the mass transducer compartment to condition the filters so that they are already equilibrated when the next filter change occurs.

When the Wizard finishes, the system will automatically test the two newly installed TEOM® filters to ensure they are firmly seated. The system will display a screen with the wait time. If the system is unable to obtain a stable frequency for one or both of the filters, it will display a screen telling which filter (or filters) needs to be re-seated. If the filters need to be re-seated, continue to follow the Wizard instructions to re-seat the filter. The system will again display the waiting screen while it is testing for stable frequencies. If it still cannot obtain a

stable frequency for one or both of the filters, it will prompt the user to re-seat the filters a second time. If it still cannot obtain a stable frequency, the Wizard will direct the user to replace the filter again; if that does not rectify the problem, the Wizard will show a failure warning and recommend appropriate service.

The back-supply of TEOM[®] sample filters should be stored inside their original carrier box, in the interior of the unit near the mass transducer to ensure they are at or near the appropriate temperature and humidity level for sampling. They are shipped with a desiccant pack to minimize the equilibration time required for the initial installation. One set of filters should be placed on the equilibration posts in the mass transducer housing to maintain a spare set of fully equilibrated filters for use.

To Install the 47-mm Purge Filters

- Locate the two doors on the left side of the TEOM[®] 1405-DF unit.
- Open one of the small filter doors (**Figure 9-8**).

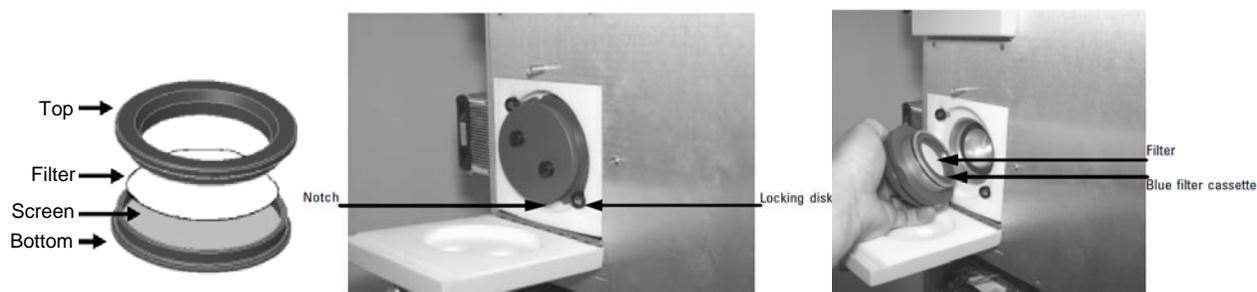


Figure 9-8. Stacking order of the 47-mm filter cassette (left), an open 47-mm purge filter door showing the filter holder (center), and the filter holder showing the cassette (right).

- Turn the filter holder counterclockwise until the notches line up with the locking disk (Figure 9-8), then pull outward to remove the holder from the unit.
- Locate the blue filter cassette and remove the used 47-mm filter.
- Insert a new 47-mm filter into the cassette. Be sure to install the 47-mm filter into the cassette with the textured face of the filter paper facing the “top” of the cassette. The “top” of the cassette fits into the “bottom” of the cassette (Figure 9-8). Note that the filter has a textured face that should be oriented into the air flow or towards the “top”; the smooth side of the filter should be placed towards the screen. Do not touch the filter with your hands if later analysis is desired.
- Close the filter cassette by pressing parts together.
- Install the filter into the filter holder with the “top” of the cassette and filter surface facing out.

- Line up the notches with the locking disks and install the filter holder into unit. Turn the holder clockwise to lock it in place. Do not over-tighten the filter holder. The O-ring creates the seal, not the force of the turn. Over-tightening may damage or distort the O-ring and cause a leak.
- Close the filter door.
- Repeat for the other 47-mm filter.

9.6.6 Select the Data Storage Options Desired

The unit stores only those variables selected by the user. If instrument variables are not set up to be logged, they will not be saved. The system default selections will need to be updated to suit the needs of each individual agency.

To select data storage variables:

- Select the Settings menu button to display the Settings screen.
- Select the Data Storage button to display the Data Storage screen.
- Select the Edit List button to display the Edit Data Storage screen.
 - Press the names of the variables you wish to log, up to a maximum of 20. Use the Next Page > and < Previous Page buttons (10 pages in all) to scroll through the entire list of variables that can be stored. Select the OK button when all the desired variables have been selected. A suggested list of variables is presented in **Table 9-3**; the complete list of variables that can be used is presented in **Table 9-4**.
 - Use the ▲ and ▼ buttons to scroll through the list of variables to save to ensure that all desired variables are selected.
 - Select the Storage Interval button to set the interval for data storage. Enter the desired data storage interval into the keypad and select the Enter button. For example, if the storage interval is 10 seconds, every 10 seconds the instrument will log (save) the data for the selected variables.
 - When all the desired variables are selected and the Storage Interval is set, select the <Back button to return to the Settings screen.
 - Upcoming version of the software (due to be released 9/15/2009) is expected to allow for storage of 30 variables and is expected to allow the user to select the order of the variables so long as ePort version 1.4 or later is used (if an earlier ePort version is used variables will be sorted alphabetically).

The internal 1405-DF data storage capacity is determined by the Storage Interval (how often values are written to memory) and by the number of variables stored. The 1405-DF standard memory allotment is 1.6GB, providing storage for approximately 30 weeks of data when the Storage Interval is set to 1 minute and the maximum of 20 variables is stored.

Table 9-3. List of suggested variables for storage.

PRC Code	Variable	Comment
8	System Status	hexadecimal code
61	Ambient Temperature	°C from outdoor sensor
63	Ambient Humidity	%RH from outdoor sensor
66	Ambient Pressure	ATM from outdoor sensor
90	Bypass Volumetric Flow	to monitor inlet flow
96	Vacuum Pump	should be <0.3 ATM
226	TEOM A Flow Rate	volumetric flow in lpm
242	TEOM A Filter Loading	OK < 80%
243	TEOM A Total Mass	total mass on filter in µg
258	TEOM A Noise	should be <0.1
271	TEOM A Dryer Temperature	should be > shelter temp & <30°C
272	TEOM A Dryer Dew Point	must be >2° below set-pt (4°C)
287	TEOM A Cooler Temperature	°C
310	TEOM B Flow Rate	volumetric flow in lpm
326	TEOM B Filter Loading	OK < 80%
327	TEOM B Total Mass	total mass on filter in µg
342	TEOM B Noise	should be <0.1
361	TEOM B Dryer Temperature	should be > shelter temp & <30°C
362	TEOM B Dryer Dew Point	must be >2° below set-pt (4°C)
373	TEOM B Cooler Temperature	°C

Table 9-4. List of variables from which up to 20 may be chosen for storage.

Operating Mode	System Status	Case heater raw output
Case temperature	Case temperature set point	Cap heater raw output
Cap temperature	Cap temperature set point	Ambient temperature
Ambient relative humidity	Ambient dew point	Ambient pressure
Enclosure temperature	Bypass flow rate	Bypass volumetric flow rate
Bypass flow set point	Vacuum pump pressure	PM-2.5 air tube set point
PM-Coarse air tube set point	Analog output #1 value	Analog output #2 value
Analog output #3 value	Analog output #4 value	Analog output #5 value
Analog output #6 value	Analog output #7 value	Analog output #8 value
Analog input #1 value	Analog input #2 value	Analog input #3 value
Analog input #4 value	PM-2.5 flow rate	PM-2.5 vol. flow rate
PM-2.5 flow set point	PM-2.5 air tube temp	PM-2.5 air tube surface temperature
PM-2.5 TEOM filter pressure	PM-2.5 TEOM filter load	PM-2.5 total mass
PM-2.5 raw MC	PM -2.5 MC	PM-2.5 unclipped MC
PM-2.5 unclipped MR	PM-2.5 30-Min MC	PM-2.5 1-Hr MC
PM-2.5 XX-Hr MC	PM-2.5 12-Hr MC	PM-2.5 24-Hr MC
PM-2.5 mass rate	PM-2.5 frequency count	PM-2.5 frequency cycles
PM-2.5 TEOM starting frequency	PM-2.5 TEOM frequency	PM-2.5 TEOM noise
PM-2.5 TEOM K0	PM-2.5 dryer temperature	PM-2.5 dryer dew point
PM-2.5 dryer RH	Current valve position	Desired valve position
PM-2.5 cooler temp	PM-2.5 cooler set point	PM-2.5 base MC
PM-2.5 reference MC	PM-2.5 30-Min base MC	PM-2.5 30-Min reference MC
PM-2.5 raw base MC	PM-2.5 raw reference MC	PM-2.5 raw base MR
PM-2.5 raw reference MR	PM-2.5 raw base unclipped MC	PM-2.5 raw reference unclipped MC
PM-Coarse flow rate	PM-Coarse vol. flow rate	PM-Coarse vol. flow set point
PM-Coarse air tube raw output	PM-Coarse air tube temp	PM-Coarse air tube surface temp.
PM-Coarse TEOM filter pressure	PM-Coarse TEOM filter load	PM-Coarse total mass
PM-Coarse raw MC	PM-Coarse MC	PM-Coarse unclipped MC
PM-Coarse unclipped MR	PM-Coarse 30-Min MC	PM-Coarse 1-Hr MC
PM-Coarse XX-Hr MC	PM-Coarse 12-Hr MC	PM-Coarse 24-Hr MC
PM-Coarse mass rate	PM-Coarse frequency count	PM-Coarse frequency cycles
PM-Coarse TEOM starting freq.	PM-Coarse TEOM frequency	PM-Coarse TEOM noise
PM-Coarse TEOM K0	PM-10 Total mass	PM-10 MC
PM-10 30-Min MC	PM-10 1-Hr MC	PM-10 XX-Hr MC
PM-10 12-Hr MC	PM-10 24-Hr MC	PM-Coarse dryer temperature
PM-Coarse dryer dew point	PM-Coarse dryer RH	PM-Coarse cooler temp
PM-Coarse cooler set point	PM-Coarse base MC	PM-Coarse reference MC
PM-Coarse 30-Min base MC	PM-Coarse 30-Min reference MC	PM-Coarse raw base MC
PM-Coarse raw reference MC	PM-Coarse raw base MR	PM-Coarse raw reference MR
PM-Coarse raw base unclipped M	PM-Coarse raw ref. unclipped M	

9.6.7 Set the Password Function, If Desired

The 1405-DF has an optional password protection system that can limit access to the operation of the machine.

- Select the Settings screen
- Select the System button

- Select the Password Protection button
 - Set the password (the default password is 100,000)
 - Initiate High Lock or Low Lock mode. (Requires entering the correct password.) In Low Lock mode, the user can view all instrument screens and can change the operating mode to perform filter changes. High Lock mode means the user cannot view any screens other than the TEOM[®] Data screen.

9.6.8 Configure the Required Communications Parameters

The final step in the setup of the 1404-DF is configuring the instrument's communication parameters to be compatible with the protocol(s) in use by the operating agency. The details of specific situations can differ greatly, so making precise recommendations is problematic. An overview of each method is provided below in Section 10, "1405-DF Communications", and additional details are given in the 1405-DF Operating Guide. It is left to the operator to decide the best way to gather the real time data available from the 1405-DF.

1405-DF Communications

There are a number of ways to communicate with the 1405-DF. The most direct, and the one used during the installation process, is the touch-screen interface allowing user access to "TEOM[®] Data", "System Status", "Instrument Conditions", "Settings", and "Service". This direct interface is the way that users interact with the instrument for verifications, calibrations, and maintenance routines. Other methods of communication must be used to download data and upload firmware.

An Ethernet connection utilizing the Thermo Scientific ePort software is the recommended method for routinely downloading data from the instrument and for installing firmware upgrades. The 1405-DF can accommodate automatic or manual data downloads of up to 20 (expected to soon change to 30) user-selected variables via the Ethernet connection through a network, a router, or directly to a PC (a direct 1405-DF/PC Ethernet connection requires a crossover cable). Alternatively, the data can be manually downloaded to a USB jump drive. A third option employs data downloads via a 9-pin RS232 port using RPSComm software (provided with the instrument) or HyperTerminal with AK protocol, and a fourth uses the 25-pin I/O port on the back of the instrument, providing 8 analog outputs, 4 analog inputs, and 2 digital outputs (contact closures). **Table 9-5** lists the data logging alternatives with references to relevant sections of the 1405-DF Operating Guide.

Table 9-5. Data logging alternatives with the 1405-DF.

Logging Method	Options	Operating Guide (pages, Revision A.003)	Comments
Thermo Scientific's ePort	ePort Setup	3-10 to 3-15	
	LAN or router	3-16 to 3-19	Standard Ethernet cable
	PC direct	–	Requires crossover cable
	Multiple Instruments	3-20 to 3-21	Each unit needs an IP address
	Manual Downloads	3-22 to 3-23	–
	Automatic downloads	3-24 to 3-27	–
USB Flash drive		3-28 to 3-29	–
Analog/Digital I/O (25-pin connector)	8 analog out	3-31 to 3-33, 4-26 to 4-28	–
	4 analog in		–
	2 digital out		–
RS232 (AK Protocol)	RPComm	4-29, Appendix B	–
	Hyperterminal		–

9.7 COMMUNICATIONS SETUP AND DATA DOWNLOAD

Depending on the user's needs, setting up communications with the 1405-DF and downloading data will involve one or more of the following tasks:

- Installing ePort software on computer or Network
- Setting up the Analog Inputs, Analog Outputs and Contact Closures
- Setting up the RS-232 serial port parameters
- Using a USB flash drive for data downloads

Note that firmware updates can only be uploaded to the instrument through an Ethernet port. Agencies that cannot use the Ethernet option must contact the manufacturer for special firmware upgrade options.

9.7.1 Install ePort Software on Site Computer or Network

Receiving data files directly from the on-board data logger via ePort is efficient, and provides complete and accurate data sets. Data files are downloaded and saved as .csv files that

can be opened and viewed with Microsoft Excel. This file format also allows for easy import into databases. The file title format is the instrument serial number followed by a date/time stamp.

The 1405-DF Operating Guide, Section 3, and technical bulletins give instructions for installing and using the ePort software (see Appendix A “Technical Bulletin – 1405 Connectivity”). This proprietary software operates on a Windows platform, so keeping current with Microsoft Windows OS upgrades is important. It may also be beneficial to register as a user with the Thermo Scientific “Air Quality Instruments Online Library”, which provides the option of automatic email notification when upgrades to products and services related to the 1405-DF are available. To register as a library user, use the link:

http://www.thermo.com/com/cda/resources/resources_detail/1,2166,200503,00.html

Download Data via the ePort Software

- Launch ePort
- Confirm that the 1405-DF has a valid IP address.
 - In the System Status screen, update, locate and record the IP address. If no IP address is listed, then check Settings > System > Network Configuration
 - Use the ePort PC software to connect to the instrument and display the ePort Main screen (See Section 3 in the Users Guide for complete details).
 - Select Download Data in the Commands window of the ePort Main screen.
 - Select the Begin Download button. The ePort software will download data based on the settings created in the Download Setup Wizard of ePort (See Section 3 in the Users Guide to set up the data downloads). When the download is complete, it will display a “Download Complete” message.

9.7.2 Set Up the Analog Outputs, Analog Inputs, and Digital Outputs (Contact Closures)

These options use I/O protocols to communicate with an external data logger through the 25-pin port on the back of the instrument. Thermo Scientific offers a 25-pin male connector manufactured by Phoenix Contact that can be wired to match to the USER I/O connector on the back of the instrument (p/n 06-004521-0025). The Operating Guide (Rev. A.003) gives the pin assignments for the 1405-DF (page 3-32,) and the user will need to ensure that the connector is properly wired and connected to the appropriate data logger input terminal.

The 1405-DF has 8 user defined analog outputs and 2 contact closures to allow the user to interface the system with an external data logger. Users may want to log analog output data to provide redundancy. The analog outputs allow collection of user-selected variables as a DC voltage. Each one of the 8 analog out channels can be configured for a 0-1 or 0-5 VDC range and assigned to any of the available instrument variables. Two digital outputs (contact closures) are available for alarm notifications.

The analog output boards should be calibrated during instrument installation, and then on an annual basis or if the voltage range is changed. The 1405-DF has an Analog Output Calibration Wizard to guide the user through the calibration process (Service > Calibration > Analog Output Calibration). Section 5 of the Operating Guide (Maintenance and Calibration Procedures) also offers step by step instructions with accompanying photos of the analog output calibration process.

The instrument can also accept and store information from up to four analog inputs. The inputs accept 0-5 VDC and can be converted to a desired scale.

Set Up the Analog Outputs

- Select the Settings screen
- Select the Analog and Digital Outputs button
 - Select the Analog Outputs button to display the Analog Outputs screen. (There are two screens, each with four configurable analog outputs)
 - Use the button associated with each analog output to select a variable
 - Set a minimum and maximum value for the output for the desired output channel
 - Repeat until all desired channels are set up.

Set Up the Analog Inputs

- Select the Instrument Conditions screen
- Select the Analog Inputs button
 - Select the desired analog input (1 to 4)
 - The monitor converts the analog input value to engineering units according to the formula: $\text{Result} = A(X*X) + BX + C$, where X is the analog input percent full scale
 - Select the button for A, B, or C and provide the constant value

The analog inputs are self-calibrating.

Set Up the Digital Outputs (Contact Closures)

- Select the Settings Screen
- Select the Analog & Digital Outputs button
- Select the Contact Closure button
 - Use the buttons to select a variable, operator and compare value for the desired contact closure channel (1-2).

The digital outputs are generally used to record alarm values.

Signal Processing of Analog Data

Signal processing of analog data requires that several issues be considered.

1. The time-stamp applied to the data is made at the bottom of the hour and most data loggers are programmed to receive the time-stamp applied at the top of the hour. Some agencies offset the time between the data logger and the instrument to compensate for this difference; the 1405-DF time is set three minutes ahead of the data logger time. Others agencies transform the time when data are post-processed.
2. If interim values are collected and averaged into hourly values by the data logger program, any time discrepancy, including an offset, may result in the analog data not exactly matching the instrument digital data.
3. The instrument calculates rolling averages; therefore, time issues are difficult to reconcile.
4. In addition, rounding or significant digits processing differences between the data logger and instrument may yield slightly different datum.
5. Only eight variables can be collected creating many challenges for field diagnostics and data validation.
6. Instrument digital and analog data may not match; the digital-to-analog conversion must be verified on a routine basis. An Analog Output Calibration Wizard is available.
7. The sampler generates status codes but they are issued in real time (while the status condition exists, the code is output). However, if the data are polled at a longer interval, such as the top of the hour, a status code may not be captured if the condition only existed for a short time period or was intermittent. These codes are critical for both field operation and data validation.

Because of these issues, collecting data digitally or augmenting analog data with periodic digital downloads from the sampler, especially during periods of sampler malfunctions, is preferable. An inexpensive method, such as using a USB jump drive, may be employed to download the digital data.

The eight most important variables to capture for purposes of data validation and remote confirmation of proper instrument operation are

1. 1-hr $PM_{2.5}$ Mass Concentration
2. 1-hr Reference Concentration (Base Concentration can be back-calculated)
3. 1-hr FEM $PM_{2.5}$ Concentration
4. Status
5. Main Flow
6. Filter Loading

7. Frequency
8. Sample Dew Point

9.7.3 Set Up the RS-232 Serial Port for Communication

The 1405-DF supports AK protocol serial communication, which enables a local or remote computer (or data logger) to exchange information with the monitor. Many users of the earlier models of the TEOM[®] may be familiar with this system. Care must be exercised when using the AK Protocol. For example, **EREG (Enter Register Command)** can assign a new value to any system variable, but the value of variables should only be changed when the monitor is in the appropriate operating mode. A complete explanation of the protocol is available in Appendix B of the Users Manual.

Program Register Codes (PRC) are labels given to the variables in the 1405-DF, and a cross reference of the codes and variable names is needed to be able to communicate with the 1405-DF. Table B-1 of Appendix B of the 1405-DF Operating Guide lists the main PRC codes for the 1405-DF.

To set up the RS232 serial port,

- select the Settings Screen,
- select the Analog & Digital Outputs button, and
- select the RS232 button to set up the unit for serial connections using AK protocol.

9.7.4 Using a USB Flash Drive

Operators may also plug a USB flash drive into USB port on the front of the unit and download the data to the portable drive. The 1405-DF will recognize the flash drive and prompt the user to choose to download all of the stored data, or data since the last download.

10. MAINTENANCE AND QUALITY CONTROL PROCEDURES

Once the 1405-DF is installed and configured, a regularly recurring protocol of maintenance and quality control procedures must be established to ensure that a continuous stream of high quality hourly PM_{2.5} concentration data is obtained.

Table 10-1 lists the Thermo Scientific maintenance and QC procedures, recommended frequencies of recurrence, and the sections of this SOP that describe the sequential steps needed to perform each maintenance procedure. In practice, it may be helpful to provide field technicians responsible for implementing the procedures with an actual calendar, or simple table, with the site-specific target dates for each protocol.

The frequencies at which these procedures are conducted are site- and agency-specific. Some agencies conduct some of these procedures at a higher frequency than listed in the table to minimize the need to invalidate data because of a failure (e.g., filter over-loading leading to a reduced sample flow rate) that may require that data be invalidated back to the last recorded acceptable value. This increased frequency is generally based on experience—if filter loading is exceeding the tolerance before the scheduled monthly visit, the logical solution is to perform the filter exchange more frequently, for example, bi-weekly, or based on real-time monitoring of the filter loading. Since most QC procedures require that the sampling cycle be interrupted, more frequent QC procedures need to be balanced against the one or two hours of lost data.

Tolerance levels for verifications of flow, temperature, pressure, and leak checks must be specified so that field technicians understand when adjustments are needed and when they are not. It is important to consider that *frequent adjustments of instruments may not be necessary* and can lead to *more* data quality uncertainty. It is left to the site supervisor to decide on the recurrence schedule and the tolerance levels that best fit the circumstances.

In general, 40 CFR Part 58 App A (U.S. Environmental Protection Agency, 2008b) and 40 CFR Part 50 App L (U.S. Environmental Protection Agency, 2006b) requirements apply to all Continuous PM_{2.5} methods. The EPA Quality Assurance Handbook Volume II, Appendix D (U.S. Environmental Protection Agency, 2008c) provides some guidance regarding QC checks, in the Continuous PM_{2.5} Local Conditions Validation Template.

Table 10-1. Thermo Scientific-recommended maintenance and QC tasks, frequencies, and SOP and 1405-DF Operating Guide section references. Maintenance items marked with an asterisk (*) have Wizard instructions in instrument firmware version 1.27, upon which this SOP is based.

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Maintenance or QC Item	Suggested Frequency	SOP Section	Operating Guide Section (Rev A.003)
Replace the TEOM filters*	Monthly or as filter loading approaches 100%	9.6.5, 10.1.9	5-4
Replace the 47-mm FDMS filters	Monthly or any time the TEOM filters are replaced	9.6.5, 10.1.10	5-16
Leak Check*	Monthly	9.6.4	Wizard: Service > Verification > Leak Check
Temperature verification/calibration*	Monthly	10.1.15	Screen: Service > Calibration > Ambient Calibration
Pressure verification/calibration*	Monthly	10.1.16	Screen: Service > Calibration > Ambient Calibration
Total Flow, One point flow verification*	Monthly	10.1.2	Wizard: Service > Verification > Flow Audit
PM _{2.5} , One point flow verification*	Monthly	10.1.12	Wizard: Service > Verification > Flow Audit
PM-Coarse, One point flow verification*	Monthly	10.1.12	Wizard: Service > Verification > Flow Audit
Bypass One point flow verification*	Monthly	10.1.12	Wizard: Service > Verification > Flow Audit
Clean the PM ₁₀ inlet	Monthly	10.1.20	5-18
Clean the virtual impactor	Monthly	10.1.9	5-22
Replace the in-line filters (PM _{2.5} , PM-Coarse, and bypass)	6 months	10.3	5-24
Clean the coolers*	Annually, or as needed	10.3.1	5-30
Clean the switching valve*	Annually, or as needed	10.3.2 App B	5-36
Replace switching valve seals and O-rings, lubricate			Separate document

Table 10-1. Thermo Scientific recommended maintenance tasks, frequencies, and SOP and 1405-DF Operating Guide section references. Maintenance items with an asterisk (*) have a Wizard in instrument firmware version 1.27, upon which this SOP is based.

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Maintenance or QC Item	Suggested Frequency	SOP Section	Operating Guide Section (Rev A.003)
Verify the clock	Monthly	10.1.22	4-24
Verify the calibration constant	Annually	10.3.6	5-64
Clean the air inlet system <i>inside</i> the mass transducer*	Annually	10.3.3	5-28
Rebuild the sample pump	18 months, or as needed	10.4	Separate document
Replace the dryer	Annually, or as needed	10.3.4	Not covered
PM2.5, 3-point flow calibration*	Upon installation then yearly and upon verification failure	10.3.5	Wizard: Service > Calibration > Flow Calibration
PM-Coarse, 3-point flow calibration*	Upon installation then yearly and upon verification failure	10.3.5	Wizard: Service > Calibration > Flow Calibration
Bypass, 3-point flow calibration*	Upon installation then yearly and upon verification failure	10.3.5	Wizard: Service > Calibration > Flow Calibration

10.1 MONTHLY MAINTENANCE AND QC

The monthly site visits and associated tasks are essential for maintaining optimal instrument performance. All data pertinent to the monthly maintenance and QC procedures should be documented, using an appropriate form. Examples of QC forms used by some agencies are provided in Appendix C. Electronic forms (e.g., MS Excel spreadsheets) are preferred by some users.

Recommended order of events for monthly QC:

1. View 1405-DF Data Screen for Warnings (SOP Section 10.1.1).
2. Deploy the temperature reference device to allow it to equilibrate.
3. Conduct “as found” total flow check (16.7 lpm; optional) (SOP Section 10.1.2).

4. Conduct “as found” leak check (SOP Sections 10.1.5 and 9.6.4).
Use the Leak Check Wizard (Service > Verification > Leak Check) or, if Advanced Users Mode is used, leak check in both reference and base cycles.
5. Replace the TEOM[®] and FDMS[®] filters (SOP Sections 10.1.8, 9.6.5 and 10.1.9).
6. Conduct “as found” flow verification on the three flow paths (SOP Section 10.1.12).
Use the Flow Audit Wizard (Service > Verification > Flow Audit).
 - Based on flow tolerances, leave as found, or proceed to temperature and pressure calibrations before making an adjustment.
7. Verify/adjust the ambient temperature sensor (SOP Section 10.1.15)
(Service > Calibration > Ambient Calibration).
8. Verify/adjust the ambient barometric pressure sensor (SOP Section 10.1.16)
(Service > Calibration > Ambient Calibration).
9. Conduct flow calibrations on three flow paths (if warranted) (SOP Section 10.3.5).
Use the Flow Calibration Wizard (Service > Calibration > Flow Calibration).
10. Clean the virtual impactor (SOP Section 10.1.18).
11. Clean the PM₁₀ inlet (SOP Section 10.1.19).
12. Remove the TEOM[®] filters and place on the equilibration posts.
13. Conduct “as left” leak check (SOP Sections 10.1.5 and 9.6.4).
14. Replace the TEOM[®] filters.
15. Install replacement TEOM[®] filters on the equilibration posts.
16. Conduct “as left” flow verification on total flow (optional) (SOP Section 10.1.2).
17. Verify/adjust the 1405-DF clock (SOP Section 10.1.22).
18. Download 1405-DF data (SOP Section 10.1.23).

10.1.1 Check for Status Codes/Instrument Warnings

During each site visit, the instrument should be checked for status condition warnings. When warnings are present, as indicated by the triangle icon and the message in the status bar on the bottom edge of the screen, the user should touch the System Status Button and then press the View Warnings Button, the icon, or the title bar. A list of the current warnings can be scrolled through by using the Next Warning and Previous Warning buttons. In addition, codes for these warnings are contained in the internal instrument data set. The status conditions can be viewed remotely if the digital data are being automatically polled. (Capturing the status codes with an analog connection is problematic because the status codes are output in real time [output while the condition exists] and not held; therefore, if the polling is not performed while the status condition exists it will not be captured.)

Appendix A of the Users Guide (Rev. A.003) explains how to decipher the codes. This process requires converting the value from a decimal number to a hexadecimal number, parsing

the resultant number, and looking up the parsed values in a table. Most agencies develop a program that performs this transformation automatically.

10.1.2 Verify the Total Flow

Users may choose to implement a “total” (the sum of the flow rates for the three paths) flow check immediately before or after the “as found” leak check to gain a general indication if the flow required to achieve the inlet cut-point is being maintained.

The Instrument Audit Screen provides a sum of the three flow fractions, labeled Total Flow (Service > Verification > Instrument Audit). In addition, this screen lists all audit parameters (within the firmware, audit is defined as a test that does not alter a value): the ambient temperature and pressure, the three flow rates, the vacuum pump pressure, and the calibration constants for the PM_{2.5} and PM-Coarse TEOMs. No adjustments, however, can be made from this screen. Firmware version 1.50 is expected to add a Total Flow value to the single point verification screen which then may be used for this comparison, as well.

Place the instrument in SETUP mode to discontinue (valid) data collection. Remove the PM₁₀ inlet and install a flow reference device, using the supplied flow adapter, if necessary. Compare and record the total flow as indicated by the instrument (Service > Verification > Instrument Audit) to the total flow as measured by the reference device.

10.1.3 Total Flow Tolerances

Maintaining the proper total flow through the inlet is necessary to ensure that the desired PM₁₀ cut-point is achieved. Generally, the flow tolerance through the inlet is set at 16.67 lpm \pm 10% but local agencies may wish to take action based on a tighter criterion to prevent data loss due to invalidation. The total flow can not be adjusted directly because it is the sum of the three flow fractions. To correct the total flow rate, the individual fractions must be adjusted or a leak, if present, corrected.

10.1.4 Equipment Needed for Total Flow Verification

- A NIST-traceable flow transfer standard capable of measuring flow rate of 16.7 lpm is required.
- Depending on the flow transfer standard used, a flow inlet adapter may be required

10.1.5 Leak Check

The leak check verification is accessed through the Leak Check Wizard (Service > Verification > Leak Check). See SOP Section 9.6.4 for full details. Note that the first step of the Leak Check Wizard will prompt the user to remove the two TEOM[®] filters from the transducer

to ensure that they are not damaged; if they are damaged, parts of the filter will be pulled into the sample path of the instrument during the leak check procedure.

10.1.6 Leak Test Tolerances

Leak check tolerances may vary by agency. Thermo Scientific recommends a tolerance of ± 0.15 lpm for the PM_{2.5} and PM-Coarse leak checks and ± 0.60 lpm for the Bypass leak check. The Wizards are set to give failure warnings based on those recommendations.

10.1.7 Equipment Needed for Leak Check

A leak check/flow adapter is provided with the instrument (Figure 9-4).

10.1.8 Replace the TEOM[®] Filters Monthly or As Loading Approaches 100%

The rate of filter loading will vary depending on ambient PM_{2.5} and PM-Coarse concentrations. While the suggested frequency for filter replacement is 30 days, this can be greatly shortened depending on local conditions. The best way to avoid data loss due to overloaded filters is to institute a strict regimen of daily (or more frequent) data review. Digital data acquisition using, for example, ePort software, makes this a routine matter, and is highly encouraged.

See Section 9.6.5, for the installation procedure for the TEOM[®] filters. It is recommended that the TEOM[®] Filter Replacement Wizard (Service > Maintenance > Replace TEOM Filters) be used until the user is thoroughly comfortable with the filter replacement process. *Bypassing the Wizard puts the onus of checking the stability of the TEOMs' frequency on the user*, and failure to do so can result in the invalidation of data.

10.1.9 Equipment Needed for TEOM[®] Filter Exchange

- TEOM filters (p/n 57-007225-0020).
- Filter exchange tool (provided with instrument).

10.1.10 Replace the 47-mm FDMS[®] (Purge) Filters

The 47-mm FDMS[®] filters must be replaced any time that the TEOM[®] filters are replaced. There is no Wizard to accompany this process, but the steps are reviewed in Section 9.6.5 (also see 1405-DF Operating Guide, Section 5) If the 47-mm filters are to be used for additional analysis, special filter handling precautions, similar to those employed for FRM filters, must be observed. Condensation should be wiped off the filter housing before the filter is reinstalled.

10.1.11 Equipment Needed to Replace the 47-mm FDMS[®] (Purge) Filters

- Standard FRM-style 47-mm filter cassette with a TX-40 filter (Teflon-coated borosilicate) p/n 10-002387-0025.
- Protective containers if filters are to be used for additional analysis.

10.1.12 Verify the Flow Rates for Each of the Three Flow Fractions

The single-point verification Wizard (Service > Verification > Flow Audit) provides step-by-step instructions on the procedure to verify the flow rate for each sample fraction.

Verify the fine, course, or bypass flow:

- In the TEOM[®] Data screen, select the Service button to display the Service screen.
- Select the Verification button to display the Verification screen.
- Select the Flow Audit button to begin the Flow Audit Wizard.

Follow the Wizard Steps to

- enter the type of flow audit device being used,
- select which flow rate (fraction) to audit, and
- connect the flow audit device to the inlet.

- To audit the PM_{2.5} flow channel, remove the inlet, inlet tube and virtual impactor, and attach the 1-1/4" flow adapter/meter to the top of the flow splitter. Disconnect the green bypass line from the side of the flow splitter (do not let it fall to the ground) and cap the bypass fitting with the 3/8" Swagelok cap provided with the system.
- To audit the PM-Coarse flow channel, remove the inlet, inlet tube and virtual impactor, and connect the 1/2" Swagelok flow audit adapter to the top of the 1/2" Coarse flow inlet. Connect the flow meter/adapter to the flow audit adapter.
- To audit the bypass flow channel, remove the bypass line from the flow splitter and connect the 3/8" flow adapter to the green tubing of the bypass line. Connect the flow meter/adapter to the flow audit adapter.

The flow rates are mathematically corrected by the instrument temperature and pressure readings and should not be adjusted until after the temperature and pressure sensors have been calibrated.

10.1.13 Tolerances for Flow Rates for Three Flow Fractions

The flow rates must be adjusted (**after the temperature and pressure calibration**) if the flow rate indicated by the instrument differs from the flow rate as measured by the flow reference device by $\pm 4\%$ or the design value (target flow rate) for the specific fraction by more than 5%. Some agencies may wish to take action based on tighter criteria to prevent data loss due to invalidation.

10.1.14 Equipment Needed to Verify the Flow Rates

- A NIST-traceable flow transfer standard capable of measuring flow rates between 1.3 lpm and 14.4 lpm is required.

The reference flow meter should have been recently calibrated to a primary standard, and should have an accuracy of $\pm 1\%$ at the flow rates of interest (3 lpm and 16.67 lpm) and a pressure drop of less than 0.07 bar (1 psi). If the flow meter does not report volumetric flow rates, the readings must be corrected to volumetric lpm at the current ambient temperature and barometric pressure.

- Flow inlet adapters (provided with instrument).

10.1.15 Verify/Calibrate the Ambient Temperature

- Select the Service button to display the Service screen.
- Select the Calibration button to display the Calibration screen.
 - Select the Ambient Calibration button to display the Ambient Calibration screen.
 - Determine the current temperature ($^{\circ}\text{C}$) at the ambient temperature sensor using an external reference thermometer.
 - If the measured value is within $\pm 2^{\circ}\text{C}$ of the temperature displayed in the Ambient Temperature button, no further action is necessary. Select the <Back button to return to the Calibration screen. If the value is not within $\pm 2^{\circ}\text{C}$ of the temperature displayed in the Ambient Temperature button, select the Ambient Temperature button. A keypad will display. Enter the actual temperature as measured by the external thermometer and press the Enter button. The Ambient Temperature Calibration screen will display with the new entered value. Select the <Back button to return to the Calibration screen.

10.1.16 Verify/Calibrate the Ambient Pressure

- Select the Service button to display the Service screen.
- Select the Calibration button to display the Calibration screen.
 - Select the Ambient Calibration button to display the Ambient Calibration screen.
 - Determine the current ambient pressure in atmospheres (absolute pressure, not corrected to sea level).
 - If the measured value is within ± 0.01 atm of the pressure displayed in the Ambient Pressure button, no further action is necessary. Select the <Back button to return to the Calibration screen. If the value is not within ± 0.01 atm of the pressure displayed in the Ambient Pressure button, select the Ambient Pressure button. A keypad will display. Enter the actual pressure as measured by the external device and press the Enter button. The Ambient Pressure Calibration screen will display with the new entered value. Select the <Back button to return to the Calibration screen.

10.1.17 Adjust the Flow Rates for Each of the Three Flow Fractions

If any of the three flow rates did not meet the verification criteria in Section 10.1.12, it (they) should be adjusted. Use the Flow Calibration Wizard (Service > Calibration > Flow Calibration). See Section 10.3.5, Calibrating the Flow Rates, for the necessary procedures.

10.1.18 Clean the Virtual Impactor Monthly

The virtual impactor is an essential component of the 1405-DF inlet system, and it is imperative that it be well-maintained. Monthly inspection and cleaning is necessary to assure efficient particle separation of the sample air stream.

10.1.19 Materials Required to Clean and Maintain the Virtual Impactor

- Ammonia-based, general-purpose cleaner or mild detergent
- Silicone-based O-ring grease
- Phillips screwdriver
- Soft brush or lint free cloth
- Cotton swabs

To clean the virtual impactor,

1. Remove the PM₁₀ inlet, and the 1-1/4" sample tube that connects the inlet to the impactor, from the top of the system.
2. Loosen the 1/2" Swagelok nut that connects the PM-Coarse flow tube inlet to the bottom of the impactor.
3. Lift the virtual impactor off the flow splitter and Coarse sample tube.
4. Place the impactor on a clean work surface and remove the four screws on each corner of the bottom section of the virtual impactor. Separate the body from its base plate (**Figure 10-1**).
5. Remove the three screws that hold the top of the virtual impactor to the body.
6. Use water and a mild detergent to wash the inside surfaces of the body, top and bottom sections of the impactor. A general-purpose cleaner can be used, if necessary. A cotton swab may be useful for cleaning the body.
7. Inspect all O-rings in each section of the virtual impactor for damage and replace them, if necessary. Apply a thin coating of O-ring lubricant onto the O-rings, if necessary.
8. Reassemble the impactor, attach it to the flow splitter and PM-Coarse tube inlet, and reinstall the PM₁₀ inlet.

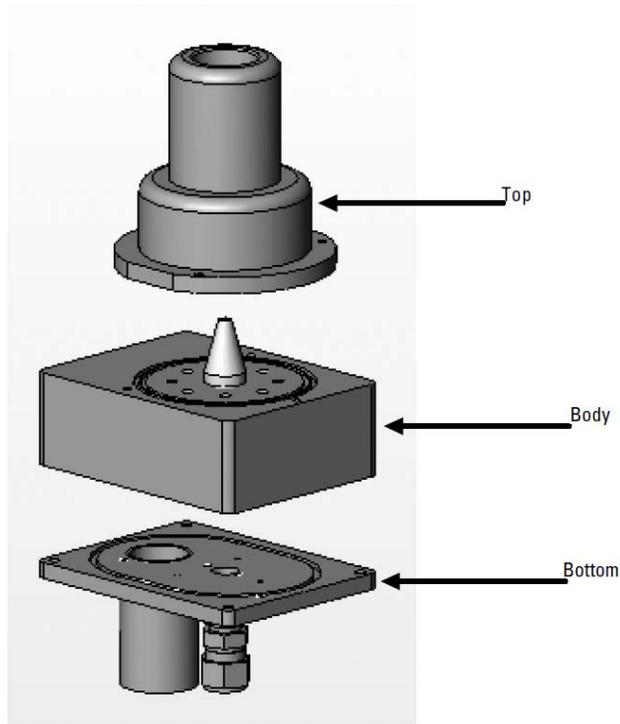


Figure 10-1. Exploded view of the virtual impactor.

10.1.20 Clean the PM₁₀ Inlet Monthly

The PM₁₀ inlet has two primary components, the Acceleration Assembly and the Collector Assembly (**Figure 10-2**). Thermo Scientific recommends cleaning both of these assemblies monthly.

10.1.21 Materials Needed to Clean the Inlet

- Soft bristled paint brush
- Lint free cloths
- Cotton swabs
- Water (or a mild solvent such as an ammonia based cleaner)
- A #2 Phillips screwdriver is needed to remove the top plates from the acceleration assembly of the inlet.

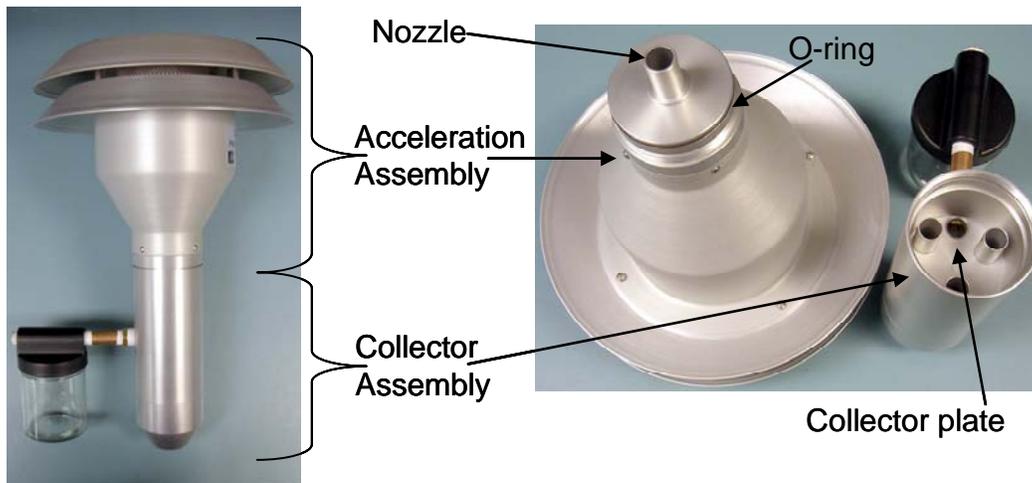


Figure 10-2. The PM₁₀ inlet has two primary components, the Acceleration Assembly and the Collector Assembly.

The 1405-DF Operating Guide has detailed instructions, accompanied by photos, detailing all aspects of the inlet cleaning procedure; they are summarized below.

To clean the inlet,

- Remove the condensation jar and set it aside.
- Unscrew the Collector Assembly (Figure 10-2 bottom portion of inlet) from Acceleration Assembly (Figure 10-2 top portion of inlet) and set it aside.
- Clean the Acceleration Assembly
 - Set the Acceleration Assembly upside down on its top plate and remove the four pan head screws on the bottom side. If the stand-offs turn, hold them in place with pliers.
 - Lift the Acceleration Assembly off the top plate.
 - Lift the lower plate up and carefully remove the insect screen.
 - Clean all the inlet parts of the Acceleration Assembly inside and out (top plates, insect screen, and the Accelerator Assembly body). Depending on local conditions, parts may only need to be wiped with brushes or a lint-free cloth, or blown out with compressed air. Alternatively, the parts may be washed with clean water, which is the best way to remove caked deposits that have accumulated in hard-to-reach places. Parts must be thoroughly dried before re-assembly. Pay special attention to the acceleration nozzle at the base of the cone-shaped body; clean the inside of the nozzle by pushing a moistened piece of cloth through it.
 - Inspect the large diameter O-ring at the base of the Accelerator Assembly. Replace if necessary. Apply a thin film of O-ring grease on the O-ring and a thin film on the aluminum threads of the acceleration assembly.

- Clean the Collector Assembly (lower portion of inlet)
 - Use a brush, lint free cloth and/or cotton swabs to clean the bottom collector plate and the collector assembly walls around the three vent tubes, and the weep hole in the collector plate. Water may be used if needed. Allow to dry.
 - Clean inside the vent tubes by running a moistened cloth through them.
 - Wipe out the area inside the bottom of the Collector Assembly where the two O-rings are located.
 - Inspect the O-rings and replace if needed. Apply a thin film of O-ring grease on the O-rings.
- Wipe out the condensation jar and the jar lid. Apply a thin film of grease to the seal inside the lid.
- Reassemble the PM₁₀ inlet taking care to avoid cross-threading.

10.1.22 Verify the Clock (Time and Date)

The TEOM[®] 1405-DF with FDMS[®] clock may drift as much as a minute per month. The EPA recommends checking the clock monthly to ensure correct sample timing. The 1405-DF clock should be permanently set for standard time and should never be reset to daylight savings time. Hourly data that needs to be expressed on a different time basis can be adjusted by post-processing the time stamp.

In addition, if the data are being collected by an outside device/or database that applies a time stamp, then the time stamps should be examined for accuracy and appropriateness on a monthly basis as well. It may be necessary to offset the times in order to properly process the data from the base and reference periods so that the mass concentration data are correct.

To set the time, use the Service > System > Set Time function and enter the time using the pop-up screen.

10.1.23 Download the 1405-DF Data Files If Not Automatically Polled

The downloading procedure will vary based on the data collection protocol of the individual agency. The 1405-DF can accommodate manual data downloads of up to 20 user-selected variables (expected to change to 30) via an Ethernet connection through a network, a router, or directly to a PC (a direct 1405-DF/PC Ethernet connection requires a crossover cable); to a USB jump drive; or via a 9-pin RS232 port using RPSComm software (provided with the instrument) or HyperTerminal with AK protocol.

10.1.24 Compare TEOM[®] 1405-DF Data to External Data Logger Data

If an external DAS is used to collect the hourly data from the TEOM[®] 1405-DF with FDMS[®], one QC protocol should be a monthly comparison of the internally stored data (assumed to be the “most correct”) with the data stored by the DAS. This is particularly important after a new installation so that any errors associated with the acquisition process can be identified and corrected to avoid continued propagation of the error. Digitally acquired data are less susceptible (although not immune) to acquisition errors than analog, and digital methods are recommended whenever possible.

The comparison of the 1405-DF internal data with DAS data should focus on time stamps and the concentration data:

- Digitally acquired concentration data in the DAS should agree exactly with the concentration data stored internally in the instrument. If it does not, there may be a time stamping problem. Compare a specific record in the data acquisition system (DAS) with the previous and following records (based upon the time stamp) downloaded directly from the 1405-DF. If one of these records matches, then there is a one-hour offset that needs to be corrected in the data acquisition protocol or in post-processing.
- Concentration data collected by the DAS from the *analog* outputs of the TEOM[®] 1405-DF with FDMS[®] should agree with the internal digital data within 1 $\mu\text{g}/\text{m}^3$ (0.001 mg/m^3).
 - Discrepancies of a few $\mu\text{g}/\text{m}^3$ may be attributable to faulty or un-calibrated DAC (digital-to-analog-converter) electronics, or simply a wiring problem between the instrument and the DAS analog inputs. The analog output calibration should be tested on the analyzer using the Wizard available through Service > Calibration > Analog Output. The analog output generally requires calibration about once per year.
 - Discrepancies between analog and digital data of more than a few $\mu\text{g}/\text{m}^3$ that are not consistent can occur if the DAS is using an averaging function and the clocks of the instrument and the DAS are not perfectly synchronized. This can result in hourly concentration values from adjacent hours being averaged together, making the resulting concentration difficult to match with digital data.
 - The above scenarios regarding analog data can be additionally confounded if there is a time stamping problem with the analog data, so be sure to factor that into troubleshooting of discrepancies between downloaded digital data and analog data.

Depending on the DAS used, the time of the instrument may need to be offset from the data logger time. For instance, some agencies using ESC data loggers set the instrument clock 3 to 4.5 minutes ahead of the DAS clock to avoid “overlap” in the base/reference period when the channels are set up as “average math channel.” These offsets will make a comparison of the data sets more difficult and further confound comparison of the data sets, because the concentration data generated by the instrument are rolling averages updated every six minutes based on the result of the base or reference measurement cycle. Verifying that a representative data set is being collected requires diligence and careful attention to detail.

10.2 SIX-MONTH MAINTENANCE AND QC PROCEDURES: REPLACE IN-LINE FILTERS

The filter elements in the small PM_{2.5} and PM-Coarse in-line filters (p/n 32-010745) and the large bypass flow filter (p/n 32-010755) should be changed every six months or as necessary. They are located on the back of the sampler. These filters prevent contamination from reaching the flow controllers. For convenience, replace the in-line filters elements immediately following one of the regularly-scheduled TEOM[®] filter exchanges during the 30-minute flow and temperature stabilization period.

To exchange the in-line filters,

1. Unplug the sample pump.
2. Unscrew and remove the small filter covers for both the PM_{2.5} and PM-Coarse flow channels on the back of the unit (**Figure 10-3**, left).

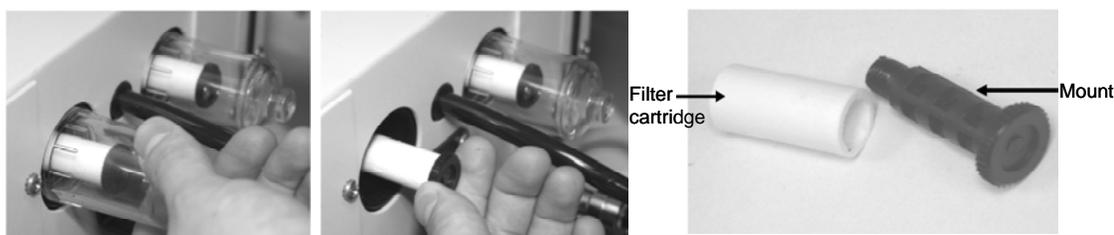


Figure 10-3. The PM_{2.5} and PM-Coarse in-line filters should be changed every six months.

3. Unscrew the filter mounts for both the PM_{2.5} and the PM-Coarse flow channels (**Figure 10-3**, center).
4. Slide the filter cartridges off the mounts and install new cartridges onto the mounts (**Figure 10-3**, right).
5. Install the mounts into the unit and install the covers.
6. Unscrew and remove the large filter cover from the bypass flow channel on the back of the unit (**Figure 10-4**).
7. Unscrew the filter mount for the bypass flow channel.
8. Slide the large filter cartridge off the mount and install a new cartridge onto the mount.
9. Install the mount into the unit and install the cover for the bypass flow.
10. Plug in the sample pump and return to normal operation.

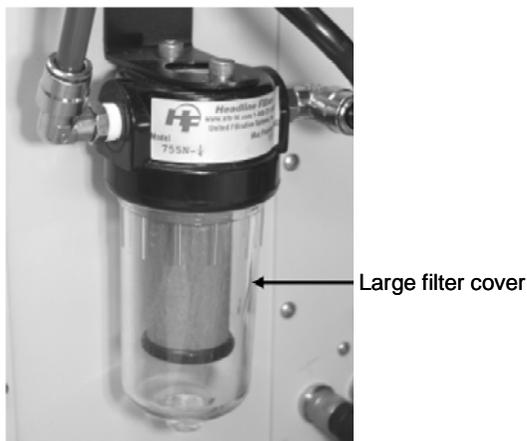


Figure 10-4. The bypass flow in-line filter should be changed every six months. This coalescing filter also serves as the water trap on the 1405-DF.

An independent audit of the system should be conducted semi-annually; it should consist of, at a minimum, a one-point flow audit for the total flow and all three fractions, a one-point audit of the temperature sensor, a one-point audit of the pressure sensor, a leak test, and a time verification.

10.3 TWELVE-MONTH MAINTENANCE AND QC PROCEDURES

A number of maintenance and QC procedures should be performed annually.

10.3.1 Clean the Cooler Assembly

The coolers should be cleaned at least once a year, or as necessary. The Cooler Cleaning Wizard provides pictures and describes all the steps necessary to clean the cooler. The 1405-DF Operating Guide (p. 5-30) mirrors the Cooler Cleaning Wizard instructions and also provides several photos to guide the user.

To clean the coolers,

- Select the Service button to display the Service screen.
- Select the Maintenance button.
 - Select the Clean Coolers button to start the Cooler Cleaning Wizard.
 - Follow the step-by-step instructions in the Wizard. The Wizard itself also has pictures.

10.3.2 Perform Switching Valve Maintenance

There are **two** switching valve maintenance routines. The switching valve should be cleaned at least once a year, or as necessary; the 1405-DF has a Valve Cleaning Wizard to guide the user through the steps. The other routine involves replacement of the seals and O-rings, and lubrication to prevent damage to the seals during the switching process. This procedure is not covered in the Operating Guide, but is available as a separate Thermo Scientific technical bulletin which is included in the SOP as Appendix A. **IMPORTANT NOTE:** At one point, the Valve Cleaning Wizard offers incorrect advice for reassembling the Swagelok connections. When reinstalling the switching valve, the user is advised to tighten the Swagelok fittings to finger tight, and then another 1-1/4 (one and one-quarter) turns with a wrench. *This instruction should be only 1/4 turn past finger tight, not 1-1/4.* When Swagelok fittings of this size are initially seated (during first assembly), they are tightened 1-1/4 turns past finger tight to *initially seat the ferrule*. Subsequent re-tightening of the fitting should only require a 1/4 turn past finger tight. Over-tightening of the fittings can ruin the ferrule and lead to leaks that are very hard to find. If a stainless steel Swagelok fitting can be turned more than 1/2 turn past finger tight, it has already been compromised.

To clean the switching valve

- Select the Service button to display the Service screen.
- Select the Maintenance button.
 - Select the Clean Switching Valve button to start the Valve Cleaning Wizard.
 - Follow the steps through the Wizard. The Operating Guide mirrors the Wizard's steps and provides photos to assist the user.

10.3.3 Clean the Air Inlet System Inside of the Mass Transducer Enclosure

The heated air inlet in the TEOM[®] 1405-DF must be cleaned once a year to remove the buildup of particulate matter on its inner walls. A dampened lint-free cloth should be pulled through the heated air inlet, using a wire or hook, to clean it.

Equipment needed

- A piece of plastic or another protective material to protect the TEOM[®] filters
- Soapy water, alcohol or Freon solution
- A 1/2-inch (or adjustable) wrench
- A soft lint-free cloth
- A length of wire

Follow these steps to clean the air inlet system:

1. Turn off the TEOM[®] 1405-DF unit.
2. Open the door of the unit and pull the black insulating cover down from the top of the mass transducer assembly. Locate the thermistors (**Figure 10-5**, left).
3. Using the 1/2" wrench, remove the thermistors from the top of the mass transducer assembly. (Note. The thermistors have short thread depths. Installation and removal should take 1-1/2 to 2-1/2 turns.)
4. Open the mass transducer compartment.
5. Place a piece of plastic or another protective material over the exposed TEOM[®] filters.
6. Using a soapy water, alcohol or freon solution, clean the entire air inlet (shown at right in Figure 10-5). A lint-free cloth may be used to remove particulate matter from the insides of the walls.
7. Allow the air inlet to dry.
8. Remove the protective material from the exposed TEOM[®] filter.
9. Close the mass transducer and latch the latch
10. Install the air thermistors into the cap of the mass transducer assembly and tighten lightly with the wrench.
11. Close and latch the door to the unit. Keep the door open for as short a time as possible to minimize the temperature change in the system.
12. Turn on the TEOM[®] 1405-DF unit.

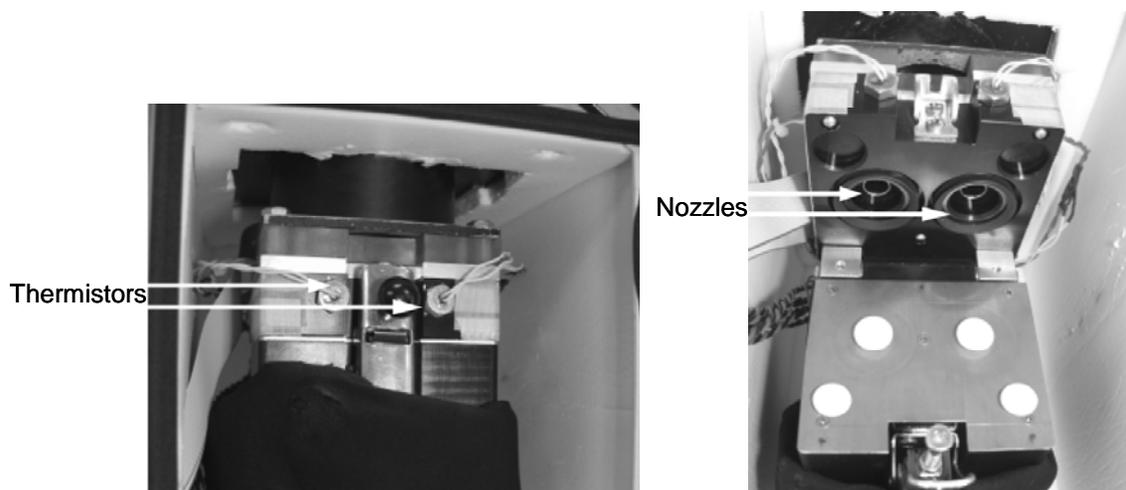


Figure 10-5. Air Inlet containing the Mass transducers, thermistors, and nozzles.

10.3.4 Replace the Dryer(s)

Replace the dryers once every year, or as necessary due to poor performance. Dryer efficiency can be estimated by monitoring the dew point of the sample stream, labeled in the instrument screens and downloads as TEOM[®] A Dryer Dew Point for the fine fraction and TEOM[®] B Dryer Dew Point for the coarse fraction. There are several indications that the dryer operation should be investigated:

- the sample dew point is positive or consistently reads near or within the 2 degrees of the chiller/conditioner set point;
- comparison of the sample dew point to the ambient dew point indicates that the sample dew point is not being controlled;
- the reference mass concentration remains below $-5 \mu\text{g}/\text{m}^3$ over a 24-hr period or the sample dew point shows large fluctuations.
- the data collected from the 1405-DF diverges from the data collected from an FRM sampler.

If the dryer is not working correctly, the 1405-DF may erroneously yield higher FEM $\text{PM}_{2.5}$ concentrations than the $\text{PM}_{2.5}$ data produced from the FRM sampler. The dryer itself may not be the cause of the problem, so a full investigation is warranted. A dryer will not function correctly if the system vacuum is not maintained correctly due to a weak pump or a leak or if the dryer temperature is not maintained appropriately. The system vacuum pressure should be less than approximately 0.4 ATM; typically a new pump would yield a system pressure of slightly greater than 0.2 ATM depending on local atmospheric pressure. The system should be leak free including the dryer purge path. Enclosure temperature and dryer temperature can negatively impact dryer performance. The dryer temperature should be maintained below 30°C , but ideally in the mid- 20° range.

Although no Wizard or instructions are available in the operator's manual, replacing a dryer is a relatively straightforward procedure.

- The sampler should be turned off and disconnected from its power source.
- The front panel of the tower must be removed to access the dryers.
- The dryers are held in place by two Swagelok fittings at the top and the bottom of the dryer; the black vacuum lines on the sides of the dryer; and the control cable which originates on the left side of the dryer. Loosen the Swage-nuts and remove the vacuum tubes from the quick-connect fittings (by pushing in on the retaining ring and then gently pulling on the tubing), and unplug the cable from below to remove the dryer.
- Install the new dryer in its place and tighten the Swage-nuts one quarter turn past hand tight and re-install the vacuum tubes and plug in control cable from the new dryer.
- Re-install the front panel.
- Plug the power cord in and turn the sampler on.

- Perform a leak check.

The sampler will run its stability process and enter into operate mode automatically.

10.3.5 Calibrations

Upon setup and then periodically, the ambient temperature and pressure sensors and flow controllers may require calibration based on the failure of a verification test. The instrument interface provides a Wizard for calibrating the PM_{2.5}, PM-Coarse, and Bypass flows. Although no Wizards are available for ambient temperature and pressure calibrations, they are accommodated via Service > Calibration > Ambient Calibration.

Calibrating the Ambient Temperature

See SOP section 10.1.15 or User's Manual p. 5-44.

Calibrating the Ambient Pressure

See SOP section 10.1.16 or User's Manual p. 5-45.

Calibrating the Flow Rates

Calibration of the PM_{2.5}, PM-Coarse, and Bypass flows is accomplished through the Flow Calibration Wizard (Service > Calibration > Flow Calibration), which leads the user through a 3-point calibration (low, high, set point; see **Table 10-2**) of each of the three system flows.

Table 10-2. Default calibration low, high, and set point flow rates for the 1405-DF PM_{2.5}, PM-Coarse, and Bypass flows.

	Low	High	Set Point
	-----lpm-----		
PM _{2.5}	2.4	3.6	3.0
PM-Coarse	1.3	2.0	1.7
Bypass	9.6	14.4	12.0

The calibration requires a 1-1/4" flow adapter, a 1/2" Swagelok flow adapter, a 3/8" Swagelok flow adapter, and a flow measurement device. The reference flow meter should have been recently calibrated to a primary standard, and should have an accuracy of ±1% at the flow rates of interest (3 lpm and 16.67 lpm) and a pressure drop of less than 0.07 bar (1 psi). If the flow meter does not report volumetric flow rates, the readings must be corrected to volumetric lpm at the current ambient temperature and barometric pressure. To audit the total flow (16.7 lpm), a 1-1/4" flow adapter is required (Figure 9-4). Note that this total flow cannot be calibrated directly, as it is the sum of three distinct flow paths.

To calibrate the fine, coarse, or bypass flow,

- Select the Service button to display the Service screen.
- Select the Calibration button to display the Calibration screen .
- Select the Flow Calibration button to start the Flow Calibration Wizard.
 - Press Next and Select either “Direct Flow Device” or FTS (an orifice-based system that measures flow based on pressure drop).
 - Choose one of the three flow paths to calibrate and complete the Wizard for that flow path. The Wizard will advise at each step.
 - Repeat the calibration steps for the remaining flow paths.

10.3.6 Calibration (K0) Constant Verification

The calibration of the mass transducer in the TEOM[®] 1405-DF Monitor is determined by the mass transducer’s physical mechanical properties. Under normal circumstances, the calibration does not change materially over the life of the instrument. Contact Thermo Scientific if the verification procedure fails. The original calibration constant is located on the “Instrument Checkout Record” or the “Final Test Record” documents that are shipped from the factory with the instrument. Before the TEOM[®] 1405-DF is shipped to the customer, it is calibrated with new, pre-weighed TEOM[®] filters installed in its mass transducer as a calibration weight. Because the mass of the filter cartridge with particulate matter differs from the mass of a new filter cartridge by only a small fraction, calibrating the system with a calibration mass equivalent to the filter mass allows all measurements to be made at essentially the same operating point as the original calibration. To audit/verify the K0 numbers requires a mass calibration verification kit (59-002107), which includes a pre-weighed filter, a filter exchange tool, desiccant and a humidity indicator, and the pre-filter with tubing that was supplied with the unit. Refill kits for the mass calibration verification kit are available from Thermo Scientific (59-002019).

To confirm the system’s K0 calibration,

- Confirm that the PM_{2.5} and PM-Coarse K0 numbers entered into the instrument and the PM_{2.5} and PM-Coarse K0 numbers on the plates on the mass transducer are the same. The K0 numbers entered into the unit can be found in the Audit screen.
- Ensure the instrument is at the normal operating temperature and condition.
- Ensure that the pre-weighed filter in the kit matches the humidity conditions for the test, as shown on the card provided with the kit. If the filter does not match the conditions listed on the humidity indicator, follow the instructions provided with the kit to dry the filter to an acceptable level.
- In the TEOM[®] Data screen, select the Service button to display the Service screen
 - Select the Calibration button to display the Calibration screen
 - Select the Mass Transducer K0 Verification button to start the K0 Verification Wizard.

- Follow the steps in the Wizard.
- The 1405-DF Operating Guide gives details on the K0 calibration process.

10.4 EIGHTEEN-MONTH MAINTENANCE AND QC PROCEDURES: REBUILD THE SAMPLE PUMP

An adequate system vacuum is integral to proper instrument operation; if the pump does not supply adequate vacuum the dryers may not function correctly and the sample filters may over-load prematurely. Rebuild the sample pump once every 18 months, or as necessary (for example, when a poor (high) vacuum pressure reading is indicated on the System Status screen). The pump rebuild kit (p/n 59-008630) contains instructions for rebuilding the pump. Note: A leak, a blocked in-line filter, or exceptionally heavy filter loading could also cause elevated vacuum readings and would not require pump servicing. The pump should be tested with a gauge after rebuilding to determine if it supplies an adequate vacuum; generally the pump pressure should be less than 66% of local pressure.

11. DATA VALIDATION AND QUALITY ASSURANCE

Generally speaking, 40 CFR Part 50 Appendix N (“Interpretation of the National Ambient Air Quality Standards for PM_{2.5}”), 40 CFR Part 50 Appendix L (“Reference Method for the Determination of Fine Particulate Matter as PM_{2.5} in the Atmosphere”), 40 CFR Part 58 Appendix A (“Quality Assurance Requirements for SLAMS, SPMs and PSD Air Monitoring”), and EPA Quality Assurance Guidance Document 2.12 (“Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods”) are all pertinent to data validation and QA protocols for FEM continuous PM_{2.5} monitoring with the 1405-DF. These documents offer extensive details about procedures intended to assure that PM_{2.5} data meet Data Quality Objectives (DQO). In practice, these procedures are based on some basic principles that, if followed diligently, will foster high rates of data capture and minimize the need to invalidate data. These core principles include the field protocols intended to keep the 1405-DF operating in accordance with FEM designation EQPM-0609-182, and with the 1405-DF User’s Manual. The field protocols aid the post-processing data validation and QA protocols, where collected data are judged under DQO criteria.

11.1 FIELD QUALITY CONTROL IMPACTS ON QUALITY ASSURANCE

The first line of defense against invalid data is the implementation of best practices in day-to-day operations affecting the data collection process:

- Understanding of the principle of operation of the equipment
- Acceptance testing of equipment
- Diligence in site selection followed by rigid installation procedures
- Scheduling and implementation of routine maintenance procedures (e.g., inlet cleaning)
- Scheduling and implementation of QC protocols (e.g., flow checks, instrument settings)
- Documentation/reporting of all field QC results and related field activities
- Daily review of real-time data
- Prompt troubleshooting of any observed operational problems

11.2 DATA VALIDATION

Four primary sources of information are directly related to validation of FEM PM_{2.5} data from the 1405-DF: (1) data generated and stored internally in the 1405-DF (the sampling attribute data); (2) the polled data set; (3) the site log information documenting local conditions and equipment operation; and (4) the standardized forms containing results from the periodic maintenance and QC protocols.

11.2.1 1405-DF Generated Sampling Attribute Data

The FEM 1405-DF internal data files should be the source files used for data validation and ultimate submittal to regulatory agencies when possible. Data acquired through an external DAS is extremely useful for real time data applications such as forecasting or daily review of operational status but are subject to the limitations and potential errors described in Section 9.7.2. Analog data should be, at least, spot checked and preferably reconciled against the internal digital data, so it suggested that the data analyst begin with the original digital data. Externally acquired (data logger) digital data proven to be a true replicate of the internally stored data can be used, with special attention to assure that data logger-applied time stamps are accurate. This scenario is becoming more common as agencies switch to real-time digital data acquisition that flows directly into a permanent database. The storage variables presented in Table 9-3 should be downloaded and utilized. Some Service Data cannot be collected through PRC codes or analog outputs so digital data collection is recommended.

11.2.2 Field QC-Generated Sampling Attribute Data

The purpose of periodic flow checks, leak checks, and other QC protocols is to provide quality assurance for the collected data; thus it is essential that the information, both qualitative and quantitative, be transmitted to the data analyst responsible for the data validation process. This information transfer should be prescribed and not left to chance.

11.2.3 Data Validation Criteria

The EPA reference documents mentioned above were originally developed for 24-hr filter-based federal reference method sampling and have been adapted in **Table 11-1** to provide suggested guidelines for data validation criteria pertinent to continuous (hourly) PM_{2.5} monitoring with the TEOM[®] 1405-DF. The table is modeled on a table in Appendix D, “Measurement Quality Objectives and Validation Templates”, of the QA Handbook, Volume II, Revision 1 (December, 2008).

The top panel of Table 11-1 lists the criteria that *must* be met to ensure the quality of the data. Failure to meet any one of these criteria is cause for invalidation, unless there is compelling justification otherwise. One example of such justification would be known wildfires contributing to excessive filter loading. High filter loading can lead to flow perturbations, but these are nonetheless highly valuable data. These criteria include the 45-minute sampling period for hourly data (and extended to 24-hr data), hourly flow rate, sampler status condition codes indicating the following sampler malfunctions (available under PRC 8) power failure (status code 1), voltage low (status code 16) cooler status (status code 32), valve position (status code 64) and dryer status (status code 128) mass transducer A failure (status code 16,777,216). The criteria for invalidation also includes failing results during a monthly flow check or leak check. Note that the leak check failure is set at 0.30/1.2 lpm here but that some agencies may invalidate at other leak rates. Leak checks are performed under a significantly greater vacuum than operating conditions and the location of the leak also determines its effect on data collected.

The bottom panel in the table has criteria that indicate that there *might* be a problem with the quality of the data and further investigation may be warranted before making a determination about sample validity. Example criteria in this category would be failure to perform manufacturer recommended maintenance. In addition, the sampler operation should be examined for over-all reasonable operation. Data should not be invalidated without a documented reason, but subtle operational problems could result in less robust data. For instance, proper system vacuum and dryer operation are necessary for optimal operation and require detailed review to detect. Developing a full data validation protocol is left to the individual agency.

Table 11-1. Critical and operational data validation criteria for PM_{2.5} continuous monitoring with the Thermo Scientific 2405-DF under FEM designation EQPM-0609-182 (top panel).

Criteria		Frequency	Tolerances	Reference
Critical Criteria: These criteria represent the most important sampling attribute data				
Sampling period	Hourly	Hourly	45 minutes	40 CFR Part 50 App L, Sec 3.3
	24-hr	Daily	1080 minutes	40 CFR Part 50 App L, Sec 3.3
Flow	Average Flow Rate	Hourly	±5% of 16.67 lpm	40 CFR Part 50 App L, Sec 7.4; Method 2.12, Sec 10.2
Verification	Single point flow (Reference Std Reading)	Monthly	±5% of Design Flow	40 CFR Part 50 App L, Sec 7.4; Method 2.12, Sec 10.2; 40 CFR Part 58, App A Table A-2
	Single point flow TEOM A (Instrument Flow Reading)	Monthly	±4% of Reference Std Reading	40 CFR Part 50 App L, Sec 9.2.5; 40 CFR Part 58, App A Table A-2
	Leak Check	Monthly	>0.30 lpm TEOM A/B, >1.2 lpm Bypass	Agency specific
Sampler Status	Significant Malfunction Codes	During occurrence	Codes 1,16,64,128, 16,777,216	Manufacturer
Sampling Mode	Out of service code	During occurrence	Codes S, X	Manufacturer

Table 11-1. Critical and operational data validation criteria for PM_{2.5} continuous monitoring with the Thermo Scientific 2405-DF under FEM designation EQPM-0609-182 (bottom panel).

Criteria		Frequency	Tolerances	Reference
Operational Criteria: These criteria represent tolerances when corrective action may be needed to reestablish optimal sampling attributes				
Verification/ Calibration	Leak Check	Monthly	>0.15 lpm TEOM A/B, >0.60 lpm Bypass	Agency specific
	Temperature Verification	Monthly	±2°C	40 CFR Part 50 App L, Sec 9.3; Method 2.12, Sec 6.4
	Temperature Calibration	Yearly or on failed verification	±0.2°C	TEOM 1405-DF Manual, Rev A.003
	Barometric Pressure Verification	Monthly	±10 mm Hg	40 CFR Part 50 App L, Sec 9.3; Method 2.12, Sec 6.5
	Barometric Pressure Calibration	Yearly or on failed verification	±10 mm Hg	TEOM 1405-DF Manual, Rev A.003
	3-Point Flow Calibration	Yearly or on Failed Flow Check	±2%	TEOM 1405-DF Manual, Rev A.003
	Time Verification	Monthly	1 min/month; ensure appropriate time stamp	40 CFR Part 50 App L, Sec 7.4
Cleaning	PM ₁₀ Inlet and Virtual Impactor	Monthly	Cleaned	TEOM 1405-DF Manual, Rev A.003
	Mass transducer air inlet	Yearly	Verified	TEOM 1405-DF Manual, Rev A.003
	Switching Valve	Yearly	Verified	TEOM 1405-DF Manual, Rev A.003
Other Mfg Recommended Maintenance	Rebuild pump	18 Months	Verified	TEOM 1405-DF Manual, Rev A.003
	Replace Dryer	12 Months	Verified, monitor performance over time	TEOM 1405-DF Technical Note
	In-line Filter Element	6 Months	Verified	TEOM 1405-DF Manual, Rev A.003

11.3 HANDLING NEGATIVE MASS DATA ARTIFACTS

Unlike criteria gaseous pollutants, airborne particulate matter (PM) can be heterogeneous. For example, it can consist of one or more elements (heavy metals such as lead and cadmium, carbon, minerals), inorganic compounds (salts), and semi-volatile components (organic carbon, secondary aerosols such as nitrates and sulfates, water). Particles can also exist in solid form, liquid form, or a mixture of both. PM is often hygroscopic, demonstrating an affinity for water at ambient relative humidity (RH) of 75-80% or higher, but stubbornly retaining that bound water

until experiencing a RH of less than 30-35%. In general, fine particles (such as PM_{2.5}) are more volatile than coarse particles. It is this complex characteristic that can lead to profound difficulty in the consistent quantification of PM air pollution. The challenge is to provide a measure of PM under well-defined thermodynamic conditions (temperature, pressure, filter face velocity, relative humidity).

Whether using a continuous monitor such as the TEOM[®] instrument or a gravimetric sampler, there always are filter dynamics occurring. When particles are collected on a sample filter their mass may be influenced by interaction with airborne gases (such as acid gases or water vapor) or other particles in the sample air stream, or possibly by the filter media. The thermodynamic conditions of the sample air stream and surrounding the sample filter influence the degree to which these ongoing reactions may occur. All of these processes define filter dynamics and may result in a positive or negative sampling artifact component of the PM mass concentration. The higher the time resolution of the PM measurement system the better the PM mass concentration change resulting from filter dynamics can be observed. The Filter Dynamics Measurement System (FDMS[®]) facilitates quantifying these dynamics, however, the precision of hourly TEOM[®] PM data is about $\pm 1.5 \mu\text{g}/\text{m}^3$. So, it is reasonable to expect some small hourly negative values (0 to $-5 \mu\text{g}/\text{m}^3$) when the true mass concentration is very low (0 to $5 \mu\text{g}/\text{m}^3$). This is not uncommon during rain events, for example. Overall, hourly mass concentration values should not routinely be lower than about $-10 \mu\text{g}/\text{m}^3$. As general guidance, small negative hourly values should be considered "clean" conditions and reported. When used to produce daily averages, all hourly values (both positive and negative) should be averaged using equal weighting. This is consistent with the physicochemical understanding of PM provided earlier.

Negative mass concentration numbers indicated by the TEOM[®] monitor can be the result of the nature of particles described above or, possibly, the result of an instrument fault. Thus, it is important to first rule out a malfunction of the monitor or instrumentation setup. Malfunctions may include system interruption due to a temporary power failure, TEOM[®] filter exchange without placing the instrument in "set-up mode", flow control or vacuum pump system fault, or failure of an electronics component (such as frequency counter board). Generally, instrument faults will produce relatively large negative spiking in the mass concentration data. Erratic mass concentration data (many positive and negative spikes) can also be indicative of an instrument problem. It is advisable to also make use of site log notes to investigate further if the suspect data points were a result of a site visit for maintenance, audit, or other reasons.

11.4 DATA VALIDATION STEPS

Table 11-2 lists suggested sequential steps, their components, and specific procedures for validating continuous PM_{2.5} mass data collected with the 1405-DF under FEM designation EQPM-0609-182.

Table 11-2. Data validation steps for TEOM 1405-DF FEM PM_{2.5} data.

Validation Step	Component	Procedure
Verify Data Source	Digital: Direct Download	Download .csv format file
	Digital: Data Logger	Collect Service Data and Data file with Concentrations (PM _{2.5} , PM ₁₀ & PM-Coarse; Ref MC and Base MC), System Status, Ambient Temperature, Ambient Humidity, Ambient Pressure, Bypass Volumetric Flow, Vacuum Pump, TEOM A Flow Rate, TEOM A Filter Loading, TEOM A Total Mass, TEOM A Noise, TEOM A Dryer Temperature, TEOM B Flow Rate, TEOM B Filter Loading, TEOM B Total Mass, TEOM B Noise, TEOM B Dryer Temperature (if 30 storage variables available add TEOM A frequency, TEOM B frequency. If FEM PM _{2.5} concentration is added in new firmware version, collect it.
		Compare time stamp to internal data
		Analog: Data Logger
	Compare concentration to internal data ($\pm 1 \mu\text{g}$)	
Compare time stamp to internal data		
Review TEOM 1405-DF Attribute Data	Convert Status Codes to Hexadecimal Number	Determine each status code present and if significant fault occurred (decimal status codes 1; 16; 32; 64; 128; 16,777,216)
	Check sampling mode	Codes S (setup) and X (stop-all) indicate the sampler is out of service and not in operational mode
	Flow rates	Fine flow within tolerance of 5% of 3.0 lpm; Coarse flow within tolerance of 5% of 1.67 lpm; Total flow within tolerance of 10% of 16.67 lpm
	Elapsed time	1080 minutes
	Average total flow (sum of fractions)	$\pm 5\%$ of 16.67 lpm
	Sample volume	Within tolerance of 23-25 m ³
	Temperature and Pressure readings	Average, Max, Min for reasonableness
Review Field QA	Flow checks	$\pm 4\%$ of transfer standard lpm, compare each of 3 flow fractions to standard
	Leak checks	> 0.6/1.2 lpm, invalidate back to last passing leak check
	Calibration	3-point flow cal every 12-months verified

Table 11-2. Data validation steps for TEOM 1405-DF FEM PM_{2.5} data.

Validation Step	Component	Procedure
Maintenance procedures	Inlet/Virtual Impactor cleaning	Verify
	Annual K0 test	Verify
	Switching Valve cleaning	Verify
	Dryer Replacement*	Verify
	Cooler cleaning	Verify
	Air Inlet (sample train) cleaning	Verify
	Sample pump rebuild	
Periodic component tests	Test: Filter T and RH, Chiller Operation, Dryer Efficiency, Analog DAC	Verify

12. DIAGNOSTICS AND TROUBLESHOOTING

The Thermo Scientific 1405-DF Manual provides a troubleshooting overview (Rev A.003, App A) explaining the error status codes recorded. In addition, Wizards in the user interface (firmware) provide troubleshooting guidance.

13. REFERENCES

- U.S. Environmental Protection Agency (1998) Quality assurance guidance document 2.12: Monitoring PM_{2.5} in ambient air using designated reference or Class I equivalent methods. Prepared by the Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, Research Triangle Park, NC, November.
- U.S. Environmental Protection Agency (2006a) Probe and monitoring path siting criteria for ambient air quality monitoring, 40 CFR Part 58, Appendix E.
- U.S. Environmental Protection Agency (2006b) Reference method for the determination of fine particulate matter as PM_{2.5} in the atmosphere, 40 CFR Part 50, Appendix L.
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- U.S. Environmental Protection Agency (2008b) Quality assurance requirements for SLAMS, SPMs, and PSD air monitoring, 40 CFR Part 58, Appendix A.
- U.S. Environmental Protection Agency (2008c) Quality assurance handbook for air pollution measurement systems, Volume II: ambient air quality monitoring program. Prepared by the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Air Quality Assessment Division, Research Triangle Park, NC, EPA-454/B-08-003, December.



AIR QUALITY SURVEILLANCE BRANCH

STANDARD OPERATING PROCEDURES

FOR

**Rupprecht & Patashnick Co., Inc.
Partisol-Plus Model 2025 Sequential Air Sampler
(R&P Sequential FRM)**

AQSB SOP 404

First Edition

MONITORING AND LABORATORY DIVISION

January 2003

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1.0 GENERAL INFORMATION

1.1 Introduction:

The purpose of these Standard Operating Procedures (SOP) is to supplement the manufacturer's Operator's Manual by describing modifications in hardware or procedures that may have been implemented by the Monitoring and Laboratory Division of the Air Resources Board. These modifications are designed to assure compliance with the Federal Reference Method for collection of particulate matter 2.5 microns or smaller (PM_{2.5}) when using the Rupprecht & Patashnick (R&P) Partisol-Plus Model 2025 PM-2.5 Sequential Air Sampler.

1.2 General Description and Principles of Operation:

The Partisol-Plus 2025 Sequential Air Sampler is designed to meet the EPA requirements for PM_{2.5} sampling. The samplers filter magazines have a capacity of 16 filters. The sampler is fully microprocessor controlled. The sampler's internal datalogger can store 16 days of 5 minute data, 50 filter data records, and 32 days of 30 minute data.

Read Section 1 of the R&P Operating Manual and see Figure 1.2: System Schematic.

1.3 Safety Precautions:

Installation, operation, maintenance, and calibration of the sampler should only be performed by properly trained personnel. High (120 volts A.C.) voltages are used to power the unit. Due to typical rooftop installations, the risks of working outdoors at elevation should also be considered.

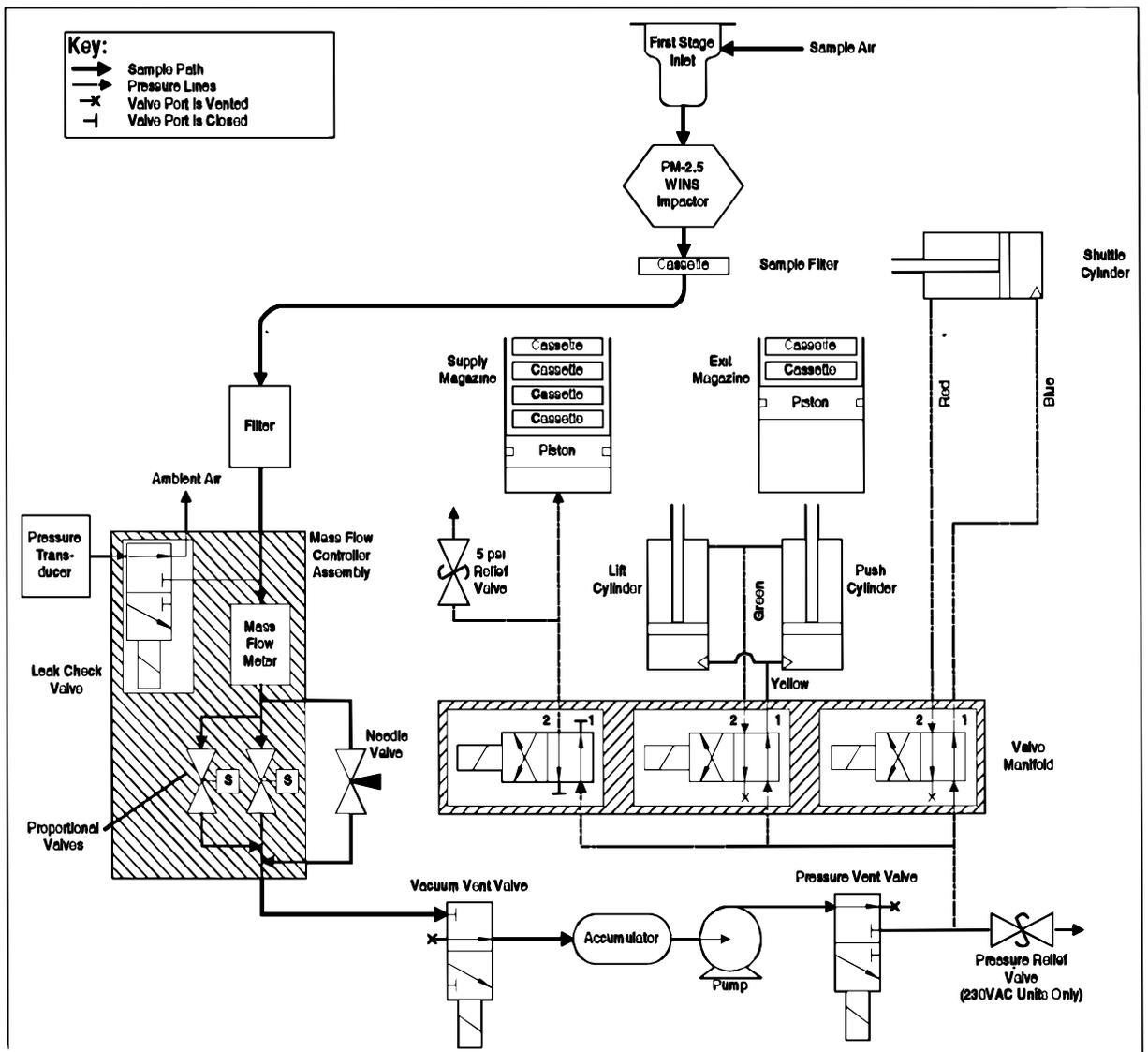


Figure 1. System Schematic.

2.0 INSTALLATION PROCEDURE

2.1 Physical Inspection:

Each R&P Partisol-Plus Model 2025 PM-2.5 Air Sampler should be supplied with the following supplies:

- 1 Partisol-Plus enclosure with WINS PM-2.5 impactor and filter exchange mechanism
- 1 1st stage PM10 Inlet
- 1 sample tube
- 3 rain hoods and associated hardware
- 1 flow audit adapter
- 3 filter cassette magazines
- 3 magazine transport containers
- 1 ambient temperature sensor and cable
- 3 sets of impactor wells and anti-spill rings
- 2 sets of inlet O-rings
- 1 bottle (100 milliliters (ml)) of WINS impactor oil
- 1 bottle (30 milliliters (ml)) of WINS impactor oil
- 3 box (25 count) of glass fiber impactor filters, 37 millimeter (mm)
- 1 AKCOMM software diskette
- 1 9-to-9 pin computer cable
- 2 Operating Manuals
- 2 Service Manuals
- 1 Quick Start Guide
- 1 cassette bulb pump
- 1 leak check plate
- 1 stand assembly
- 1 cassette removal sleeve

Upon receipt of the sampler(s), inspect sampler and accessories for shortage and for shipping damage. If shortage or damage is found, immediately notify your supervisor, and/or your agency's shipping department.

2.2 Rain Hood Installation:

There are three rain hoods that must be attached to the sampler. Attach the gaskets to the rain hoods by peeling the paper backing off of the gaskets and apply the gaskets to the appropriate rain hood. Install the rain hoods with the included thumbscrews. The two small rain hoods are interchangeable.

2.3 Temperature Sensor Installation:

Remove the phillips screws on the upper left side of the sampler. Use these screws to mount the temperature sensor. When mounting the temperature sensor, insert the washer and gasket between the sensor bracket and the enclosure, not under the head of the screw (see figure 2). Plug the three-pin connector into the connection marked "Ambient Temperature" on the back of the sampler.

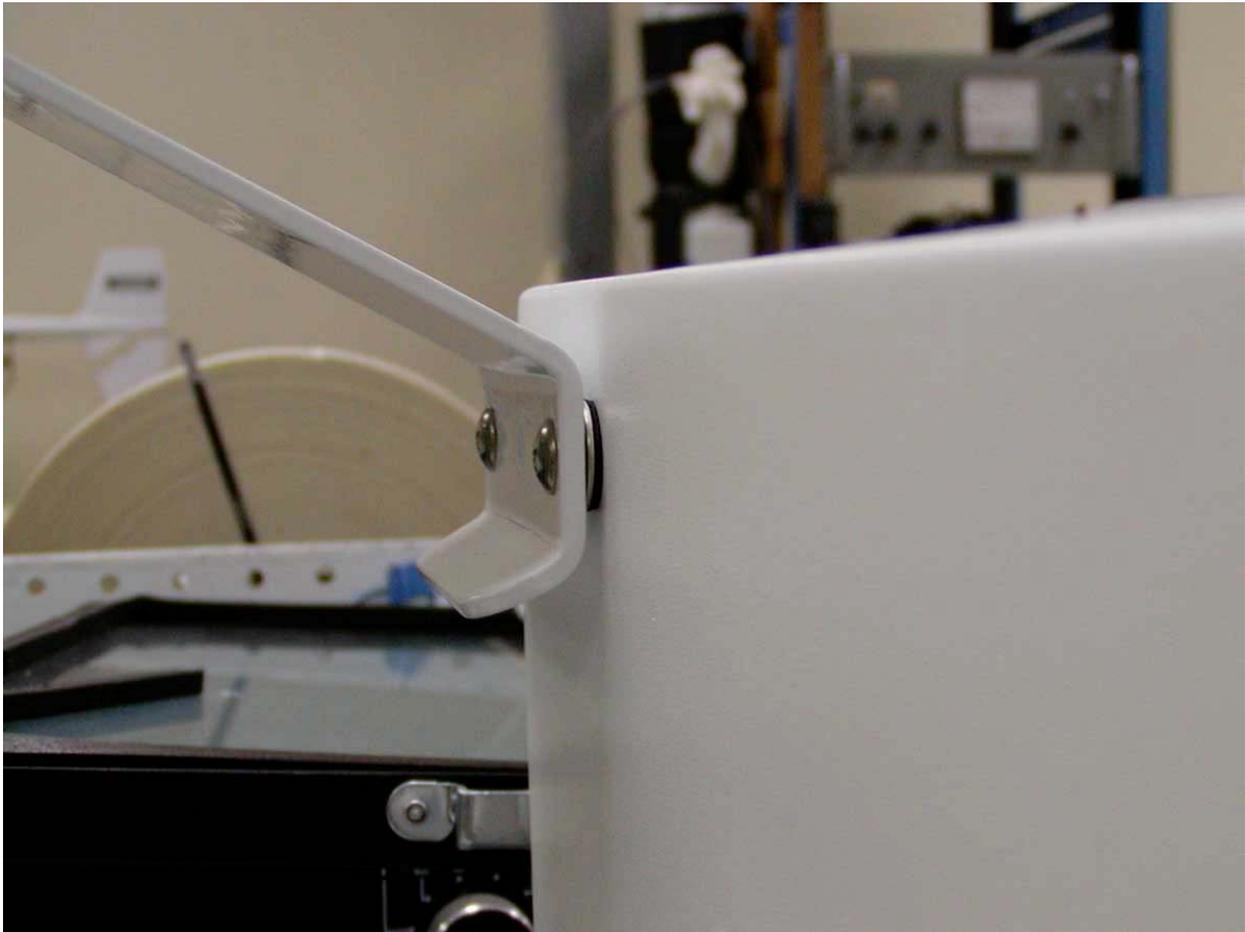


Figure 2. Ambient Temperature Sensor Installation.

2.4 WINS Impactor Installation:

Open the top cover of the sampler. Remove the WINS impactor by pulling it upwards. Unscrew the middle section of the impactor to expose the well. Remove the 37 mm filter if present and wipe down the well with a paper towel until there is no visible residual oil. Insert a new 37 mm filter and place 42-44 drops of impactor oil onto the filter. Reassemble the impactor and reinstall. Close and latch the top cover.

2.5 Very Sharp Cut Cyclone (VSCC) Installation:

Open the top cover of the sampler. Remove the WINS impactor if present. Install the VSCC by pushing it down completely on the mounting tube. Close and latch the top cover.

2.6 1st Stage Inlet Installation:

Insert the 1 ¼" OD sample tube into the instrument bulkhead. Ensure that the tube is pushed past both the lower and upper o-rings until it stops. Tighten the dome connector to ensure a tight and leak-free grip. Place the first stage inlet onto the tube. Make sure the inlet is inserted past the first and second o-rings until it stops.

2.7 Stand Assembly:

Follow the stand assembly diagram included with the sampler. The diagram can be found on page 2-5 in the operator's manual or in the quick start guide.

2.8 Supply Magazine Loading and Installation:

Obtain an empty magazine from its transport case. Remove the orange cap on the supply magazine. Use the bulb pump to move the piston in the supply magazine to the top of the magazine. The top of the piston should be level with the top edge of the canister. Detach the bulb pump from the magazine. Place one filter cassette on the piston and push it down until the top of the cassette is level with the top of the magazine. Repeat with additional filter cassettes if loading multiple filters. Note the order of filter placement from top to bottom for future reference. Replace the orange cap when finished to protect the filters from contamination. Place the magazine back in the transport case for transport to the site.

Open the sampler door to access the filter transport assembly. The left magazine mount is the supply side (clean filters). The right mounting position is the storage side (loaded filters). Remove the orange cap on the magazine. Align the grooves on the top of the cassette with the mounting studs on the left

mounting ring. Mount the magazine so that the hose connection faces outward. Push the magazine upward and twist counterclockwise to lock it in place. Connect the air supply tube to the supply (left) canister by pushing it onto the connector until it snaps into place. See Figure 3.

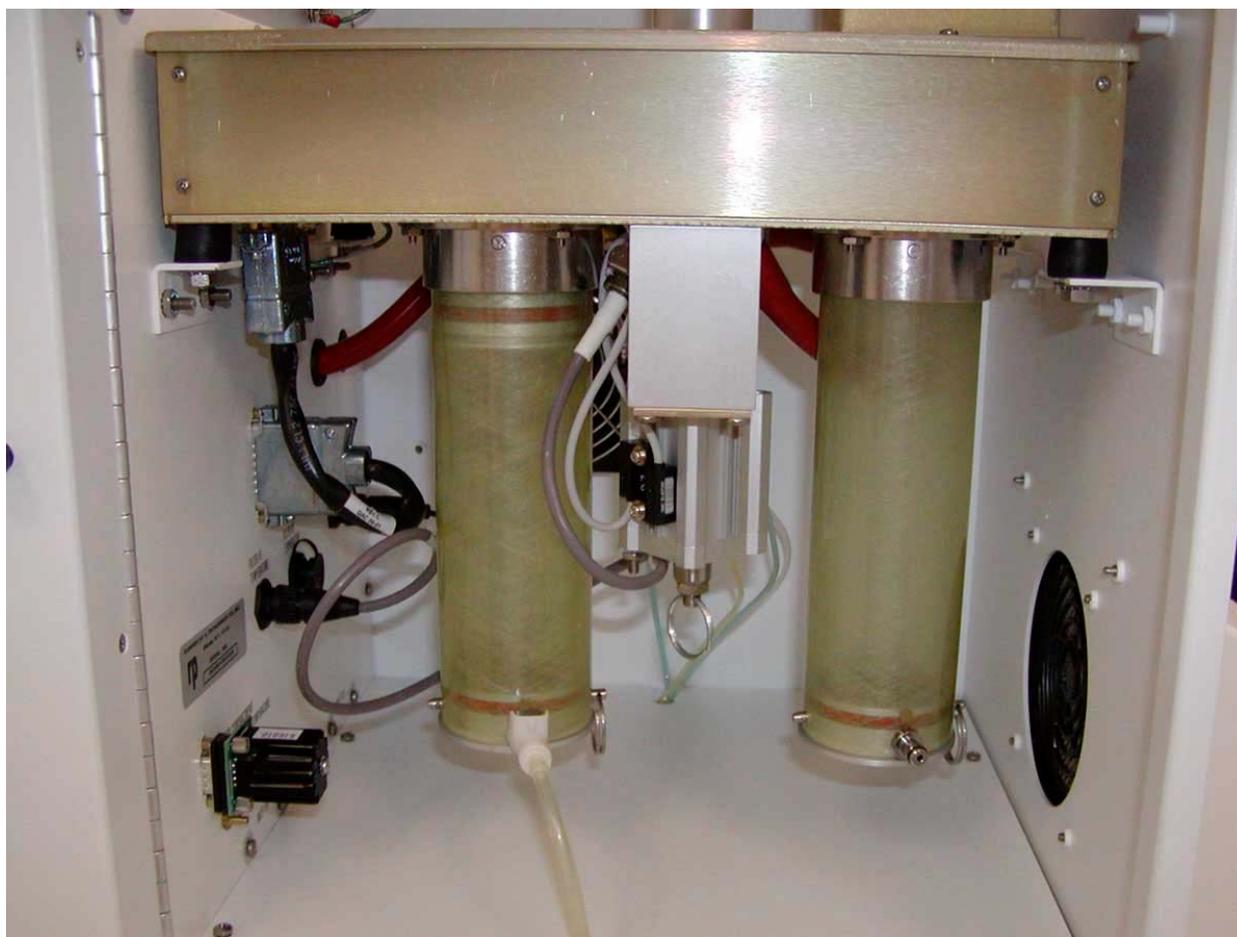


Figure 3. Sampler Compartment Layout.

3.0 CONFIGURATION

3.1 Sampling Train Operating Principles:

The sampling train transfers cassettes between parts of the sampling chamber at different times depending on the state of the sampler. If the sampler is placed into run mode from stop mode, the filter in the sampling position will move to the storage canister and the next filter in the supply canister will move into the sampling position at the sampling start time. In run mode, the sampler moves the sampled filter into the storage magazine at the end of the run. The next sampling filter is moved into the sampling position. When the next scheduled run starts the filter is already in place and no movement of filters occurs. If the sampler is set to run mode from audit mode, the sampler begins sampling with the filter currently in sampling position. Knowing the sampler's filter transport cycles is essential to avoiding sampling on the incorrect filter.

3.2 Main Screen and Menu Screen:

Most setup functions can be reached from the main screen on the sampler display. The exception is the service mode screen, which must be selected at the menu screen. To get to the main menu, press <Esc> until the main screen is reached. <Esc> can also be used to go back one screen. Pressing the <Menu> key at any time accesses the menu screen.

3.3 Clock and Time Setup:

Enter the main screen. Press <F5:Setup> to enter the Setup menu. Press <F5:System> to enter the system screen. Move the cursor to the "Curr Time" field and press <edit> to change the time. Move the cursor to the "Curr Date" field and press <edit> to change the date. The default date format is yy/mm/dd. Use the default date format. There may be software issues with other date formats.

3.4 Average Time Interval Setup:

The Average Time parameter in the System Setup field defines the time interval that is averaged by the sampler when storing data. 30 minute averages are the default.

3.5 Site Identification Setup:

Press <F3: Site ID> in the "System Setup" screen to enter the site identification screen. "ID1" and "ID2" can be edited to identify the site and sampler.

3.6 Resetting Status Codes:

Press <F2:Stats> in the main screen. The current and average values for temperature and pressure will be displayed. Pressing <F1:StCode> will bring up the status code display. Pressing <F1:Reset> will reset the status of the sampler and clear the error states.

3.7 Sample Set-up Procedures:

The following steps describe procedures for programming the R&P Partisol-Plus Model 2025 PM-2.5 Air Sampler for a sampling run. A loaded filter cassette must be installed prior to starting the sample run.

1. Place the sampler in the Stop operating mode (the right corner of screen shows STOP). Press <Run/Stop> to put sampler in STOP mode.
2. Press <F5:Setup> from the main screen.
3. Select the “BASIC” sample definition method. Set the sampling start time, sampling duration, repeat time, filter type, flow rate, flow error mode, and separator. Pressing <F2: Set EPA> programs settings for EPA FRM PM2.5 setting on a 1/1 schedule. If parameters other than the default settings are desired, use the arrow keys to move the cursor to the desired parameter and press <Edit> to change a parameter. The repeat time defines the time period in which the stored program repeats. It should be changed to 72 hours for 1:3 sampling and 144 for 1:6 sampling. Flow Error Mode “ERR” stops all sampling after a flow error code. Flow Error Mode “WAIT” stops sampling on flow errors and resumes sampling on the next programmed run.
4. Verify the “Set Flow” parameter is set to 16.7 lpm.
5. Press <ESC> to return to the main menu. Press <F3:FiltSet> to set the start date for the next run. The sampling program will repeat at the interval specified in the Setup menu.
6. Prepare a supply canister. Note the AIRS and LIMS numbers for each filter in the order that they are inserted in the canister, going from top to bottom.
7. In the “Filter Setup” menu press <F4:FilterLst>. Enter or verify that the site AIRS Number is in the ID1 field. Enter Filter LIMS Number (sample barcode number) in the ID 2 field. These values will be attached as a header to all data files pertaining to the associated sampling run. Press <ENTER> to accept information. Repeat for all the filters in the sampler. The entries should be done with the top filter in position 1 and the following filters in 2, 3, etc. **(Note: The Filter LIMS Number will need to be entered for each sampler run.)**

8. Press <ESC> key to return to main menu. Press <Run/Stop>. The “Mode:” flag in the right corner will display WAIT. The instrument is now in the wait mode and will begin sampling when the programmed start time is reached.

3.8 Resetting Memory:

Turn the sampler off and on. The sampler will display a startup screen before entering the main screen of the display. In the startup screen, press <F5: Reset>, then <F4: Yes> to reset the memory.

WARNING: RESETTING THE MEMORY ERASES ALL CALIBRATION AND SAMPLER SETTINGS AND RESTORES ALL SETTINGS TO DEFAULT VALUES. RESETTING THE MEMORY ERASES ALL STORED RUN DATA. USE THIS OPTION ONLY WHEN NECESSARY. RECORD ALL CALIBRATION OFFSETS BEFORE RESETTING TO AVOID RE-CALIBRATING THE SAMPLER AFTER RESET.

<F1: Rdfault> resets all sampler settings to the default values while retaining the run data stored in the internal datalogger. <F2: Rdata> deletes all stored run data in the internal datalogger while retaining the sampler settings.

4.0 DATA RETRIEVAL

4.1 General Information:

Field personnel will have the responsibility of ensuring the PM2.5 sampling information for each filter run is properly retrieved. The sampling information for the FRM samplers can be obtained either manually or electronically.

To manually record data, field personnel will complete a CARB 24-Hour Sample Report-Field Data Sheet, Appendix B (see attachment). The sample report will contain all information required by 40CFR58 Appendix L, Table L-1.

Electronic data can be downloaded via an RS-232 data output connection through which digital data will be exported to and external data storage or transmission device.

4.2 Manually Record Data:

Press <F4:Data> from the main screen. The data for the latest sampling period will be displayed onscreen. Other sampling runs can be accessed by pressing <F1:-Rec> and <F2:+Rec>. Additional data can be accessed by pressing <F3:MoreDat>, <F4:IntvDat>, or <F4:InptDat> in the Interval data screen. Record sample information in appropriate locations on the sample data sheet. After recording data, return to the main menu by pressing <ESC>.

4.3 Electronic Data Download Setup:

The Partisol-Plus Model 2025 PM2.5 Air Samplers have serial communications ports that can be used to communicate to PC's, modems, and printers. The Partisol-Plus Model 2025 PM2.5 Air Samplers communications use 8-N-1 protocol (8 stop bits, no parity, 1 stop bit). The default baud rate is 9600. However, the samplers are capable of communications over a large baud rate. The primary way to download data from the samplers is via laptop PC with RPSComm. Data can also be downloaded using a terminal program such as hyperterminal but is not recommended.

4.4 Apparatus:

1. Laptop PC with communications software, terminal program, or RPSComm software.
2. Serial cable with D-9 male plug with female pins on one end and a D-9 female plug with male pins on the other. The serial cable must be a "straight through" cable.

4.5 Download Procedure (Using RPComm):

1. Section 10 of the operator's manual contains detailed instructions for using the RPComm software. This procedure only outlines the necessary steps for a simple download. Refer to the manual for instruction on the advanced features of the RPComm software.
2. Connect the serial cable from the PC to the serial port on the sampler.
3. The sampler can be in any mode when using RPComm to download data. The RS232 port on the sampler must be set to AK protocol. AK protocol is the 2-way communication format for RPComm communication with R&P samplers. From the main screen press <F5: Setup>, then <F5: System>, then <F2: I/O>, then <F1: A/I>, and then <F3: RS232> to change the RS232 protocol.
4. Start RPComm. If a connection has not been defined for the Partisol-Plus 2025, create a connection. Choose New Connection from the file menu. Choose the 2025 sampler from the menu, and press the settings button. Make sure the software is set to 9600 baud, 8-N-1. See Section 10.2.2 in the operators manual for more information. Once a connection has been created, select the Connection Icon in the tool bar. A 2025 window should pop up with the serial number of the sampler at the top of the window if the connection is successful. If the 2025 window does not have a serial number, recheck the connection settings and try again.
5. To download data, select the download data tab. Set the storage pointer to the appropriate place if necessary (see section 10.2.3 in the operators manual for more information) and then select the appropriate data set icon in the menu bar. Select either the "Download all data" or "download from storage pointer" icon to begin the download. See section 10.2.3 "Downloading Stored Data" for more information.
6. The RPComm software has many other features designed specifically for the 2025, including a virtual keypad and the ability to define filter lists for the sampler. See section 10 "Direct Communications Using RPComm" for additional information.

4.6 Download Procedure (Using Hyperterminal):

1. Connect the serial cable from the PC to the serial port on the sampler.
2. Open hyperterminal or another terminal program and configure it to operate using the N-8-1 protocol and baud rate set on the sampler (default value 9600). Enable the text logging capability of the software package.

3. The RS232 port communication protocol must be set to “AK” to download the data for a completed run manually. From the main screen press <F5: Setup>, then <F5: System>, then <F2: I/O>, then <F1: A/I>, and then <F3: RS232> to change the RS232 protocol. Refer to sections 9.2 to 9.5 in the manual for more details on the parameter settings and their functions. The “protocol” parameter should be changed to AK. Press <Esc> to go back to the main screen. Press <F4: Data> to enter the filter data screen. Use the <F3: MoreDat> and <F4> keys to navigate to the desired data. Press the <F5: DwnLoad> button to begin downloading data. Pressing <F5: DwnLoad> before the transfer is complete interrupts the download. The event summary information is found in the filter data set.
4. The terminal window of the communications software should show the data being transmitted.
5. After transmission is completed, disable the file capture capability of the communications software to close the capture file. Disconnect serial cable from the sampler and PC. Return the sampler to the main menu.
6. The data is downloaded as a comma-separated text file. Most commercial spreadsheet programs can convert these files to spreadsheets.
7. The downloaded data from hyperterminal contains no data headers. The order of the data can be found in sections 9.3-9.5.

5.0 DATA SUBMITTAL (Field to Laboratory)

5.1 General Information:

Once field personnel have retrieved sampling information either manually or electronically, the data will be forwarded to the laboratory. If the sampling information was recorded manually, the CARB 24-Hour Sample Report-Field Data Sheet will accompany the sampled filter(s) to the laboratory. If the sampling information was recorded electronically, the sampling information will be sent to the lab via file transfer protocol. An abbreviated 24-Hour Sample Report-Field Data Sheet will still accompany the sampled filter(s) to document chain-of-custody and additional sampling information.

5.2 Sample Chain-of-Custody:

The chain-of-custody process begins once the filter is pre-conditioned and inspected by laboratory personnel. After pre-conditioning is complete, filters will be pre-weighed, placed in filter rings and prepared for shipping. Each filter will be associated with a bar code number that will be attached to a 24-Hour Sample Report-Field Data Sheet (Appendix B). Laboratory personnel will annotate the pre-weight of the filter, date and initials on the 24-Hour Sample Report-Field Data Sheet. The sample report sheet and filter will be shipped to the field. Within 30 days of pre-conditioning, the filter will be used for sampling. When the filter is loaded on the sampler, field personnel will document the date, time, and name of person loading the sampler. After sampling, field personnel will document date, time and name of personnel removing the sample from the sampler. The temperature of the filter will also be documented at this time. If the filter is not being shipped to the laboratory right away, the filter will be placed in a refrigerator for storage until shipping. Field personnel will document date, time and filter temperature when the filter is placed in refrigerator. When the filter is shipped to the laboratory, the date, time, filter temperature and personnel shipping the filter will be documented on the sample report. When the filter arrives at the laboratory, the date, time, filter temperature and person receiving the filter will be noted on the sample report. Laboratory personnel will then enter the filter information into the Laboratory Information Management System (LIMS). LIMS will generate a LIMS sample identification number that will be documented on the sample report. The filter will then be prepared for post conditioning or placed in a refrigerator for storage until post-conditioning. The date, time, filter temperature and name of analyst will be documented once post-conditioning begins.

6.0 SAMPLE FILTER HANDLING PROCEDURES

6.1 General Information:

Federal regulations stipulate specific time frames and environmental conditions for FRM PM_{2.5} sample filters at various stages in the sampling program. If these time frames and conditions are not met, sample filters may be flagged or invalidated by the receiving laboratory. In addition to these requirements, operators should practice the usual care to prevent or minimize contamination of the sample filters, filter cassettes, or anything else which may come in contact with the sample filters.

6.2 Presampling Filter Handling Procedures:

Sample filters must be used within 30 days of the preweighing procedure. Sample filter temperature must be within 5 °C of ambient temperature while installed in the sampler.

6.3 Post sampling Filter Handling Procedures:

Sampled filters must be removed from the sampler within 96 hours of the end of sampling and placed in cold storage as soon as practical.

Sampled filters must be kept at a temperature of less than 4 °C during storage and shipping which allows the laboratory up to 30 days from the end of sampling for analysis. If this temperature is exceeded but is kept at no greater than 25 °C, the laboratory has up to 10 days to analyze.

The storage environment will have its temperature constantly monitored and recorded.

Sampled filters and CARB 24-Hour Sample Report-Field Data Sheets will be shipped in an insulated shipping container containing sufficient Blue Ice or other chilled media to assure that sample filters arrive at the laboratory at a temperature no greater than 25 °C or preferably 4 °C. Other methods may also be employed if they comply with these requirements.

Shipping containers will contain a min/max thermometer, temperature data logger, irreversible temperature indicators (3M, 5 °C and 26 °C) or other suitable means to determine whether temperature requirements of the sample filters have been exceeded during transit. This requirement also applies when sampled filters are being transported from remote or satellite sites to central or main locations.

Sampled filters will be shipped to the laboratory weekly on Monday, Tuesday, Wednesday or any other day that avoids Saturday or Sunday arrivals as well as assures a short as possible transit time.

6.4 Filter Blank Handling Procedures:

Upon receipt and identification of filter blanks, treat these filters the same as filters to be sampled with the exception that they will not be used to collect samples. They are to be installed in the sampler for the same time period as a filter sample, stored in a cooler and returned to the laboratory with the sampled filters. Fill out the CARB 24-Hour Sample Report-Field Data Sheet with exception of run data and submit with rest of sample reports.

7.0 CALIBRATION OVERVIEW

7.1 Introduction:

This section describes the calibration procedure for the Rupprecht & Patashnick Partisol-Plus Model 2025 PM-2.5 Air Sampler (R&P PM2.5 FRM). The procedures listed are in reference to the R&P FRM Operating Manual and are not intended to replace the operating manual.

7.2 Overview:

The calibration of the fine particulate matter samplers whose mass has an aerometric diameter of less than 2.5 microns (PM2.5) must be performed on a six month basis. There are several parameters that must be calibrated with this new generation of fine particulate matter samplers. These parameters include flow or volume, temperature, pressure and time.

The calibration procedure in Section 3 of the R&P Service Manual is fairly complete, accurate and easy to follow. The primary purpose of the verification/calibration is to determine and/or verify that the volumetric flow of the PM2.5 sampler is at 16.67 liters per minute (LPM), or that the sampler collects a volume of 1 cubic meter of air per hour. Refer to 40 CFR Part 50, Appendix L for further information.

7.3 Apparatus for R&P PM2.5 FRM Sequential Channel Sampler Calibration:

- NIST-traceable flow transfer standard
- NIST-traceable temperature standard
- NIST-traceable pressure standard
- R&P inlet flow adapter
- Calibration forms or laptop computer
- Empty filter cassette
- Leak check filter cassette with filter
- Leak check plate and filter cassette

8.0 CALIBRATION PROCEDURE

8.1 General Information:

The calibration of the R&P PM2.5 FRM sampler should be performed in the following steps:

1. Temperature sensor calibrations
2. Pressure calibration
3. Leak test
4. Flow calibration
5. Verify calibration parameters

All calibration information and data will be recorded on the Calibration Data Sheet (Appendix C).

8.2 Ambient Temperature Sensor Calibration:

Press <Esc> until the sampler is in the Main Screen. The device must be in the “Stop” Operating Mode to perform an ambient temperature sensor calibration.

1. Press <Menu> and select “Enter Service Mode”, then choose “calibration/audit” when in the Service Menu to access the calibration screen. Press <F3: SensCal>.
2. Place the reference thermometer in the radiation shield of the ambient temperature probe. Determine the current temperature in °C at the ambient temperature sensor using the reference thermometer.
3. Use the arrow keys to move the cursor to the Actual column in the “Amb Temp” row. Hit <Edit> to change the entry.
4. Enter the current temperature in °C and press <ENTER> to leave the edit mode.
5. Upon receiving the actual temperature, the system’s microprocessor automatically computes the offset for the ambient temperature sensor.

8.3 Filter Temperature Sensor Calibration:

1. Press <Menu> and select service mode, then choose “calibration/audit” when in the Service Menu to access the calibration screen. Press <F4: FiltCal>.
2. Remove the filter temperature probe and place it in close proximity to the reference thermometer. Determine the current temperature in °C at the location of the sample filter in the FRM using the reference thermometer.

3. Use the arrow keys to move the cursor to the Actual column in the “Filter” row. Hit <Edit> to change the entry.
4. Enter the current temperature in °C and press <ENTER> to leave the edit mode.
5. Upon receiving the actual temperature, the system’s microprocessor automatically computes the offset for the filter temperature sensor. Note this number for future reference.

8.4 Filter Compartment Temperature Sensor Calibration:

1. Press <Menu> and select service mode, then choose “calibration/audit” when in the Service Menu to access the calibration screen. Press <F4: FiltCal>.
2. Place the reference thermometer in close proximity to the filter compartment sensor. Determine the current temperature in °C at the location of the filter compartment temperature sensor in the FRM using the reference thermometer.
3. Use the arrow keys to move the cursor to the Actual column in the “Filter Comp” row. Hit <Edit> to change the entry.
4. Enter the current temperature in °C and press <ENTER> to leave the edit mode.
5. Upon receiving the actual temperature, the system’s microprocessor automatically computes the offset for the filter temperature sensor. Note this number for future reference.

8.5 Barometric Pressure Calibration:

1. Press <Menu> and select service mode, then choose “calibration/audit” when in the Service Menu to access the calibration screen. Press <F3: SensCal>.
2. Determine the current ambient barometric pressure in mm Hg with the NIST-traceable pressure standard.
3. Use the arrow keys to move the cursor to the Actual column in the “Amb Pres” row. Press the <Edit> key to change the entry.
4. Enter the current pressure in mm Hg and press <ENTER> to leave the edit mode.
5. Upon receiving the actual pressure, the system’s microprocessor

automatically computes the offset for the ambient pressure sensor. Note this number for future reference.

8.6 Leak Check:

Before verifying/calibrating the flow of the sampler it is important to ensure that the sampling train does not have a leak. Internal and External leak checks should be performed. Additional information can be found in sections 12.1.5 and 12.1.7 in the operator's manual.

8.7 External Leak Check:

1. Insert the leak check filter cassette into the supply filter magazine. This cassette should contain a filter and the support screen.
2. If the sampler is in "Run" mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in "Stop" mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. If the sampler is in "Audit" mode, press <Menu> and choose the audit selection. Press <F4:FiltAdv> to place the leak check cassette in the sampling chamber.
3. Remove the PM10 inlet and place the flow audit adapter on the sample tube. Close the adapter inlet.
4. Press <F5: LeakChk> to display the leak check screen.
5. Choose "external" for the type.
6. Press <F2: Start> to begin the leak check.
7. Press <F1:External> to start the external leak check sequence.
8. Press <F1: Yes> at the "Filter in place" screen.
9. Follow the onscreen instructions. The sampler will display either a pass or fail message when complete as well as a pressure drop value.
10. If fail is displayed, check the leak check cassette for filter holes or malfunctions and repeat the test. If it fails again, the unit needs servicing.
11. If a "pass" message is displayed, slowly open the valve on the flow audit adapter and replace the PM10 inlet.
12. Record the leak rate on the calibration worksheet.

8.8 Internal Leak Check:

1. Prepare a leak check cassette by inserting the leak check plate into a filter cassette. This cassette should only contain the leak check plate. No filter or screen should be in the cassette.
2. Insert the leak check cassette into the supply magazine.
3. If the sampler is in "Run" mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in "Stop" mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. If the sampler is in "Audit" mode, press <Menu> and choose the audit selection. Press <F4:FiltAdv> to place the leak check cassette in the sampling chamber.
4. Press <F5: LeakChk> to begin the leak check.
5. Select <F2: Internal> to start the internal leak check sequence.
6. Press <F1: Yes> at the "Cassette in place" screen.
7. Follow the onscreen instructions. The sampler will display either a pass or fail message when complete as well as a pressure drop value.
8. If a fail message is displayed, check the leak check cassette and repeat the test. If it fails again, the unit needs servicing.
9. If "pass" is displayed, slowly open the valve on the flow audit adapter and replace the PM10 inlet.
10. Record the leak rate on the calibration worksheet.

8.9 Flow Rate Calibration:

The flow rate of the R&P PM2.5 FRM sampler must be 16.67 LPM to correctly select particulate matter smaller than 2.5 microns in diameter. The purpose of the flow rate calibration is to ensure that the sampler draws the correct volumetric air flow rate. Section 3.2.8 of the R&P PM2.5 FRM Service Manual discusses the sampler flow calibration. The sampler must be in the STOP mode to perform a calibration. The R&P PM2.5 FRM sampler is flow rate calibrated by testing the flow rate at 3 points using a NIST-traceable flow meter.

1. Carefully remove the PM10 inlet from the sampler.
2. Install a filter cassette into the supply cassette.

3. Enter the service mode by pressing the <Menu> key and selecting the “Service Mode” option. Select the “System Maintenance Routines” and press <F1: Audit>. Press <F4: FiltAdv> to place the leak check filter cassette into the filter chamber.
4. Return to the Service Menu. Select the “Calibration/Audit” option.
5. Display the Flow Calibration Screen by pressing <F5:FlowCal>.
6. If using a Streamline FTS flow transfer standard, enter the m and b constants of the FTS into the “Const m” and “Const b” parameters.
7. Remove the PM10 inlet and place the transfer standard onto the sample tube.
8. Edit the desired minimum and maximum flow rates as well as the number of calibration points desired using the arrow and edit keys.
9. Press <F5: More> and then <F4: Start> to begin sampling.
10. Wait for the flow to stabilize. Press <Edit> and enter the pressure drop (inches H₂O) if using the Streamline FTS in the “pressure” parameter, or enter the volumetric flow in the “Act. Flow” parameter if using another standard. Press <Enter>. The sampler will move on to the next calibration point. Repeat this step until the sampler has completed all the points.
11. Once all points have been complete, the sampler will adjust the Offset and Span values automatically.
12. Remove the flow transfer standard and reinstall the PM10 inlet.

8.10 Clock/Timer Verification:

Units of time are used in several aspects of sampler operation. Examples are the start and stop times, volume/flow calculations, run dates, etc. Therefore, it is necessary to document the time setting of the sampler.

Observe the sampler time from the Main Screen. Enter this value onto the calibration data sheet. At the same time, enter the value of your time keeping device. Identify your time keeping device on the calibration data sheet.

Include the make, model, ID number, date last certified, and bias of your clock.

The requirement in 40 CFR Part 50, Appendix L, Section 7.4 states that the sampler must not lose more than 1 minute per month.

If the sampler is off by more than ± 10 minutes from true time, reset the system

clock.

To reset the clock, from the Main Screen select <F5: Setup>, then select <F5: System>. Enter the correct time to ± 1 minute from true. Enter the corrected time on your calibration data sheet.

Enter all data on the appropriate datasheets and record any repairs or changes for future reference.

9.0 VERIFICATION PROCEDURES

9.1 General Information:

If the sampler is in "Run" mode and is currently sampling, do not use place the sampler into "Stop" mode. Placing the sampler in "stop" mode will result in the loss of the current sampling event. All of the following verification procedures can be done in the "Audit" mode that allows the user to resume the sampling event.

9.2 Ambient Temperature Sensor Verification:

1. Press <Esc> until the sampler is in the Main Screen. The device should be in the Audit Operating Mode to perform ambient temperature sensor verifications.
2. If the sampler is in "Run" mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in "Stop" mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. In Audit mode, press <Menu> and choose the audit selection.
3. Place the reference thermometer in the radiation shield of the ambient temperature sensor. Determine the current temperature in °C at the ambient temperature sensor using the external thermometer.
4. Verify that the value for the temperature displayed as Ambient Temp in the Audit Screen is within ± 2 °C of the external thermometer.

If the ambient temperature sensor reading is not within ± 2 °C of the external thermometer, the ambient temperature sensor must be re-calibrated. Follow the steps in section 8, Calibration Procedures for more information.

9.3 Filter Temperature Sensor Verification:

1. Press <Esc> until the sampler is in the Main Screen. The device must be in the Audit Operating Mode to perform the ambient temperature sensor verification.
2. Remove the filter temperature sensor by releasing it from the quick release. Place the reference thermometer as close as possible to the temperature sensor and allow them to equilibrate.
3. Determine the current temperature in °C at the location of the sample filter in the FRM.

4. Verify that the value for the temperature displayed as Filter Temp in the Audit Screen is within ± 2 °C of the external thermometer.
5. If the filter temperature sensor reading is not within ± 2 °C of the external thermometer, the filter temperature sensor must be re-calibrated. Follow the steps in section 8, Calibration Procedures for more information.

9.4 Filter Compartment Temperature Sensor Verification:

1. Press <Esc> until the sampler is in the Main Screen. The device must be in the Audit Operating Mode to perform the ambient temperature sensor verification.
2. If the sampler is in “Run” mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in “Stop” mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. In Audit mode, press <Menu> and choose the audit selection.
3. Determine the current temperature in °C at the location of the filter compartment sensor in the FRM using the external thermometer. The sensor is clearly labeled and is located along the inner left wall of the compartment.
4. Verify that the value for the temperature displayed as Filter Comp Temp in the Audit Screen is within ± 2 °C of the external thermometer.
5. If the filter temperature sensor reading is not within ± 2 °C of the external thermometer, the filter temperature sensor must be re-calibrated. The calibration procedure can be found in section 8, Calibration Procedures.

9.5 Barometric Pressure Verification:

1. Press <Esc> until the sampler is in the Main Screen. The device must be in the Audit Operating Mode to perform a barometric pressure sensor calibration verification.
2. If the sampler is in “Run” mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in “Stop” mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. If the sampler is in “Audit” mode, press <Menu> and choose the audit selection.
3. Determine the current ambient barometric pressure in mm Hg.
4. Verify that the value for the “Ambient Pres” parameter in the Audit Screen is within ± 10 mmHg of the measured ambient pressure.
5. If the sampler ambient pressure is not within ± 10 mmHg of the measured

ambient pressure, the barometric pressure sensor must be re-calibrated. The calibration procedure can be found in section 8, Calibration Procedures.

9.6 Leak Check:

Before verifying/calibrating the flow of the sampler it is important to ensure that the sampling train does not have a leak. External leak checks should be performed during the verification procedure. Additional information can be found in sections 12.1.5 and 12.1.7 in the operator's manual.

9.7 External Leak Check:

Insert the leak check filter cassette into the supply filter magazine. This cassette should contain a filter and the support screen.

1. If the sampler is in "Run" mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is in "Stop" mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. If the sampler is in "Audit" mode, press <Menu> and choose the audit selection. Press <F4:FiltAdv> to place the leak check cassette in the sampling chamber.
2. Remove the PM10 inlet and place the flow audit adapter on the sample tube. Close the adapter inlet.
3. Press <F5: LeakChk> to display the leak check screen.
4. Choose "external" for the type.
5. Press <F2: Start> to begin the leak check.
6. Press <F1:External> to start the external leak check sequence.
7. Press <F1: Yes> at the "Filter in place" screen.
8. Follow the onscreen instructions. The sampler will display either a pass or fail message when complete as well as a pressure drop value.
9. If fail is displayed, check the leak check cassette for filter holes or malfunctions and repeat the test. If it fails again, the unit needs servicing.
10. If a "pass" message is displayed, slowly open the valve on the flow audit adapter and replace the PM10 inlet.
11. Record the leak rate on the appropriate worksheet.

9.8 Flow Rate Verification:

Press <Esc> until the sampler is in the Main Screen. The device must be in the Audit Operating Mode to perform a flow rate calibration verification.

1. If the sampler is in "Run" mode, press <Run/Stop> and place the sampler in audit mode. If the sampler is already in "Stop" mode, press <menu> and choose service mode. In the service menu, press <F1: Audit>. In Audit mode, press <Menu> and choose the audit selection.
2. Install the filter cassette containing a 47 mm filter into the supply filter magazine.
3. Press <F4: FiltAdv> to place the a filter cassette into the flow path. This cassette should contain a filter and the support screen. Select the "Calibration/Audit" option.
4. Carefully remove the PM10 inlet from the sampler.
5. Attach the transfer standard to the sampler.
6. If the Streamline FTS flow transfer standard is being used, enter the m and b of the standard in the "Const m" and "Const b" on the display.
7. Turn on the pump by pressing <F1: Pump>, and then turn on the sample flow valve by pressing <F2: Valve>.
8. Determine the flow in units of actual (volumetric) LPM using the flow rate verification device. If the Streamline FTS is being used, enter the pressure drop in inches of H₂O in the "FTP Pres" selection. The calculated volumetric flow will be displayed in the "FTS flow" parameter.
9. Verify that the value for the flow rate displayed in the Flow Rate field of the Audit Screen is within $\pm 4\%$ of the flow rate verification device.
10. If the flow rate reading is not within $\pm 4\%$ of the flow rate verification device, a flow rate calibration must be performed.
11. Finish the flow check by Pressing <F2: Valve> and then <F1: Pump> to shut off the flow. Remove the transfer standard and install the PM10 inlet.

10.0 ROUTINE SERVICE CHECKS

10.1 General Information:

See section 11 of this document "Maintenance Procedures" and Appendix G of the Operator's manual "Maintenance of Inlets" for further routine service check information.

10.2 Daily Checks:

After each run, review summary data for compliance with Measurement Quality Objectives for FRM PM_{2.5}. Complete and return the sample report form with the appropriate filter. Inspect WINS impactor and clean if necessary. See section 11.4 "PM_{2.5} WINS Impactor Maintenance" in this document for more information.

10.3 Weekly Checks:

Inspect the water trap on the PM₁₀ inlet and empty if necessary. Ship sampled filters.

10.4 Bi-Weekly Checks:

Perform flow verification checks. The flow rate should be within $\pm 4\%$ of the transfer standard.

10.5 Monthly Checks:

1. Disassemble, clean and inspect PM₁₀ inlet.
2. Check the o-rings and replace if necessary on the PM₁₀ inlet.
3. Check "V" seals at the top and bottom WINS impactor junctions.
4. Clean interior compartment and the sample downtube.
5. Clean or replace air intake filters.
6. Clean VSCC inlet.
7. Perform temperature sensor verifications for both the filter and ambient sensors. The sensors should be within ± 2 °C of the transfer standard. Perform pressure sensor verification. The pressure sensor should be within ± 10 mm Hg of the transfer standard.

8. Perform a clock and date verification check. The clock should be within ± 10 minutes of the time standard and the date should be correct. Record results for all verification procedures. Perform leak check and record results.

10.6 Semiannual Checks:

Clean the screens under the rainhoods. Check the particle trap filter and replace as necessary. Perform temperature, pressure, flow, and clock calibrations.

11.0 MAINTENANCE PROCEDURES

11.1 General Information:

Read the operators manual for more detailed information regarding sampler maintenance.

11.2 Sampler Maintenance:

The sampler should be wiped down with a clean wet cloth when required. Clean the filter compartment with a wet cloth when required. Clean the sampler downtube as necessary. Check "V" seals and replace when necessary. See operators manual, section 3.1.5. "Inspect V Seals" for more information.

11.3 PM10 Inlet Maintenance:

Clean the PM10 inlet as necessary. Refer to section G.1. in the operators manual for further instructions.

11.4 PM2.5 WINS Impactor Maintenance:

Determining the state of the WINS impactor requires removing the impactor and examining the particulate cone in the impactor well. If the cone is more than 2 cm tall or the if the top of the cone has broken off the WINS impactor needs cleaning to minimize re-entrainment of particles larger than 2.5 microns. Refer to section G.3. for further instructions on the cleaning procedure.

11.5 VSCC Maintenance:

The VSCC should be cleaned once a month. Disassemble the entire VSCC and clean with a kimwipe or compressed air. Check all o-rings for wear or damage and replace if necessary.

12.0 TROUBLESHOOTING

12.1 General Information:

If review of the R&P Operating Manual does not result in correction of the problem, notify your area engineer, specialist, and/or repair facility technician.

12.2 Filter Cassette Problems:

Using the proper filter cassettes is critical in this sampler. If the wrong filter cassettes are used, the sampler will jam. The proper filter cassettes have a beveled edge along the top outer rim of the ring. If the edges of the filter cassettes are unbeveled, contact the laboratory for replacements.

CALIFORNIA AIR RESOURCES BOARD
MONTHLY QUALITY CONTROL MAINTENANCE CHECK SHEET
R&P PARTISOL-PLUS MODEL 2025 PM-2.5 AIR SAMPLER

Site Name: _____ Month/Year: _____
 Site Number: _____ Sampler I.D. Number: _____
 Agency: _____ Sampler Serial Number: _____
 Operator: _____ Primary, Collocated, Audit, or Other: _____

Maintenance Instructions for Daily Sampling:

- After Each Run: Remove sampled filter; Download, record, and review sample data; Inspect WINS impactor and clean if necessary; Install new sample filter; Program sampler for next run.
- Weekly: Inspect water collector bottle and drain if necessary; Ship sampled filters along with the sample data to the originating laboratory.
- Monthly: Disassemble, clean, and inspect O-rings of PM10 inlet; Clean interior cabinet and downtube; Clean or replace air intake filters; Inspect "V" Seals; Perform flow, temperature, pressure, and clock verification checks and record results; Perform leak check and record results. DATE LAST PERFORMED: _____
 FORWARD THIS CHECK SHEET AND COPIES OF ALL SAMPLE FIELD DATA SHEETS TO SECOND LEVEL REVIEWER.
- Semiannually: Perform flow, temperature, and pressure calibrations; DATE LAST PERFORMED: _____

Results

ACTION	Indicated	Actual	Sampler	% Difference	Control Limits*
Flow Rate					16.50 to 16.83 L/min
Ambient Temp.					±2 °C
Ambient Press.					±10 mm Hg
Filter Temp.					±2 °C
Clock Time					±1min/mo
Leak Check					<25 mm Hg

*If check exceeds limits, investigate to determine cause and repeat check at later time or date.
 If second check also exceeds limits, request a re-calibration.

Standards

Standard	Make/Model	Serial/I.D.Number	Date Certified	Slope	Intercept
Flow Rate					
Temp.					
Pressure					
Clock					

Appendix A. Monthly Quality Control Maintenance Check Sheet

CARB 24 Hour – FIELD SAMPLE REPORT
Federal Reference Monitor (FRM) PM 2.5 Samplers

Bar Code: _____
LIMS Sample ID: _____

Site Name: _____
 AIRS Site Number: _____
 Field Technician: _____
 Agency: _____

Cassette I. D. Number: _____
 Scheduled Sampling Date: _____
 Sampler Property #: _____

SAMPLE SUMMARY

Start Date / Time: _____ / _____
 Total Elapsed Time: _____ Hr:min
 Volume: _____ M³
 Flow CV: _____ %

	MIN	AVG	MAX
Ambient Temp(°C):			
Filter Temp (°C):			
Pressure (mmHg):			

Local Condition Codes: _____

Sampler Flag Codes: _____

A. High Winds	E. Forest Fire
K. Farming Nearby	J. Construction Nearby
N. Sanding/Salting Streets	L. Highway Construction
P. Roofing Operations	Q. Prescribe Burn

F. Flowrate 5-min average, out of spec	T. Filter Temp differential, 30 minutes interval out of spec
E. Elapsed sample time, out of spec	

Operator Comments: _____

Chain of Custody

ACTION	DATE	TIME	FILTER TEMP °C	NAME
Sample Load				
Sample Removal				
Sample placed in freezer				
Sample shipped to Lab				
Sample received at Lab				
Start post-conditioning				

FOR LABORATORY USE ONLY

	Mass:	Dup Mass:	Date:	Analyst:
Postweigh by: _____	Preweight			
	Postweight			

Lab Comments:	

Appendix B. PM2.5 Field Data Sheet

R&P Partisol-Plus 2025 PM2.5 Sampler

ID Information:

Station Name:	Sacramento	Make:	R&P
ARB Station Number:	xxxx	Model #:	Model 2025
Station Address:	1927 13th St	Property #:	20020022
Agency:	ARB	Serial #:	5524
Operator:			

Calibration:

"As Is"	X
"Final"	X
Calibration Date:	04/15/02
Report Date:	04/15/02
Prev. Cal. Date:	NA

Pressure/Temperature STD:

Make & Model:	BGI Deltacal
Property Number:	20020853
I.D. #:	981133
Cert. Date:	01/29/98
Cert. Exp.:	01/01/00

Time Standard:

Make & Model:	Casio
Identification No.:	
Cert Date:	

Time:	Sampler:	Standard:
Date:	3/7/01	3/7/01
Hours:Minutes:Secs	10:30:00	10:28:48

Temperature: (deg. C)			Differ. from True:	% Difference	Span	Offset
Ambient	23.5	23.7	0.2	0.84	1.02	2.2
Filter	25.1	24.8	-0.3	-1.21	1.05	1.5

Pressure: (mm Hg)			Differ. from True:	% Difference	Span	Offset
Ambient	760	761	1.0	0.13	1	1.01

Leak Test: (LPM)	Pressure Drop (mm Hg)
External	10.0
Internal	10.0

Target Volumetric Flow (LPM)	Sampler Display:	Transfer Standard Display:	Volumetric Flow vs Design Flow: (+/- Percent)	Volumetric Flow vs Sampler Display (+/- Percent)	Span	Offset
15	15.00	15.02	0.00	-0.13	2.3	0.85
16.7	16.70	16.80	0.00	-0.60	2	0.9
18	18.00	17.90	0.00	0.56	2.5	0.7

Comments:			
Calibrated by:	MPQ	Checked by:	

Appendix C. R&P Sequential FRM Calibration Worksheet

1.0 GENERAL OPERATIONS

1.1 Purpose of Procedure

This standard operating procedure describes the operation of the Micro-Orifice Uniform Deposit Impactor (MOUDI) for the collection of suspended particulate matter on substrates which are amenable to different chemical analyses. The MOUDI is a cascade impactor which allows air to be drawn through a series of micro-orifice nozzles; particles with different aerodynamic diameters are collected onto a series of impaction plates.

1.2 Measurement Principle

The principle of operation of MOUDI is the same as any inertial cascade impactor with multiple nozzles. At each stage, jets of particle-laden air are impinged upon an impaction plate and particles larger than the cut size of each stage are collected on the impaction plates. Smaller particles with less inertia follow the air streamlines and proceed onto the next stage. The nozzles of each succeeding stage are smaller than the prior stage, giving a higher velocity through the nozzles, and a smaller particle size cut. The air flow continues through a series of eight impactor stages until the smallest particles are removed by the after-filter.

The basic sampler is an eight-stage cascade impactor operated at a flow rate of 30 liter per minute (lpm), controlled by a ball valve downstream of the sampler. The specifications for the MOUDI Model 100 series Units A and B are given in Tables 1-1 and 1-2. The 50% cut points are 0.105, 0.148, 0.37, 0.54, 1.0, 1.8, 3.2, 5.6, and 15 μm . Nominal collection efficiency curves for a typical MOUDI sampler are shown in Figure 1-1. For this study, only the four smallest stages will be analyzed.

1.3 Measurement Interferences

The micro-orifice nozzles in the lower stages are quite small and can become partially clogged due to particle deposition by impaction or Brownian/turbulent diffusion. This could cause an increase in pressure drop. Periodic cleaning is required to minimize particle deposition.

Particle bounce between the nozzle plates and impaction plate may become significant after a long sampling period (i.e., 24 to 48 sampling hours). Material collected on the impaction plate can become re-entrained in the air flow. Circular patterns of deposit corresponding to air flow streamlines around the nozzle jets may be observed after each sampling period. The nozzle plates should be cleaned with a methanol-soaked Kim Wipe prior to each sample loading.

Parameterized and Measured
Stage Efficiencies for MOUDI

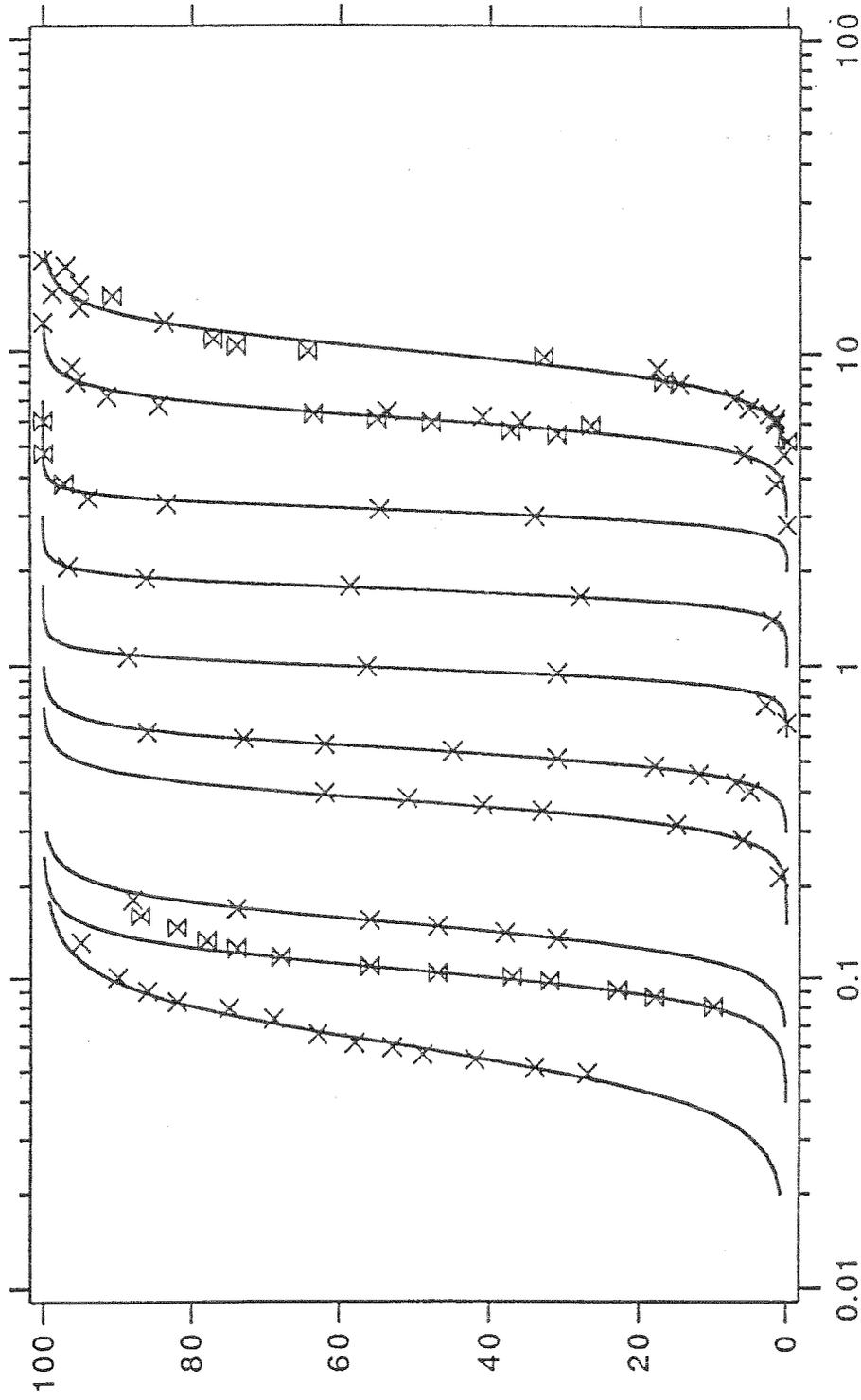


Figure 1-1. Nominal Collection Efficiency Curves.

Title: Micro-Orifice Uniform Deposit
Impactor (MOUDI) Field and
Laboratory Operations

Table 1-1

Desert Research Institute MOUDI Specifications for Unit A

Model No. 100 (Unit A)

Serial No. MDI-011

Flow rate: 30 lpm

Pressure reading:

Upper gauge - 13.1 inch water

Lower gauge - inch water

Particle aerodynamic diameter 50% cut-points

Inlet cut-point:	15	μm
Stage 1	5.6	μm
Stage 2	3.2	μm
Stage 3	1.8	μm
Stage 4	1.0	μm
Stage 5	0.54	μm
Stage 6	0.37	μm
Stage 7	0.148	μm
Stage 8	0.105	μm
37 mm after-filter		

DRI STANDARD OPERATING PROCEDURE

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Title: Micro-Orifice Uniform Deposit
Impactor (MOUDI) Field and
Laboratory Operations

Table 1-2

Desert Research Institute MOUDI Specifications for Unit B

Model No. 100 (Unit B)

Serial No. MDI-012

Flow rate: 30 lpm

Pressure reading:

Upper gauge - 13.3 inch water
Lower gauge - inch water

Particle aerodynamic diameter 50% cut-points

Inlet cut-point:	15	μm
Stage 1	5.6	μm
Stage 2	3.2	μm
Stage 3	1.8	μm
Stage 4	1.0	μm
Stage 5	0.54	μm
Stage 6	0.37	μm
Stage 7	0.148	μm
Stage 8	0.105	μm
37 mm after-filter		

1.4 Ranges and Typical Values

The range of concentrations measured by this method is limited by the sensitivity of the analysis instrument and the standard deviation of the values obtained by the dynamic blank.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

For mass concentration, the typical lower quantifiable limit is $1.0 \mu\text{g}/\text{m}^3$ for 6-hour sampling. The precision is calculated from replicate laboratory analyses and flow rate performance tests. This precision is generally within $\pm 10\%$ for mass concentrations greater than $1.0 \mu\text{g}/\text{m}^3$. Accuracy is generally within the measurement precision.

1.6 Responsibilities

The field technician is responsible for carrying out this standard operating procedure and for the completion and submission of all documents.

The field operations supervisor is responsible for scheduling the field technician's visits, reviewing documentation, identifying and correcting deficiencies, and receiving samples from and transmitting samples to the laboratory.

The laboratory supervisor is responsible for preparing samples, transmitting them to the field, and receiving them from the field.

1.7 Definitions

- Nozzle Plate: Metal plate with 10 to 2,000 nozzles machined by computerized mechanical drilling. The number and diameters of the nozzles determine the particle cut size of each impaction stage.
- Impaction Plate: Metal plate downstream of the nozzle plate which holds the filter/foil substrate by means of a metal clamping ring. The impaction plate is magnetically secured on top of each impactor stage. It serves to collect particles from nozzle jets from the stage above.

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- Rotator: The device for rotating the impactor stages to provide a uniform deposit. It consists of an electric motor connected to a shaft with sprocket gears.
- Cascade Impactor: The basic assemblies of MOUDI which consists of eight impaction stages, plus an inlet and an after-filter located in the base.
- Goose-neck Inlet: U-shaped brass tube which connects the MOUDI inlet with the rotameter. It is used to check the total flow rate through the system. A bug screen is used to cover the upper part of the inlet.
- Denuder: The devices are attached to the inlet. The nitric acid denuder uses parallel plates of anodized aluminum to remove gaseous nitric acid and the organic vapor denuder uses parallel strips of prefired quartz fiber filter material to remove organic material that may adsorb on the quartz after filter.

1.8 Related Procedures

- DRI SOP # 2-102.2 Gravimetric Analysis Procedures
- DRI SOP # 2-202.2 Extraction of Ionic Species from Filter Samples
- DRI SOP # 2-203.2 Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
- DRI SOP # 2-207.2 Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetric Analysis
- DRI SOP # 2-208.2 Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy
- DRI SOP # 2-204.3 Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples

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2.0 APPARATUS, INSTRUMENTATION, SUPPLIES, AND FORMS

2.1 Instrumentation

2.1.1 MOUDI Unit

The MOUDI consists of three basic assemblies: a gas denuder (for either nitric acid or organic carbon vapor), the cascade impactor and the rotator. A schematic diagram of a typical MOUDI stage is shown in Figure 2-1. Each impactor stage consists of an impaction plate for the stage above it and a nozzle plate for the stage below.

The rotator unit, which rotates the stages to provide a uniform deposit on the impaction plate substrate, consists of an electric motor connected to a shaft with sprocket gears. These sprocket gears mesh with four ring gears which have been pressed onto the bodies of four alternate stages of the cascade impactor as shown in Figure 2-2. As the gear motor drives the sprocket gears, the stages with the ring gears are rotated. The stages which do not rotate are equipped with a ring and a pin which rests against the drive shaft of the rotating unit to prevent their rotation. By rotating alternate stages of the impactor and holding the others stationary, every nozzle plate/impaction plate will have relative rotation. Thus, only alternate stages need to be rotated to provide a uniform deposit on the substrate of the impaction plate.

The rotator also houses with two pressure gauges. The upper gauge monitors the pressure drop across stages 1 to 4 to provide an indication of the flow rate through the impactor. The lower gauge monitors the pressure drop across the final stage. A flow rate of 30 lpm from the inlet through the cascade impactors is achieved with a GAST 1022 pump. A ball valve downstream of the MOUDI unit is used to adjust the flow rate. A timer box with two elapsed time meters is equipped with both MOUDI units. In operation, the timer sends a current at a pre-specified time to activate the pump for sampling.

2.1.2 Impaction Plate Holder

A filter/foil substrate is loaded on top of each impactor plate and clamped into the holder by a metal clamping ring. Each impaction plate is capped with a blue color metal cover. The sealed cover minimizes evaporative loss or any contamination of the sample during storage. A set of eight impaction plates with an after filter cassette is secured by a metal holder which consists of two 2x2 inch metal plates and four long screws.

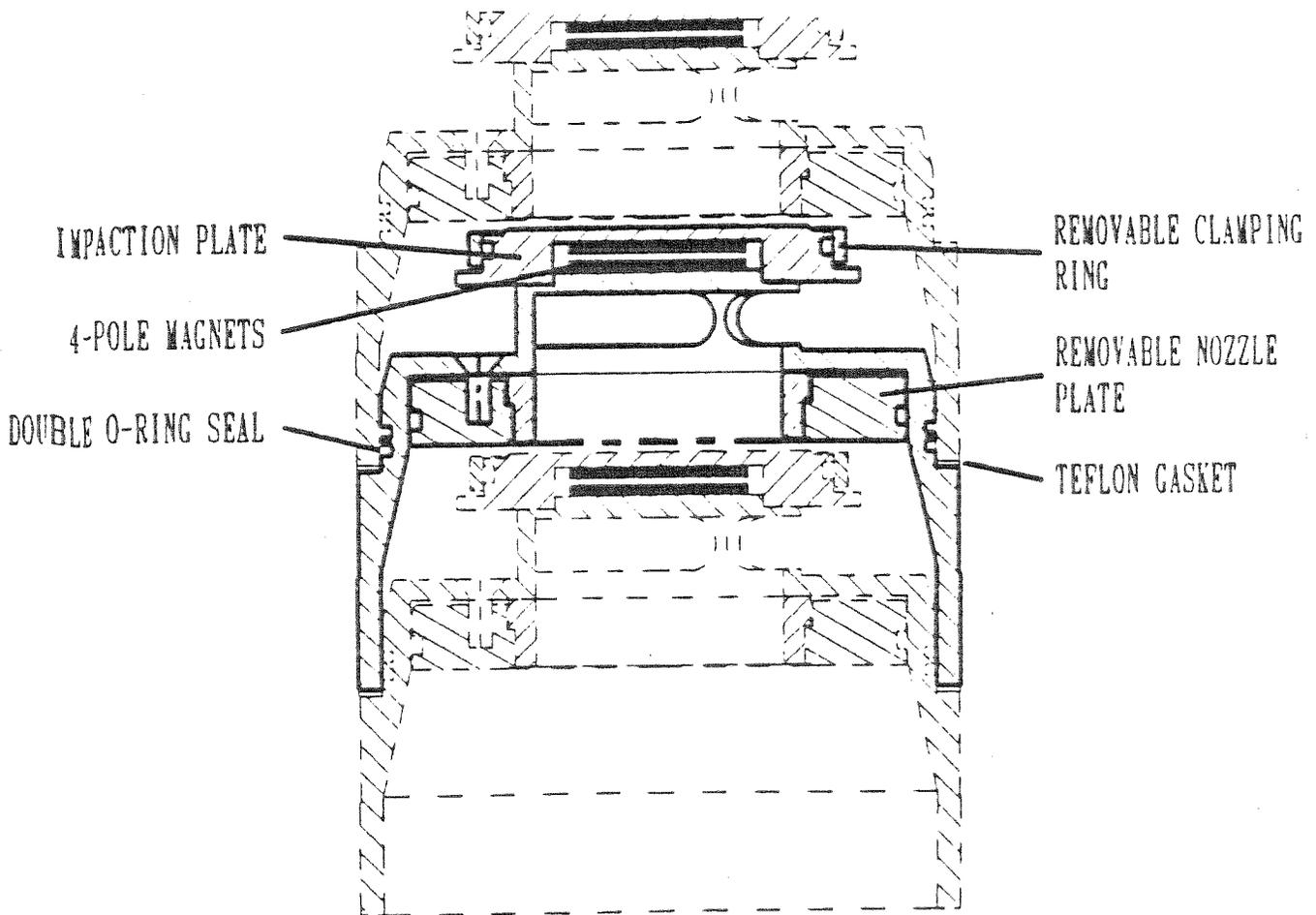


Figure 2-1. Schematic Diagram of a Typical MOUDI Stage.

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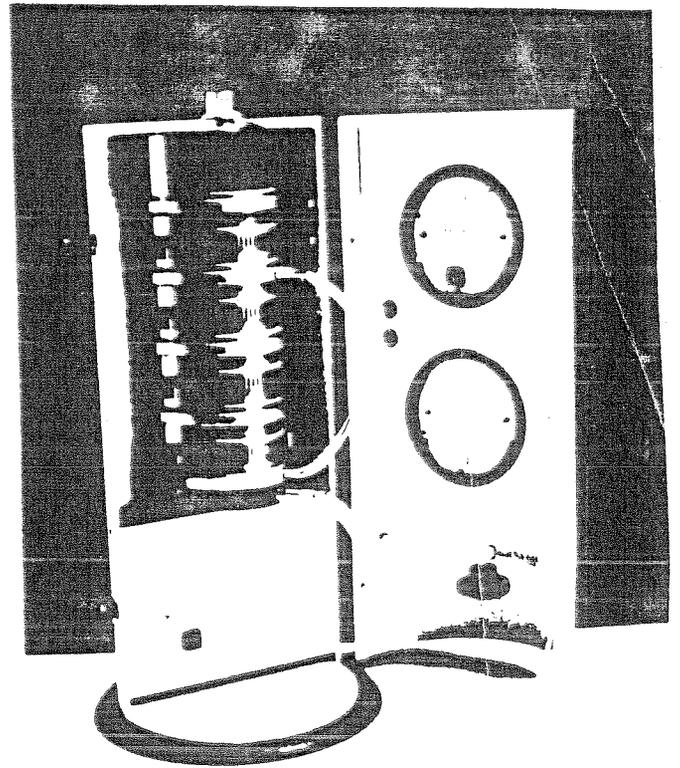
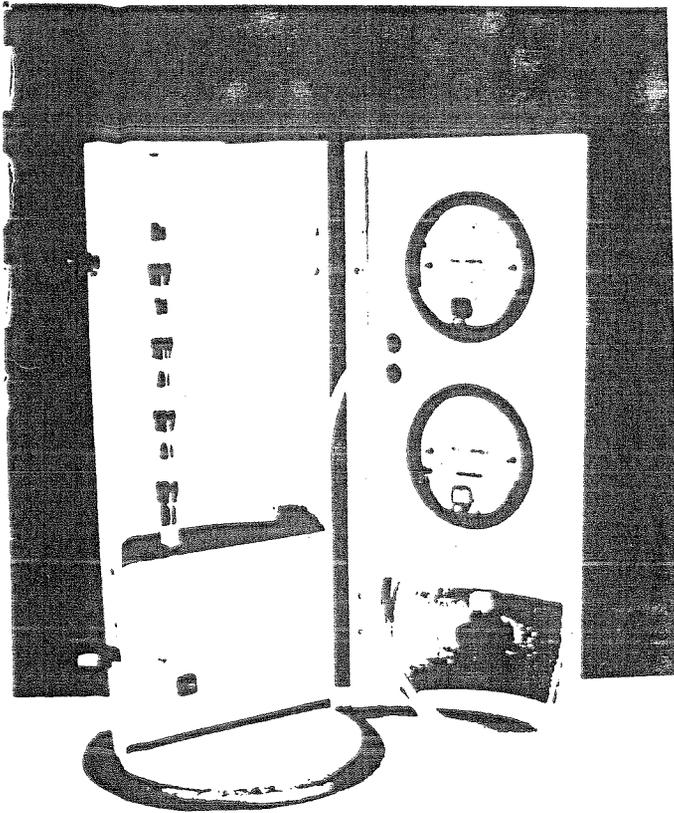


Figure 2-2. Rotator Unit and Fully Assembled Unit for Rotameter.

2.1.3 Dwyer 10 to 100 SCFH Rotometer

This rotometer is used to set and verify flow rates through each MOUDI unit.

2.1.4 Sonicator (Branson Model 5200)

The ultrasonic bath is used to clean nozzle plates after each 48 hours of sampling or when the pressure drop across the impaction plate has increased and adequate pressure drop can not be achieved for sampling.

2.1.5 Spare Parts Accessories

Each MOUDI is accompanied by a carrying case with the spare parts and accessories listed in Table 2-1. Table 2-2 is a summary of the parts list for the impactor and rotator unit and the vendor's address and phone number.

2.2 Supplies

- 2.2.1 Forceps: Forceps are used to load and unload filters from the filter holders and to place them in their numbered PetriSlides.
- 2.2.2 18 x 24 inch Laboratory Bench Cover: The bench cover is the work surface used to place the filters in their numbered PetriSlides.
- 2.2.3 Methanol in Wash Bottle: To clean forceps and cutting board prior to filter unloading, and to clean nozzle plates between sampling.
- 2.2.4 Kim Wipes: To wipe methanol from working surfaces and forceps.
- 2.2.5 47 mm PetriSlides: Filters are placed into these slides and samples with the equivalent ID labels are transferred from the filter holder to the Petri Slide after sampling.
- 2.2.6 Bar-Code Labels: Bar-code labels are attached to the cover of each impaction plate holder for identification.
- 2.2.7 Disposable Gloves: Gloves are worn whenever filters are loaded or unloaded. Gloves are discarded when they have come into contact with any contaminant and after each loading/unloading session.
- 2.2.8 Teflon FEP 200A (fluorocarbon, heat sealable, 0.002 inch thick) (Cadillac Plastic and Chemical Company, Birmingham, MI): The substrate used for sample collection.

Table 2-1

MOUDI Spare Parts and Accesories

<u>Item No.</u>	<u>Description</u>	<u>MSP Part #</u>	<u>Quantity</u>
1	O-ring (body)	MOUDI-1-039 Urethane	2
2	O-ring (body)	MOUDI-1-038-Urethane	2
3	O-ring (filter post)	MOUDI-1-020-Viton	2
4	O-ring (filter holder)	MOUDI-1-025-Viton	2
5	O-ring (impaction plate)	MOUDI-1-028-Viton	2
6	O-ring (nozzle plate)	MOUDI-1-035-Viton	2
7	O-ring (trans. cover)	MOUDI-1-031-Viton	2
8	Machine screw	MOUDI-108	3
9	Teflon washer	MOUDI-109	2
10	Chem-plex silicon lub.	MOUDI-201	1
11	Cling-Surface silicone spray	MOUDI-202	1
12	Aluminum substrate 47 mm	MOUDI-203	300
13	Substrate holder ass'y	MOUDI-204	1
14	Substrate holder cover	MOUDI-205	9
15	Coating mask for 47 mm	MOUDI-206	3

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Table 2-2

Summary of Parts List for MOUDI

I. Impactor (size= 35 X 8 cm, weight 3 kg)

<u>Item No.</u>	<u>Description</u>	<u>MSP Part #</u>	<u>Quantity</u>
1	Filter base	MOUDI-101	1
2	Filter base cover	MOUDI-102	1
3	Stage body	MOUDI-103	8
4	Cover	MOUDI-104	1
5	Pressure tap	MOUDI-105	2
6	Impaction plate ass'y	MOUDI-106	8
7	Filter holder ass'y	MOUDI-107	1
8	Inlet nozzle plate, 15 μ m	MOUDI-110	1
9	Nozzle plate, 10 μ m	MOUDI-111	1
10	Nozzle plate, 5.6 μ m	MOUDI-112	1
11	Nozzle plate, 3.2 μ m	MOUDI-113	1
12	Nozzle plate, 1.8 μ m	MOUDI-114	1
13	Nozzle plate, 1.0 μ m	MOUDI-115	1
14	Nozzle plate, 0.56 μ m	MOUDI-116	1
15	Nozzle plate, 0.32 μ m	MOUDI-117	1
16	Nozzle plate, 0.18 μ m	MOUDI-118	1
17	Nozzle plate, 0.10 μ m	MOUDI-119	1
18	Nozzle plate, 0.05 μ m	MOUDI-120	1
19	Machine screw	MOUDI-108	24
20	Teflon washer	MOUDI-109	9
21	O-ring (body)	MOUDI-1-039 Urethane	10
22	O-ring (body)	MOUDI-1-038 Urethane	9
23	O-ring (filter post)	MOUDI-1-020-Viton	1
24	O-ring (filter holder)	MOUDI-1-025-Viton	1
25	O-ring (impaction plate)	MOUDI-1-028-Viton	9
26	O-ring (nozzle plate)	MOUDI-1-035-Viton	8
27	O-ring (trans. cover)	MOUDI-1-031-Viton	9

Table 2-2 (continued)

Summary of Parts List for MOUDI

II. Rotator (size= 50 X 22 cm, weight 6 kg, power 110-12V, 50Hz or 60Hz, 0.3 amp)

<u>Item No.</u>	<u>Description</u>	<u>MSP Part #</u>	<u>Quantity</u>
1	Shell back	MOUDI-151	1
2	Shell front	MOUDI-152	1
3	Panel, gauge mount	MOUDI-153	1
4	Panel, motor cover	MOUDI-154	1
5	Plate, motor mount	MOUDI-155	1
6	Plate, impactor support	MOUDI-156	1
7	Plate, base	MOUDI-157	1
8	Bearing	MOUDI-158	1
9	Bearing	MOUDI-159	1
10	Shaft ass'y	MOUDI-160	1
11	Coupling	MOUDI-161	1
12	Motor	MOUDI-162	1
13	Capacitor	MOUDI-163	1
14	Hinge	MOUDI-164	2
15	Draw latch	MOUDI-165	2
16	Keeper	MOUDI-166	2
17	Switch, on/off/mom	MOUDI-167	1
18	Light, neon	MOUDI-168	1
19	Line cord	MOUDI-169	1
20	Valve, control	MOUDI-170	1
21	Bracket, valve	MOUDI-171	1
22	Magnehelic 0-180"H20	MOUDI-172	1
23	Magnehelic 0-20"H20	MOUDI-173	1

III. Vendor's Address and Phone Number

MSP Corporation
1313 Fifth Street, S.E., Suite 206
Minneapolis, MN, U.S.A. 55414
Tel: 612/379-3963
Fax: 612-379-3965

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2.2.9 Aluminum Foil: Commercial grade heavy duty aluminum foil.

2.2.10 47mm Metal Punch (McMaster Carr, Sante Fe Springs, CA): Used to cut 47mm substrate discs from the FEP Teflon Sheet.

2.2.11 Teflon Tape, 1/2" width x 20 ', available at hardware store: Wrap on top of the O-ring of the impaction plate to keep the metal clamping ring tightly in contact with the impaction plate holders.

2.2.12 37 mm Teflon Membrane Filter (Gellman Sciences Inc., Ann Arbor, MI, #R2PJ037).

2.2.13 37 mm Quartz-Fiber Filter (Pallflex Corp., Putnam, CT, #2500 QAT-UP)

2.2.14 Glass-Fiber Filters (Pallflex Corp., Putnam, CT, #TX40H120-WW)

2.3 Data sheets

Figure 2-3 illustrates an example data sheet as it comes in the carrying case prior to sampling. Figure 2-4 is an example of a data sheet after it has been filled out by the field technician after sampling. MOUDI data sheets are prepared in triplicate. The pink copies are retained in the laboratory after unexposed substrates are loaded in the carrying case as part of the sample chain-of-custody. The yellow copies are kept in the field office after sampling. The original data sheets are returned to the laboratory with the exposed substrates.

3.0 CALIBRATION STANDARDS

The transfer standards for MOUDI flow rates are the rotameters specified above which have been calibrated against a Roots meter prior to the beginning of the sampling program. Figures 3-1 and 3-2 present the calibration curves for 760 mm Hg and 25° C for the rotameters used in this project. Elapsed time meters are calibrated against a stopwatch.

4.0 SAMPLER OPERATION

4.1 Flow Diagram

Figure 4-1 summarizes the routine operating procedure for the MOUDI. Filter changing and flow rate performance tests are performed between each sampling period and require approximately 20 to 25 minutes per Moudi unit.

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DRI MOUDI Field Data Sheet

Network: _____ Moudi ID: AS9 Date Shipped From DRI: 12/12/89 By: AWT
 Site Name: EDISON Cassette ID: _____ Date Shipped To DRI: _____ By: _____
 Technician: _____ Date Received From DRI: _____ By: _____

Filter ID	Stage No.	Start Sampling		End Sampling		Start Elapsed Time (min)	End Elapsed Time (min)	A Time (min)	Rotameter Reading		Upper Gauge AP (in H ₂ O)		Lower Gauge AP (in H ₂ O)		Flag	Comments
		Date (YYMMDD)	Time (HHMM)	Date (YYMMDD)	Time (HHMM)				Initial	Final	Initial	Final	Initial	Final		
	1															
	2															
EDMI408																
	3															
EDMI409																
	4															
EDMI410																
	5															
EDMI411																
	6															
EDMI412																
	7															
EDMI413																
	8															
EDMI414																
	A.F.															
EDMT059																

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Figure 2-3. DRI MOUDI Field Data Sheet.

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DRI MOUDI Field Data Sheet

Network: _____
 Site Name: AUSPEN
 Technician: EDISON
 MOUDI ID: _____
 Cassette ID: B-59
 Date Shipped From DRI: 12/12/89 By: SL
 Date Shipped To DRI: _____ By: _____
 Date Received From DRI: _____ By: _____

Filter ID	Stage No.	Start Sampling		End Sampling		Start Elapsed Time (min)	End Elapsed Time (min)	Δ Time (min)	Rotameter Reading		Upper Gauge AP (in H ₂ O)		Lower Gauge AP (in H ₂ O)		Flag	Comments
		Date (YYYYMM)	Time (HHMM)	Date (YYYYMM)	Time (HHMM)				Initial	Final	Initial	Final	Initial	Final		
	1															
 EDMA408	2	900911	0700	900911	1400	07626	11229	360.3	64	64	>15.0	>15.0	115	115		
 EDMA409	3															
 EDMA410	4															
 EDMA411	5															
 EDMA412	6															
 EDMA413	7															
 EDMA414	8															
 A.F.																
 EDMQ059																

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Figure 2-4. Example DRI MOUDI Field Data Sheet Entries.

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Calibration system: ROOTSMETER Model 1.5M S/N: 8623119
 Date: 06/08/90 Project: AUSPEX Operator: DEWITT
 Rotameter manu/model: DWYER RMC 104 S/N: DRI 401

Press temp mmHG	Qind C	Qind SCFH	P mmHG	P mmHg	ROOTS ON	ROOTS OFF	VOL m3/ft3	Time Min.	Qc CFH	Qr CFH	
				<u>Exhaust</u>							
1	37.5	21.5	100.00	10.00	0.00	35111	35136	25.0	14.07	104.59	96.36
1	36.0	21.4	150.00	15.00	0.00	35235	35274	39.0	14.47	154.55	142.24
1	35.8	21.5	200.00	23.00	0.00	35319	35369	50.0	14.12	203.63	187.35
1	35.5	21.4	250.00	36.00	0.00	35411	35476	65.0	14.12	259.09	238.36
1	35.0	21.7	280.00	47.00	0.00	35581	35656	75.0	14.30	287.37	264.14
1	35.0	21.8	70.00	7.00	0.00	35722	35740	18.0	15.10	70.42	64.72
0	0.0	0.0	0.00	0.00	0.00	0	0	0.0	0.00	0.00	0.00
0	0.0	0.0	0.00	0.00	0.00	0	0	0.0	0.00	0.00	0.00

Slope: 0.946900
 Intercept: -0.1865
 Corr.Coeff.: 0.999793

$Q_r = Q_c [(P_c / 760) * (298 / T_c)]^{1.5}$ Where:
 $Q_c = (Vol / Time) [(P_c - \Delta P) / P_c] * 60$
 From linear regression of Indicated flow, Qind vs. Qr in CFH:
 $Q_r = A * Q_{ind} + B$

To obtain ACTUAL FLOW (CFH) and STANDARD FLOW (SCFH)
 at site conditions, P2, T2:
 $Q_{act} = Q_r [(760 / P_2) * (T_2 / 298)]^{1.5}$
 $Q_{std} = Q_r [(P_2 / 760) * (298 / T_2)]^{1.5}$

To obtain flows in LPM multiply by 0.472
 * = Enter a 1 to include in calculations.

Figure 3-1. DRI Rotameter Calibration Log Sheet.

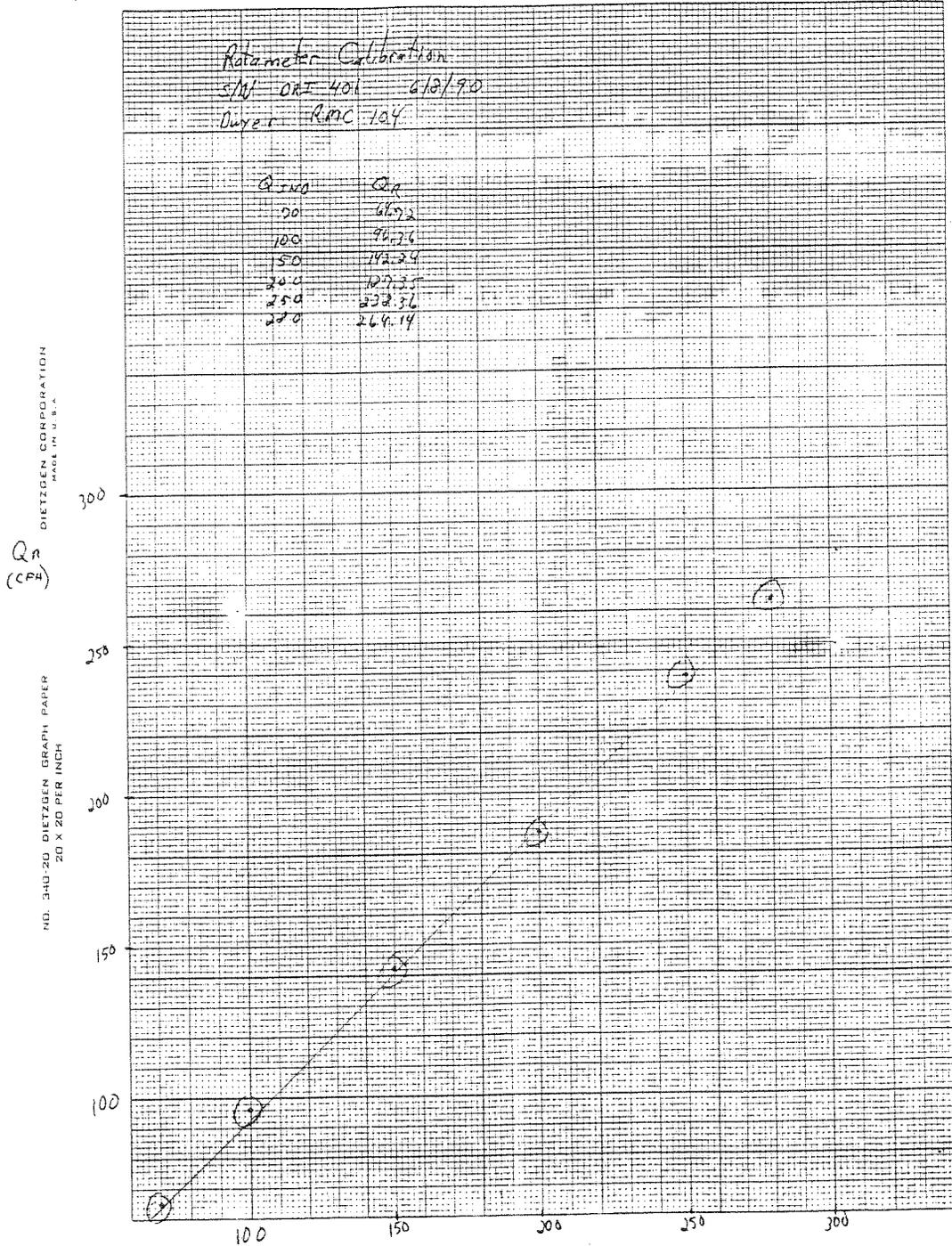


Figure 3-2. Dwyer RMC-102 Rotameter Calibration.

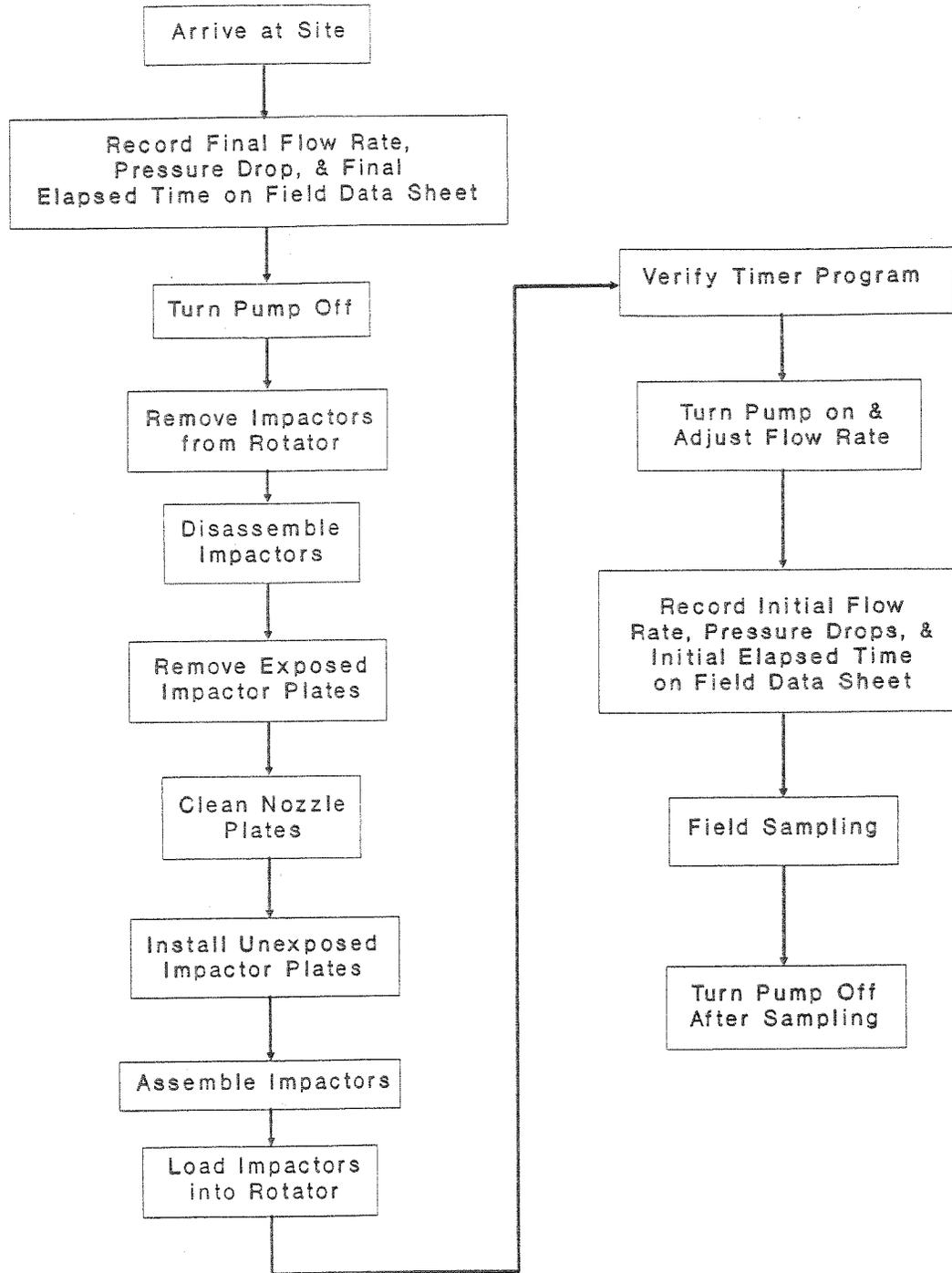


Figure 4-1. MOUDI Sampler Operations Flow Diagram.

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Nozzle plates should be cleaned with methanol soaked Kim Wipes during each sample change.

4.2 Start Up

4.2.1 Laboratory Operations

- Preparation of Sampling Substrate

The substrate used in the impactor must be thin enough to be clamped in the holder by the metal clamping ring. No commercially available substrate is suited for MOUDI sampling and analysis.

FEP (fluorocarbon) 200 A (0.002" thickness) Teflon sheet is purchased from Cadillac Plastic and Chemical Company (Birmingham, MI), and punches are used to prepare 47 mm substrate discs. These discs are then soaked in methanol overnight, rinsed thoroughly with distilled-deionized water, and dried in a vacuum oven prior to submission for sample pre-weigh. Pre-weighed Teflon sheets are stored in the individual PetriSlides with pre-assigned barcode labels.

The aluminum foil is purchased in the grocery store and a stainless steel punch is used to prepare 47 mm substrate discs. Batches of aluminum foil substrates are pre-fired at 600° C for 3 hours and acceptance tested for background organic and elemental carbon levels. Aluminum foil substrates are stored in pre-assigned barcode labelled PetriSlides and refrigerated prior to sample loading.

- Preparation of Impaction Plates

The impaction plates are loaded in the laboratory and inserted into the impactor sampler prior to sampling. Metal filter holder covers are provided for each impaction plate to minimize sample contamination.

Normally, Unit A uses pre-cleaned 47 mm diameter FEP Teflon sheets as impaction plate substrates and Gelman (Ann Arbor, MI) polymethyl pentane ringed, 2.0 μ m pore size, 37 mm PTFE Teflon membrane filters (#R2PJ037) as after-filter substrates for mass and ion analyses. Unit B uses pre-fired 47 mm diameter aluminum foil (Reynolds Aluminum, Gresham, OR) as impaction plate substrates and pre-fired Pallflex (Puttnam,

CT) 37 mm diameter quartz fiber filters (#2500 QAT-UP) as after-filter substrates for carbon analysis.

DRI MOUDI Field Data Sheets (Figure 2-3) with pre-assigned barcode labels and filter holder cassette IDs are prepared; impaction plates are cleaned with a methanol-soaked Kim wipe prior to substrate loading.

A set of 8 impaction plates and one after-filter cassette is arranged sequentially on top of a cleaned laboratory counter. Each filter retainer ring is marked with 1 to 8 black dots which correspond to the stage number. The barcode label is placed on each filter holder cover, and corresponding PetriSlides with sampling substrate are placed in front of each impaction plate.

With gloved hands and a methanol cleaned forceps, load the sampling substrates one by one for each set of 9 filter holder cassettes. Substrates are put into the impaction plate holders by removing the retainer ring, inserting a substrate, and the pressing the ring back onto the holder. The filter is inserted in the after-filter holder in the same fashion. Care must be taken to align the pin on the filter holder to the hole in the ring. Complete the field data sheet before proceeding to the next cassette.

Removal of impaction plate substrates and after-filter is also done in a laboratory. To remove the impaction plate substrates, the retainer rings are lifted from the holders and the substrates removed. The same procedure is required to remove the after-filter from its holder. However, on the filter holder, there is a pin between the holder and the rings so the ring must be lifted straight up.

4.2.2 Field Operations

- Install the Denuder.

The nitric acid denuder is installed on unit A and the organic vapor denuder is installed on unit B.

- Plug in the Sampler

Each MOUDI unit uses approximately 8 amps of current during normal operation, though it can draw 20 amps or more when the pump starts. A 20 amp circuit is needed for each MOUDI. Where possible, the unit should be directly plugged into an

outlet. If an extension cord is needed, it should be extra heavy duty (10 or 12 gauge) and not more than 25 feet in length. If the pump relay chatters when the pump is switched on, the voltage drop along the extension cord is probably too high. A heavier gauge or shorter cord usually eliminates this chatter. When two MOUDI units are operated on the same circuit, set the current times one minute apart so that they will not draw starting currents at the same time.

- Program the Timer

Detailed instructions for the Grasslin 56-72 timers are described below. Read them. Channels one and two control the pumps and the elapsed time meters for Unit A and B, respectively. Four features must be noted on the timer readout: 1) time of day; 2) am or pm; 3) day of week; and 4) on/off (or I/O). The on/off indicator refers to the current status of a channel -- "ON" indicates that power is on and "OFF" indicates that it is not. "I" is used in a program to turn power on and "O" is used to turn it off. The sequence of program steps is not controlled by the order in which they occur, but by the times at which they are set to occur. The timer contains a rechargeable backup battery which should last for as long as two days after a power outage.

- Set the Current Time

Press the "Set Time" button and keep it depressed during the entire procedure. Press the button under the current day of the week until a bar appears over the day marker. Press the "h+" or "h-" button until the current hour appears in the center of the LCD display. Make certain that the "am" or "pm" designation on the left edge of the display is correct. Keep pressing the button until it is. Press the "m+" or "m-" button until the current minute appears on the display. Release the "Set Time" button and the current time should be displayed.

- Program the Start and Stop Times

Push the "READ" and "CANCEL" buttons several times in succession until a blank display appears. This clears all previous programming steps. Push "Set Time" and the timer is prepared for programming. For example, to program the channel 1 morning start time, push "h+" until 5 am is displayed in the hours column. Push "m+" until "01" is displayed in the

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minutes column. Push the button corresponding to the day of the week on which bar on the LCD display should appear over each day. Press the Channel 1 "I/O" button until the Channel 1 LCD marker is on "I". Press the "WRITE" button to record this program step. To program the morning stop time, press the appropriate buttons to obtain a time of 11:00 am on the same day and press the Channel 1 "I/O" button until the Channel 1 display marks "O". Press the "WRITE" button to record this program step. For the next sampling period of the same day, repeat the previous steps with different start and stop times. Push "h+" until 11:00 am is displayed in the hour column. Push "m+" until 01 is displayed in the minute column. Press the Channel 1 "I/O" button until the Channel 1 LCD marker is on "I". Press the "WRITE" button to record this program step. To program the afternoon stop time, press the appropriate buttons to obtain a time of 5:00 pm on the same day and press the "I/O" button until the Channel 1 display reads "O". Press the "WRITE" button to record this program step. Repeat the same procedure for Unit B on Channel 2.

• Program Verification and Modification

Press "READ" to sequence through each step in the program in order. When a change is desired in a step, press the appropriate buttons to make that change and then press "WRITE" to record the changes. Pressing "READ" will start at step number one when it is pressed following a "WRITE".

The programs should read as follows for Channel 1 on each sampling day. The same programs are applied for channel 2:

Step 1: 05:01 am, on sampling day, Channel 1 on I.
Step 2: 11:00 am, on sampling day, Channel 1 on O.

• Test the Timing and Switching Sequence

Flip the power switch to "ON". This supplies power to all sampler components. Press the channel 1 "OVERRIDE" to turn the pump on and the pump should start. Repeat the same steps for Channel 2.

• Impaction Plate Removal and Installation

Remove the impactors from the rotator by plugging the rotator into a 110 volt outlet and holding the switch on the rotator panel to "reverse." The drive shaft will rotate clockwise and the impactor will be pushed out of the rotator.

Disassemble the impactor by first removing the cover and then removing each stage of the impactor, starting with the upper stage and working downward to the base. Figures 4-2 and 4-3 show the partially disassembled impactor unit and parts of an individual MOUDI stage, respectively. Each stage of the impactor consists of the body, the impaction plate for the stage above and the nozzle plate for the stage below. The impaction plate is held onto the pedestal of the body by two magnets; one magnet on the pedestal and the other on the impaction plate. Normally this is all the disassembly of the stages that is required. However, if necessary, the nozzle plates can be removed by removing the three screws holding the nozzle plate to the body and pushing downward on the nozzle plate ring through the three screw holes. Caution: Never push directly on the nozzle plate, which is quite thin and can be damaged.

The final step in disassembly is removal of the after-filter holder from the base. To do this, unscrew the top of the base from the bottom and remove the top. Remove the filter holder from the base by pulling upward. After disassembling the cascade impactors, a new set of filter holders can be loaded on stages 5-8; stages 1-4 are merely wiped clean. Place the impaction plates on the pedestals of the base for each stage. Assemble the stages in the reverse order of disassembly. Assemble the smallest cut-size stage first. Progressively larger cut size stages are placed on top as one goes from bottom to top of the impactor. The impactor cut sizes are etched into the ring of the nozzle plate and can be read from the bottom of the stage. The stage ID is also labelled on the outside of the impactor. The final step in the impactor assembly is to place the cover onto the uppermost stage.

The impactor can now be placed into the rotator. By turning the rotator switch "On" for a few seconds, the gears on the drive shaft will pull the impactor into the rotator. Connect the pressure gauges to the impactor (upper gauge to the upper pressure tap and the lower gauge to the lower pressure tap) and the MOUDI is fully assembled.

Caution: apply a moderate amount of grease to the O-ring between stages when reassembling. If these O-rings become dry, the torque required to rotate the MOUDI may increase enough to damage the motor.

Title: Micro-Orifice Uniform Deposit
Impactor (MOUDI) Field and
Laboratory Operations

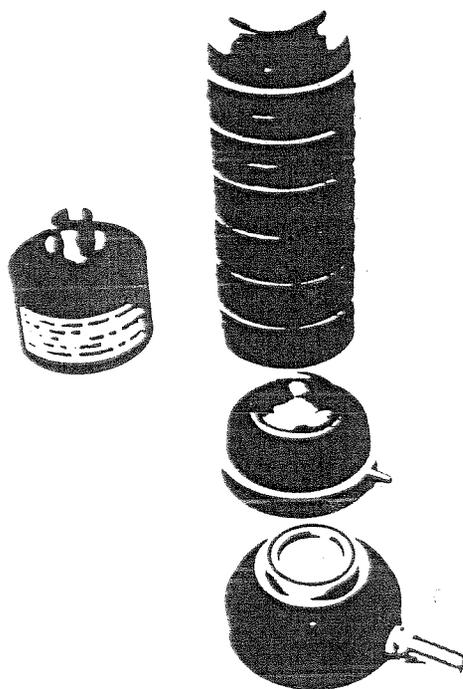


Figure 4-2. Partially Disassembled Impactor Unit.

DRI STANDARD OPERATING PROCEDURE

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Title: Micro-Orifice Uniform Deposit
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Laboratory Operations

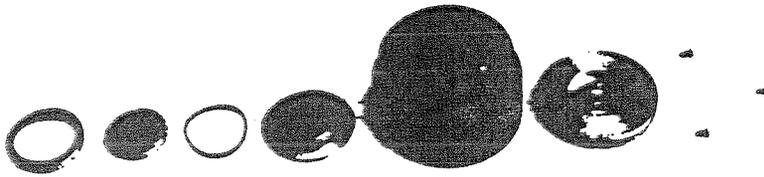


Figure 4-3. Parts of an Individual MOUDI Stage.

- Operating Procedure

Connect the MOUDI outlet to a vacuum pump. Turn on rotator and the vacuum pump. Adjust the flow to 30 lpm. The upper gauge pressure drop should read between 1 to 2 inches of water, and the lower gauge pressure drop should read 15 inches of water. Complete the field data sheet. The MOUDI is now ready to sample aerosol.

4.3 Routine Field Operations

As shown in Figure 4-1, routine field operations consist of the following steps:

- Upon arrival at the sampling site just before 11 am, insure that the units are operating.
- Turn pump off.
- Make sure both flow rates and pressure drops are within specified tolerance (i.e., $\pm 10\%$ from the initial setting). Just before 11 am connect the rotameter with the gooseneck inlet. Record the final flow rate, final pressure drop, and final elapsed time on the MOUDI field data sheet. Verify that total sampling time is within $\pm 10\%$ of the pre-specified duration.
- Turn pump off.
- Remove impactor from rotation unit by disconnecting the tubing between the pump and impactor, and between the impactor and pressure gauge.
- Disassemble impactor from the top to bottom.
- Cap each exposed impaction plate with the corresponding cover and remove the impaction plate from the pedestals of the base for each stage. Secure the entire set of 8 impaction plates and one after-filter cassette in the cassette holder.
- Wipe the nozzle plate with a methanol-soaked Kimwipe or disassemble the nozzle plate as stated in Section 4.2.2 and place it in a distilled water filled ultrasonic bath. Sonicate in distilled water for 10 minutes.
- Repeat the above steps for the second MOUDI.

Title: Micro-Orifice Uniform Deposit
Impactor (MOUDI) Field and
Laboratory Operations

Date: 10/21/92

Number: 1-208.3

Revision: 3(TUUH.92)

- According to the field data sheet, install a new set of unexposed impaction plates. Starting from the bottom stage, load the impaction plate stage by stage.
- Assemble the impactors.
- Load the impactors in the rotator unit and connect the tubing between the impactor and the pressure gauge.
- Verify the program steps on the Grasslin timer.
- Turn the pump on and adjust the flow rate for 30 lpm.
- Connect the rotameter and record the initial flow rate, initial pressure drop, and initial elapsed time on the new set of field data sheets.
- Prepare the equipment for field sampling.
- The pump will be turned off at the end of each sampling period.

4.4 Shutdown

At the end of the sampling program, conduct a performance test on the flow and pressure drop prior to dismantling the sampler. Record the condition of the sampler in the station logbook. Check all equipment and parts against the check-out sheet and assure that all are packed for shipment back to the Desert Research Institute in Reno, NV.

5.0 QUANTIFICATION

5.1 Calibration Procedures

5.1.1 Mark rotameter scales with correct readings

The actual flow rate through each rotameter is

$$Q_{act} = (0.472) (aQ_i + b) ((760/P_2)(T_2/298))(0.5)$$

where

$$Q_{act} = \text{actual flow rate at temperature } T_2 \text{ and pressure } P_2 \text{ in lpm.}$$

Title: Micro-Orifice Uniform Deposit
Impactor (MOUDI) Field and
Laboratory Operations

- a = linear regression slope for the relationship between the rotameter reading and the true flow rate at standard conditions.
- b = linear regression intercept for the relationship between the rotameter reading and the true flow rate at standard conditions.

Actual flows can be located on a piece of tape applied to the rotameter scale for typical temperatures and pressures in the sample area. Slopes and intercepts are found on the DRI rotameter calibration log sheet (Figure 3-1).

5.1.2 Connect the Rotameters

Connect the 0 to 100 SCFH rotameter to the gooseneck inlet for flow measurement.

5.1.3 Adjust Flows

Adjust the ball valve downstream of the MOUDI unit until the actual flow reads 30 lpm. Record the flow rate in the logbook.

6.0 QUALITY CONTROL

6.1 Calibration Checks

An initial and final flow rate measurement is made and recorded at every sample change.

6.2 Pressure Drop Checks

An initial and final pressure drop measurement is made and recorded at every sample change.

7.0 QUALITY AUDITING

Audits of flow rates are performed by an independent auditor with independent standards at the beginning and end of the field program.

Standard Operating Procedure for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

Prepared by: Lisa C. Greene Date: 2-16-2009
Reviewed by: James B. Flay Date: 2/18/2009
Approved by: W.F. Sultknecht Date: 2-19-09



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

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Procedures for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters

1.0 Purpose and Applicability

This document outlines procedures for procurement and acceptance testing of Teflon, nylon, and quartz filters for their use in chemical speciation of PM_{2.5}. Research Triangle Institute (RTI) has contacted the below-mentioned manufacturers/suppliers to confirm their ability to supply the needed filters. The mention of specific suppliers or trade names does not constitute endorsement by RTI.

Teflon (Whatman PTFE, Part Number 7592-304), nylon (Part Number 7410-004), and quartz (Part Number 1851-047) filters will be purchased from the McConnell Group. RTI will have the capability to pre-fire the quartz filters.

2.0 Procedures for Filter Procurement

The individual task leaders along with the sample custodian will have the responsibility for determining project materials and supply requirements, including those of filters needed for collecting ambient aerosol samples. The number of filters ordered will be sufficient for all planned field activities, planned acceptance testing protocols, and field and laboratory quality assurance and quality control activities. Due to extended lead times often required for large filter procurements and the accompanying acceptance testing, filters will be ordered at least 90 days prior to the expected day of field use. The procedure for ordering filters is as follows:

- 2.1 Contact the filter supplier and obtain a written (or documented verbal) price quote for the intended quantity of filters required. The quote should include per unit price, expected ship date, and expected delivery date. Ensure that the quote is based on the vendor's understanding that all procured filters will be from the same manufacturing lot.
- 2.2 Complete an eProcurement request containing the following information:
 - Filter manufacturer's product number.
 - Supplier's product number.
 - Complete product description and specifications.
 - Unit size.
 - Number of units required.
 - Unit price and extended price.
 - Specification that all filters must be supplied from the same manufacturer's lot number.
 - Statement that the supplier can ship partial orders.

- Required receipt date for a completed order.
 - Copy of written price quote and/or name and date of supplier's customer service representative who provided the verbal quote.
 - Supplier's name, address, telephone number, fax number, and contact name.
 - Desired procurement priority.
 - RTI project and overhead number.
 - Names of individuals requesting and approving the procurement.
- 2.3 Retain a copy of the completed eProcurement request for future reference. Deliver the original eProcurement request to the designated PM_{2.5} eProcurement requestor, who will enter the requisition into *Procure+*, which is a Web-based procurement application that automates RTI's procurement process, from order placement to fulfillment and receipt.
- 2.4 Upon receipt of each filter shipment, inspect the shipment to verify that the items appear to be in good condition and that the receiving order accurately represents the shipment's actual contents. If so, sign and date the receiving order, make a photocopy for the RTI Project Leader, and submit the original to the RTI Program Administrative Assistant. If a discrepancy in shipment contents or condition is noted, complete and submit an online RTI Materials Discrepancy Report (MDR). If defective materials need to be returned to the supplier, complete and submit an online MDR. Following receipt of the MDR for any reason, RTI's Office of Purchasing will contact the supplier to arrange for the return of the incorrect or damaged item(s) and shipment of the correct item(s).
- 2.5 Store acceptable procured filters in their original bulk containers in a climate-controlled environment until required for use. Maintain copies of lot documentation in the filter storage location.

3.0 Filter Acceptance Testing

Filters procured for research purposes typically have project-specific testing and acceptance requirements. Regardless of the filter type or the project's specific analytical requirements, filters must be examined individually prior to use to ensure that defects do not exist.

Teflon: Teflon filters procured for PM_{2.5} compliance measurements have detailed specifications and acceptance testing requirements (e.g., subsequent chemical analysis of collected aerosol deposits places additional acceptance testing requirements on the filters depending on the analytical technique used and the analytes of interest). Teflon filters for use in the chemical speciation program are received from the filter vendor monthly. A number of filters equal to 10% of the total quantity of filters received each month are visually inspected with the aid of magnification and enhanced lighting for an initial determination of acceptability.

In addition to the initial screening inspection, filters must be examined individually prior to use to ensure that one or more of the following defects does not exist:

- **Pinhole**—A small hole or tear in the filter matrix that appears when examined over a light table.
- **Loose material**—Any 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, which rely on the uniformity of aerosol deposition (e.g., X-ray fluorescence), 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.

If any of the above defects are found on a filter prior to sampling, the filter will be discarded and replaced with another. Pre-sampling inspection and acceptance testing for Teflon filters are described in the standard operating procedure (SOP), *Standard Operating Procedure for PM_{2.5} Gravimetric Analysis*.

Defects detected on a filter during the post-sampling phase of a field study will be noted on the filter's chain-of-custody record or in the laboratory database and the defect will be brought to the attention of the appropriate Task Leader. The type and severity of the defect will dictate what corrective actions are necessary regarding further use of the filter and interpretation of the filter's test results. For example, a slight post-sampling separation of a Teflon filter's reinforcing ring would typically invalidate gravimetric test results but may not adversely affect the quality of X-ray fluorescence analysis performed on the filter's center section. For this reason, post-sampling defects in field filters must be evaluated on a case-by-case basis.

Nylon: Cleaning and acceptance for nylon filters are described in the SOP, *Standard Operating Procedure for Cleaning Nylon Filters Used for the Collection of PM_{2.5} Material*.

Quartz: Cleaning and acceptance procedures for quartz filters are described in the SOP, *Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer*

Standard Operating Procedure for Sample Handling and Archiving Laboratory (SHAL)

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

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Date: 2/18/09

Reviewed by: James B. Flannery

Date: 2/18/2009

Approved by: W. Dutknecht

Date: 2/19/09



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

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Standard Operating Procedure for Sample Handling and Archiving Laboratory (SHAL)

1.0 Introduction

1.1 Scope and Application

The Sample Handling and Archiving Laboratory (SHAL) is responsible for the preparation of filter media to be sent to sampling sites in the Chemical Speciation Network. Filters are prepared, packaged, and shipped from the SHAL to the field sites prior to the scheduled sampling dates. Following the sampling event, the field site returns the filter media to the SHAL, where the filters are removed from their modules and sent to laboratories for analysis. Following analysis, the filters or filter extracts are archived in appropriate storage for a specified time by the individual laboratory. This Standard Operating Procedure (SOP) presents the methods used by personnel working in the SHAL to accomplish these tasks.

2.0 Training of SHAL Personnel

2.1 Summary of Task

All personnel must be trained prior to working in the SHAL. This procedure describes the training of all SHAL workers.

2.2 Procedure

1. The SHAL Supervisor will orient all new workers to the SHAL facility. This will include explanation of all safety and security information.
2. The first step in training new workers is the presentation of a training video that highlights the various filter types and modules in the program and their handling and cleaning. All new workers must watch this video.
3. A new worker will be paired with an experienced worker, who will instruct them in the various SHAL tasks. During this time, the new worker will be required to review the current SHAL SOP.
4. As the new worker becomes familiar with a specific task and is able to complete the task unassisted, he will be deemed competent in that task. This will be recorded on the SHAL Personnel Training Record (see Figure 1).
5. The SHAL Personnel Training Record will be kept in the Training File located in the Program Office.
6. Periodically, workers will be trained in new tasks or retrained in common tasks. This extra training will be documented and a record placed in the worker's SHAL Personnel Training Record.

SHAL Personnel Training Record

The SHAL worker listed below has completed instruction in the specific activities shown in the table. The listed activities are those tasks required in the SHAL as part of the PM 2.5 Speciation project.

Activity	Date Completed
1. RTI Safety and Occupational Health Orientation	
2. Review of Standard Operating Procedure for SHAL. Revision 8, Dated July 11, 2005..	
3. Review SHAL training video on filter handling and module processing.	
4. Hands-on instruction in filter handling and module loading/unloading.	
5. Hands on instruction in use of the PM2.5 Speciation database relating to SHAL data entry.	
6. Instruction in cooler packaging and unpacking.	
7. Instruction in creating aliquots and transfer of aliquots to analytical laboratories including Chain-of-Custody issues and documentation.	

Acknowledgment of Initial Training

_____	_____	_____
Printed Name	Signature	Date
_____	_____	_____
James O'Rourke SHAL Supervisor	Signature	Date

Note: Additional training beyond the initial training will be acknowledged by initialing and dating additions to the above table.

Figure 1. SHAL Personnel Training Record. *This figure shows training all SHAL personnel have received. A copy of this is kept in each person's training folder.*

3.0 Batch Label Printing

3.1 Summary of Task

This procedure describes printing batches of identification labels, which are used in various parts of sampler processing and shipping.

3.2 Procedure

- 3.2.1 Review printed labels inventory to determine need to print more labels.
- 3.2.2 Print labels as needed using label printing program.
- 3.2.3 Review label stock inventory, reorder as needed.
- 3.2.4 Distribute labels to user(s), as needed.

4.0 Log-In Parts from Client

4.1 Summary of Task

This procedure describes receipt of incoming sampler accessory parts from clients.

4.2 Procedure

- 4.2.1 Receive package with parts. Record shipping information in SHAL Incoming Package Notebook.
- 4.2.2 Identify each part in shipment and assign inventory number to identifier part of module.
- 4.2.3 Label a bin with a Bin Label. Enter bin location into database.
- 4.2.4 Create Bin Folder and Bin Inventory Form. Label each with Folder Copy and Form Copy of Bin Label. The unique Bin number is now associated with the bin, the Bin Folder, and the Bin Inventory form.
- 4.2.5 Disassemble each module and verify that all parts are included. If not, note on Bin Inventory Form and notify SHAL supervisor.
- 4.2.6 Label each module with an Inventory Label. Place the Form Copy of the Inventory Label on the Bin Inventory Form.
- 4.2.7 Color code each module according to the current coding scheme for each sampler by affixing a colored dot to the module.
- 4.2.8 Place a corresponding colored dot on the Bin Inventory Form next to the Module Inventory Label.

- 4.2.9 Complete the Bin Inventory Form. Include client, sampler, and/or location information.
- 4.2.10 Note any unusual items in comments at bottom of form.
- 4.2.11 Enter inventory information into database from Bin Inventory Form.
- 4.2.12 Place modules and other items into correct bin.
- 4.2.13 Compare actual bin contents to list; make appropriate corrections.
- 4.2.14 Put inventoried bin on shelf in bin storage area.
- 4.2.15 Place Bin Inventory Form into the Bin Folder.
- 4.2.16 File the Bin Folder in the file cabinet containing all of the Bin Folders in the SHAL.

5.0 Prepare Sampler Modules for Shipment

5.1 Summary of Task

This procedure describes the assembly of sampler modules prior to shipment. Details specific to individual sampling modules are covered in separate sections of this procedure.

5.2 Procedure

- 5.2.1 Schedule work for processing period.
- 5.2.2 Generate Measurement Request Forms (see Figure 2).
- 5.2.3 Identify storage bin(s) containing modules to be assembled.
- 5.2.4 Remove bins from storage and place in SHAL work area.
- 5.2.5 Assemble each module, placing the correct filter/filters in each as described on Measurement Request Form.
- 5.2.6 Specific assembly instructions for each module type are covered in separate sections of this procedure.
- 5.2.7 Record ID and batch number of pre-weighed Teflon filter for mass determination on Measurement Request Forms.

- 5.2.8 Record batch number(s) of other filters on module assembly form.
- 5.2.9 Package assembled module in shipping box. The shipping box is an insulated container designed to keep contents cold when packed with frozen blue ice.
- 5.2.10 Complete Measurement Request Form.
- 5.2.11 Generate Field Sampling Chain-of-Custody (FSCOC) form. Prepare a Chemical Speciation Trends Network Field Sampling Null Value and Validity Coding Form (see Figure 3) for this sampling event.

**Chemical Speciation Network
Field Sampling Null Value and Validity Coding Form**

c. White (return to lab)
c. yellow (site retains)
c. pink (lab)

Chain of Custody Sampling Request ID _____ Sampling Date _____

Date Received in SHAL _____

Instructions to Field Sampling Operator: For the sampling event identified by the Chain of Custody Sampling Request ID indicated above please circle all applicable flags in the tables below. If no flags apply to this sampling event, please check the box below the tables.

Table A. Null Value Codes
* selection of any flag in this table will invalidate sample

FLAG	DESCRIPTION
AA	SAMPLE PRESSURE OUT OF LIMITS
AB	TECHNICIAN UNAVAILABLE
AC	CONSTRUCTION/REPAIRS IN AREA
AD	SHELTER STORM DAMAGE
AF	SCHEDULED BUT NOT COLLECTED
AG	SAMPLE TIME OUT OF LIMITS
AH	SAMPLE FLOW RATE OUT OF LIMITS
AI	INSUFFICIENT DATA (CAN'T CALCULATE)
AJ	FILTER DAMAGE
AK	FILTER LEAK
AL	VOIDED BY OPERATOR
AM	MISCELLANEOUS VOID
AN	MACHINE MALFUNCTION
AO	BAD WEATHER
AP	VANDALISM
AQ	COLLECTION ERROR
AU	MONITORING WAIVED
AV	POWER FAILURE (POWR)
AW	WILDLIFE DAMAGE
BA	MAINTENANCE/ROUTINE REPAIRS
BB	UNABLE TO REACH SITE
BE	BUILDING/SITE REPAIR

Table B. Validity Flags
* samples marked with any of these flags will be analyzed and reported with flags noted

FLAG	DESCRIPTION
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.
W	Flow Rate Average Out of Spec
X	Filter Temperature Difference out of Spec
Y	Elapsed Sample Time Out of Spec

No flags assigned to this sampling event. _____

Signature _____ Date _____

Figure 3. Chemical Speciation Network Field Sampling Null Value and Validity Coding Form. This form is used by the site operator to assign any flags.

- 5.2.12 Generate a return air bill.
- 5.2.13 Each month, RTI will include one or more Field Audit forms with a shipment to each sampling location. This form will be completed by the site operator when he does his monthly audit of the sampler. The form will then be returned to RTI for data entry and inclusion in the monthly data reports.
- 5.2.14 Complete the validity coding form for this sampling event. Sign/date the FSCOC Form, transferring custody to receiving party.
- 5.2.15 Place the FSCOC, validity coding form and the monthly Field Audit Form (if scheduled) in the shipping box. The FSCOC will be placed on top of the modules, clearly visible to the person receiving the shipment, with the date of the sampling event prominently displayed on the top of the form.
- 5.2.16 Enter the outgoing shipment information into the database.
- 5.2.17 Record the outgoing air bill number on the Measurement Request Form. Attach copies of the FSCOC, the Validity Coding Form, and the return air bill to the Measurement Request Form.
- 5.2.18 Package the shipping box with the appropriate number of ice packs. Include all necessary paperwork.
- 5.2.19 A shipping clerk will check the contents of the package using the SHAL Cooler Checklist (see Figure 4) to verify that the contents are correct. Any problems will be corrected before proceeding.
- 5.2.20 After the box has been checked and the inspection completed satisfactorily, the cooler will be taped securely, and the outgoing shipping air bill attached.
- 5.2.21 The completed SHAL Cooler Checklist will be stapled to the copies of the Measurement Request Form, FSCOC, Validity Coding Form, and the return air bill. This paperwork will be filed in the SHAL.
- 5.2.22 Place the box in the designated area for outgoing shipments.

SHAL COOLER CHECKLIST

- Sampling date, Site name and "Q" number(s) on Custody form match with those on the Measurement request(s).
- Site indicated on Custody form agrees with airbill shipping address.
- Compare outgoing airbill to return airbill. Both airbills show the same "Q" number.
- Tracking sticker is removed from outgoing airbill and attached to measurement request.
- Custody form(s), Flag validation form(s), Operator instructions, and any extra information is included in shipment.
- Custody form(s) is/are signed/dated in Section A, #1 "Laboratory Out".
- Modules in bin are correct type of module as indicated on Custody form(s).
- Correct number of modules are in bin. Memory card is included if needed.
 - URG- 2 modules
 - MetOne- 3 modules
 - Andersen- 3 modules
 - R&P- 3 modules
 - MetOne+IMPROVE- 3 MetOne + 1 IMPROVE + Memory Card
 - MetOne+IMPROVE -- 2 MetOne + 1 IMPROVE + Memory Card
- Bin number agrees with bin listed on Measurement Request(s).
- Correct number of freeze packs in cooler.
- All packing materials are present.
- All modules and icepacks are placed in ziplock bags.
- Every Ziplock bag is in good condition

Measurement request number: _____

Inspected by: _____

Date: _____

Figure 4. SHAL Cooler Checklist. *This checklist is used to ensure that all packing materials and paperwork are included in the cooler. A second person (not the assembler) checks the cooler.*

6.0 Receive Incoming Sampler Modules

6.1 Summary of Task

This procedure describes the receipt of incoming sampler modules. Disassembly and processing of pieces are not covered in this procedure, but are included as separate procedures.

6.2 Procedure

- 6.2.1 Receive packages from delivery service.
- 6.2.2 Look for container number; identify and separate incoming samples from other items.
- 6.2.3 Process sampler modules first.
- 6.2.4 Open shipping containers. Measure temperature of received filter modules using an infrared sensor or other appropriate thermometer or sensor. Record received temperature on Chemical Speciation Trends Network Level 0 Validation Form (see Figure 5).
- 6.2.5 Transfer containers to cold room area for storage.

7.0 Disassemble Incoming Sampler Modules and Associate with Sampling and Analysis Events

7.1 Summary of Task

This procedure describes the overall steps needed to disassemble incoming sampler modules. Details of disassembly for a specific module are not included in this procedure, but are contained in individual instruction sheets.

7.2 Procedure

- 7.2.1 Remove containers of filter modules from the cold room. Place in SHAL module processing area.
- 7.2.2 Remove module(s) from box. Crosscheck the ID of the modules received with those listed on the FSCOC. Notify the SHAL supervisor of any discrepancies before proceeding.
- 7.2.3 Place all of the module(s) from the box on the table along with the FSCOC forms and Level 0 Validation forms.
- 7.2.4 Allow module(s) to thermally equilibrate before proceeding.
- 7.2.5 Enter package contents and incoming air bill into SHAL database.

Chain of Custody Sampling Request ID: Q _____ Cooler Number: C _____

**Chemical Speciation Network
Level 0 Validation - SHAL**

Date Received in SHAL: 
Wednesday, May 14, 2008

OBSERVATION	STATUS	FLAG ASSIGNED	COMPONENT ID's FLAGGED
1. Cooler received intact with all ice packs and bin components?	Y / N / NA		
2. Contents received at = 4 degrees C? Time Temp. Measured: _____	Y / N / NA		
3. All modules present and intact?	Y / N / NA		
4. Custody and Field Data Form received in cooler? A. All required data properly filled in? B. Signed and dated by field operator?	Y / N / NA Y / N / NA Y / N / NA		
5. Module numbers agree with numbers on Custody and Field Data Form?	Y / N / NA		
6. Modules appear undamaged?	Y / N / NA		
7. Module end caps in place, threaded properly (if applicable)?	Y / N / NA		
8. Visible filters inspected and appear undamaged?	Y / N / NA		
9. All filters unloaded and assembled into batches for laboratory analysis?	Y / N / NA		
10. Filter aliquot numbers entered onto Laboratory Chain of Custody forms?	Y / N / NA		

_____ Aliquot flags entered
_____ Aliquot flags reviewed
_____ First data entry complete
_____ Second data entry complete

Comments: _____

Signature Date Completed

Figure 5. Chemical Speciation Network Level 0 Validation Form. *This form is used by the SHAL to note the temperature when the cooler arrives. It is also used to note any flags or unusual conditions.*

- 7.2.6 Sign and date FSCOC forms to indicate receipt of contents at the SHAL. Enter the date received on the Field Sampling Null Value and Validity Coding forms.
- 7.2.7 Determine sampling configuration from FSCOC form and/or database.
- 7.2.8 Compare individual modules to those specified on FSCOCs.
- 7.2.9 Note any discrepancies between received module set and those on FSCOC forms.
- 7.2.10 Notify SHAL Supervisor of discrepancies. Resolve discrepancies before proceeding.
- 7.2.11 Document any discrepancies and corrective actions. Notify QA Officer if major problems are found.

- 7.2.12 Disassemble modules, remove parts and filters. Place the filters into pre-labeled petri slides. The filters will now be called aliquots for internal tracking purposes.
- 7.2.13 Determine analysis list for sampling event from sampling event form or database.
- 7.2.14 Generate Aliquot Creation forms (see Figure 6) in database. Print the form. Handwrite the aliquot information on the Aliquot Creation forms.
- 7.2.15 Transfer information from the Aliquot Creation forms into the SHAL database.
- 7.2.16 Store aliquots in SHAL refrigerator or freezer, as appropriate for filter type.
- 7.2.17 Determine correct bin for module storage.
- 7.2.18 Clean module parts and allow to dry. Reassemble modules. Place cleaned modules in Ziploc bags. Put bags with cleaned modules in correct bin(s) for storage.
- 7.2.19 Return bin(s) to bin storage area.
- 7.2.20 Staple the FSCOC forms, Chemical Speciation Network Level 0 Validation Form, Chemical Speciation Network Field Sampling Null Value and Validity Coding Forms, Aliquot Creation forms, and Return Air bill together. If the site has returned the monthly Field Audit Form in the package, include this form with the others.
- 7.2.21 Place the forms in the tray for transfer to data entry.



Measurement Request: R159059N **Sampling Request:** Q152998M
Location: San Jose - Jackson Street **Sample Date:** 2/24/2008

114133 SASS cassette (Teflon filter) (GREEN)

13076283 Teflon Filter

	<i>Analysis</i>	<i>Laboratory</i>	<i>Aliquot ID</i>
GRAV	Mass - PM2.5	Gravimetric Analysis Lab	_____
Metals	Trace elements	Chester LabNet	_____

114144 SASS cassette (MgO denuder, nylon filter) (RED)

Nylon Filter

	<i>Analysis</i>	<i>Laboratory</i>	<i>Aliquot ID</i>
NO3nylon	Nitrate - PM2.5	Ion Analysis Lab	_____
SO4	Sulfate - PM2.5	Ion Analysis Lab	_____
Cations	Cations - PM2.5 (NH4, Na, K)	Ion Analysis Lab	_____

114155 SASS cassette (quartz filter) (ORANGE)

Quartz Filter

	<i>Analysis</i>	<i>Laboratory</i>	<i>Aliquot ID</i>
3EXT/OC EC Ext3 PM2.5	Organic and elemental carbon	OC/EC Analysis Lab	_____

Aliquot Created By: _____ **Creation Date:** _____

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Figure 6. Aliquot Creation Form. This form, labeled Measurement Request R426171, has three sections. The first section starts with I1566J. This is the Aliquot Creation Form and is used in the SHAL during the disassembly process to ensure that the filters are sent to the correct laboratories.

8.0 Flag Events

8.1 Summary of Task

This procedure describes how any unusual events are identified and marked accordingly for reporting purposes

8.2 Procedure

- 8.2.1 If any of the AIRS null value codes are assigned by the site operator, the event will be invalidated for reporting purposes. The SHAL supervisor (or his designee) will be informed, and he will decide if the filters will be sent to laboratories for analysis.
- 8.2.2 If marked “don’t run” or otherwise voided by operator in the comments section of the FSCOC, make decision to analyze aliquots. Mark the Level 0 Validation Form appropriately.
- 8.2.3 Send aliquots to analytical laboratories or to the “Do Not Analyze” bin in the SHAL refrigerators, as appropriate.
- 8.2.4 During disassembly, note any unusual issues on the Level 0 Validation form. Contact the SHAL supervisor for guidance.
- 8.2.5 Pass form to Form Evaluator.
- 8.2.6 The Form Evaluator will review site operator and SHAL comments along with site operator marked flags. The Evaluator will determine which flags are appropriate and mark them for data entry.

8.2.6.1 Treatment of Samples That Were Not Run as Scheduled

1. Samples that were scheduled as Routine, but were not run by the operator:
 - A. If the sample did not run, but will be invalidated, (for example a machine malfunction or power failure), do not convert it to a blank. Add the indicated flags and mark it as invalid.
 - B. If there was a Field or Trip blank scheduled for the same date and you know that the operator ran the Blank instead of running the Routine, convert the Blank to a Routine and the Routine to a Blank (simply swap the sample types).
2. Samples that were scheduled as Blanks, but were run as Routine samples by the operator:

- A. If the event appears to be a valid Routine sample, then convert the sample type to Routine. (This means that the sampling time is between 23 and 25 hours, etc.)
 - B. If the sample was run, but must be invalidated, do not change the sample type; invalidate it by assigning the appropriate flags.
- 8.2.7 For a complete description of the flagging procedure see *Standard Operating Procedure for Assigning Data Validation Flags for the Chemical Speciation Network*, May 14, 2008.
- 8.2.8 Add billing flags, where appropriate, and mark them on the data entry form.
- 8.2.9 A group of forms ready for data entry will now be assigned to a Batch.
- 8.2.9.1. Setting Level 0 and Level 1 Validation
- 1. Form batch creation
 - A. While assigning flags for each batch of forms, make sure you check the “Flags Reviewed” box (see Figure 7).
 - 2. Data Entry
 - A. While doing first data entry, review the level 0 and level 1 boxes. Verify they are checked and initialed.
- 8.2.10 Batches will be kept together during the data entry process and as each step of the data entry process is completed - the batch will be marked in the database accordingly (see Figure 8). All forms may be tracked during data entry using this batch process.
- 8.2.11 The Form Reviewer will then transfer a batch of forms to data entry to begin the entry of the information from the Custody Forms (see Figure 9) into the database. (For a detailed description of the data entry process, refer to the Database Operation SOP).

Form Batch: E12674P	Comment(s)
DATE_CREATED: 2/7/2008	Aliquots on Lab COC
Flags Reviewed: <input checked="" type="checkbox"/> by Boose, Larry, 2	
Entry 1 <input checked="" type="checkbox"/> by Wall, Constance, 2753 Entry 1 date: 2/12/2008	
Entry 2 <input checked="" type="checkbox"/> by Boose, Larry, 2 Entry 2 date: 2/7/2008	
Completed <input checked="" type="checkbox"/> Completed date: 2/13/2008	
Archived <input type="checkbox"/> by Entry 2 date:	
	Form CO
	Q151458V
	Q151459W
	Q151492X
	Q151526Q
	Q152789F
	Q1528230
	Q152857A
	Q152858B
	Q152891C
	Q1529255
	Q152991F
	Q153019K
	Q154105L
	Q154139V
	Q154140O
	Q154174Y
	Q1542774
	Q154311P
	Q154345Z
	Q1543460
	Q1544496
	Q154477A
	Q154505X
	Q154587F
	Q155481A
	Q1555153
	Q1555164
	Q155549D
	Q155583F
	Q155651A
	Q155719D
	Q1557206

Figure 7. An Example of the Data Entry Form Batch Creation Page. *This includes the Level 0 and Level 1 Validation acknowledgement.*

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

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Figure 8. Form Batch Chain of Custody. Forms listed in order added to batch. This form is used to track the Chain of Custody form. All forms are scanned into a batch before the data entry process.

 Q84261F	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)		Bin ID: B1649M Set: 3						
1. Laboratory, Out _____	3. Site, Out _____							
2. Site, In _____	4. Lab, In _____							
B. SITE AND SAMPLER INFORMATION								
1. Site AIRS Code <u>123456789</u>	5. Site Name <u>Test Site</u>							
2. Sampler S/N _____	6. Intended date of use Thursday, July 29, 2004							
3. Sampler Type <u>SASS</u>	7. Date of Sampler set-up _____							
4. Sampler POC <u>5</u>	8. Operator's name _____							
C. SAMPLER CHANNEL COMPONENTS								
Channel No.	Component ID No.	Component Description						
1	Kept at Site	SASS cyclone						
1	I3319E	SASS cassette (Teflon filter) (GREEN)						
2	Kept at Site	SASS cyclone						
2	I33207	SASS cassette (MgO denuder, nylon filter) (RED)						
3	Kept at Site	SASS cyclone						
3	I33218	SASS cassette (quartz filter) (ORANGE)						
D. START, END, AND RETRIEVAL TIMES								
Channel No.	Start date	Start time	End date	End time	Retrieval date	Retrieval time		
1								
2								
3								
E. SAMPLER CHANNEL INFORMATION (Post-Sampling)								
Channel No.	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								
2								
3								
Channel No.	Δ T Flag	Avg. Filter T (°C)	Max. Filter T (°C)	Min. Filter T (°C)	Avg. BP (mm Hg)	Max. BP (mm Hg)	Min. BP (mm Hg)	
1								
2								
3								
F. Comments _____ _____ _____								

Figure 9. PM_{2.5} CSN Custody and Field Data Form.

9.0 Ship Aliquots to Laboratories

9.1 Summary of Task

This procedure describes aliquot shipment to laboratories (both inside and outside RTI).

9.2 Procedure

- 9.2.1 Remove a group of filters (by filter type) from the SHAL refrigerator.
- 9.2.2 Generate a Laboratory Chain of Custody (LCOC) form (see Figure 10) for the group of filters.
- 9.2.3 Enter the information for the group of filters in the Laboratory Aliquot Tracking Notebook. Also, mark in the database the date the filters were transferred from the SHAL to the laboratory.
- 9.2.4 If filters are transferred to an RTI laboratory (or a local subcontractor), obtain a signature of the receiving laboratory on the LCOC Form. Retain one copy of the LCOC Form in the SHAL in the designated area.
- 9.2.5 For filters transferred to a subcontractor at a distance from RTI, sign and date the LCOC Form and keep one copy in the SHAL for RTI's records.

10.0 Sending Filters to an Offsite Subcontractor Laboratory for Analysis

10.1 Summary of Task

This procedure describes the process of packaging and shipping filters to an offsite laboratory for analysis.

10.2 Procedure

- 10.2.1 Determine the subcontractor to receive a particular type of filter.
- 10.2.2 Retrieve a batch of filters from the refrigerator or freezer to be shipped.
- 10.2.3 In the SHAL database, generate a LCOC form. Sign and date the LCOC form. Mark the date that the batch is being shipped from the SHAL.

 H279392		Page 1 of 3	
		RTI PM 2.5 Laboratory Chain of Custody Form (LCOC) Research Triangle Institute Gravimetric Analysis Lab	
Bar Code	Identification Number	Filter Type	Analysis Requested
Delivery Order: 0023		RTI Task: 08858	
	A556105D	Teflon Filter B 13071379	GRAV
	A556234L	Teflon Filter B 13071288	GRAV
	A564539W	Teflon Filter B 13071551	GRAV
	A573171L	Teflon Filter B 13071471	GRAV
	A573877C	Teflon Filter B 13070558	GRAV
	A573895E	Teflon Filter B 13071664	GRAV
Delivery Order: 0024		RTI Task: 08858	
	A556164O	Teflon Filter B 13071697	GRAV
	A556229O	Teflon Filter B 13071299	GRAV
	A562482O	Teflon Filter B 13071631	GRAV
	A564525Q	Teflon Filter B 13070832	GRAV
	A564534R	Teflon Filter B 13071722	GRAV
	A568734D	Teflon Filter B 13070536	GRAV
	A568737G	Teflon Filter B 13071528	GRAV
	A573174O	Teflon Filter B 13070194	GRAV
	A573260L	Teflon Filter B 13070296	GRAV
Custody Record (Name, Date)			
1. RTI SHAL, Out		Laboratory, In	
2. Laboratory, Out		RTI SHAL, In	
Comments _____			

Figure 10. RTI PM_{2.5} Laboratory Chain of Custody Form (LCOC). This form is used to track filters as they move through the analytical laboratories. The SHAL keeps a copy of the form and the receiving laboratory keeps the other two copies.

- 10.2.4 Package the samples in an appropriate container. Use a carrier appropriate to the type of filters being shipped. Complete the carrier's waybill, charging to the correct task.
- 10.2.5 Retain copies of the LCOC form, the waybill, and the cover letter.
- 10.2.6 Ship the samples via the carrier to the laboratory.

11.0 Receiving Filters From an Offsite Laboratory

11.1 Summary of Task

This procedure details the receipt of filters from an offsite laboratory.

11.2 Procedure

- 11.2.1 Verify that the package received is intended for the RTI SHAL. Remove the carrier waybill and retain for record keeping, or note the waybill number if the waybill cannot be removed from the packaging.
- 11.2.2 Inspect the package for damage. Note any damages. Open the package and removing any packing materials and freeze packs. Store the freeze packs in the freezer for future use.
- 11.2.3 Compare the filters to the custody form or packing list, if included. Note any discrepancies. Sign and date the custody form or packing list, acknowledging receipt of the package contents.
- 11.2.4 Store all filters appropriately. If filters are to be sent to another laboratory, follow the procedures for sending filters to RTI laboratories or offsite laboratories.

12.0 Return Unused Parts to Owner

12.1 Summary of Task

This procedure describes the steps needed to return unused sampler parts to their owner.

12.2 Procedure

- 12.2.1 Identify part(s) to be returned.
- 12.2.2 Prepare shipping paperwork, including air bill.
- 12.2.3 Associate container(s) with shipment.
- 12.2.4 Associate part(s) with container(s) in database. Carefully package each part in the appropriate container.

- 12.2.5 Verify actual contents of bins with printed list; make appropriate corrections.
- 12.2.6 Ship package, and add shipment date and airbill number to database.
- 12.2.7 Update Inventory in database to show which parts have been returned to owner.

13.0 Filter Types and Handling

13.1 Summary of Task

This procedure describes in general terms the handling of filters in the SHAL.

13.2 Procedure

- 13.2.1 Before assembling modules with clean filters, examine filters for tears, holes, etc. If any are damaged, record and discard. Wear gloves when handling filters and modules. Use forceps when handling the filters.
- 13.2.2 At least five different types of filters may be handled in the SHAL: Teflon, Nylasorb, Quartz, Polycarbonate, and XAD-impregnated.
- 13.2.3 Filters will be pretreated in the laboratories prior to being received in the SHAL.
- 13.2.4 Teflon and polycarbonate filters are equilibrated at a constant temperature and humidity and preweighed.
- 13.2.5 Quartz filters are pre-fired at high temperature to remove any carbon.
- 13.2.6 Nylasorb filters may be washed to remove ions. XAD-impregnated filters are treated with XAD.
- 13.2.7 Post treatment of filters will be done in the SHAL and the analytical laboratories.
- 13.2.8 Teflon and polycarbonate filters are post-treated by equilibrating in a temperature- and humidity-controlled room and reweighing the filter.
- 13.2.9 Quartz filters are kept frozen prior to analysis.
- 13.2.10 Nylasorb filters are kept refrigerated before analyzing.
- 13.2.11 XAD filters are refrigerated before analyzing.
- 13.2.12 Orientation and appearance of filter types: Teflon filters have an outer ring and an inner delicate Teflon membrane. The filter top will curve down. Teflon filters have a unique identifying number stamped on the outer ring.

- 13.2.13 Nylasorb filters are thin, curved filters with no outer ring. Both sides appear the same. Place these filters in the holders such that the curved downside of the filter collects the particulate matter.
- 13.2.14 Quartz and XAD filters are thicker than Teflon filters with no outer ring. The top has a bumpy texture, and the bottom has a grid pattern.
- 13.2.15 Polycarbonate filters are very thin with no outer ring. The top is shiny in appearance, and the bottom is dull.
- 13.2.16 Handling of Filter types (always use forceps and gloves): Teflon – pick up by the ring because the inner Teflon tears easily. Quartz, XAD, and Nylasorb – use forceps under edge. Polycarbonate – use forceps under edge and handle in a static-free environment.

14.0 Module Cleaning and Drying

14.1 Summary of Task

This procedure describes the cleaning of the disassembled modules.

14.2 Procedure

- 14.2.1 Once the module is disassembled, wipe down all parts using DI water wipes. Do not use soaps or other cleaners. Discard and replace the wipe with a fresh one as needed. Clean each module separately to keep parts from individual modules together.
- 14.2.2 Spread out the parts on a clean table surface. Allow all parts to air dry.

15.0 MET ONE (SASS) Module Disassembly/Assembly

15.1 Summary of Task

This procedure describes the handling of MET ONE modules in the SHAL.

15.2 Procedure

- 15.2.1 Place the white module holder on the work area in front of you. Take the yellow end caps off the MET ONE module and turn it so that the screw on the top is facing towards you.
- 15.2.2 Place the MET ONE module into the holder by placing the two long screws at the bottom of the module into the two holes on the module holder. Take the MET ONE wrench and unscrew all three screws only half way. Then remove them completely.

- 15.2.3 While keeping the screws and washers in the module, lift up and remove the metal covering of the MET ONE. Place it to the side. Then remove/open each piece placing the pieces in order on the table from first to last. Leave the base piece in the holder.
- 15.2.4 Remove filters and place in petri dishes.
- 15.2.5 Clean all of the module parts and allow to air dry completely.
- 15.2.6 Clean and dry the module and each individual piece. (See cleaning instructions.)
- 15.2.7 Place the closed bottom white filter ring back in the base, empty. Place the metal divider piece on top of it.
- 15.2.8 Open the next ring and place the appropriate filter on top of the screen, using tweezers. Securely close the ring and place it on the spacer.
- 15.2.9 All Teflon filters in the MET ONE modules will be placed into blue plastic cassettes - NOT the white Delrin plastic cassettes.
- 15.2.10 Place the empty metal ring or the denuder on top of the white ring with filter, then the top metal piece on top of that. Finally, place the metal covering over the pieces lining it up in the same direction it was taken off.
- 15.2.11 Tighten all the screws half way down then all the way down securely. This is done to make sure the module is closed evenly to prevent leaks during sampling. Place the module in a plastic Ziplock bag.

16.0 Andersen (RAAS 2.5-400) Module Disassembly/Assembly

16.1 Summary of Task

This procedure describes handling of the Andersen modules in the SHAL.

16.2 Procedure

- 16.2.1 Remove the Andersen modules from the bin. Place them on a clean work area for disassembly.
- 16.2.2 Unscrew the threaded center piece of the module. Take out the filter cassette from the center of the module. Remove the filter from the cassette. Place the filters into petri slides.
- 16.2.3 Clean each part of the Andersen filter module, including the white Teflon end caps. (See cleaning instructions.) Allow all pieces to air dry completely.

- 16.2.4 Place the appropriate filter on top of the screen in the bottom piece of each white ring. Close the cassette and reassemble the module.
- 16.2.5 Make sure the filter is oriented properly according to the direction of airflow through the module.
- 16.2.6 Place all modules into Ziplock bags and return them to the bin.

17.0 URG (400 and 450) Module Disassembly/Assembly

17.1 Summary of Task

This procedure describes the handling of URG modules in the SHAL.

17.2 Procedure

- 17.2.1 URG 400 - Turn the module so that the metal quick connect end is down and the male screw on top is up. Screw off the white Delrin screw sleeve and place it aside. Remove the filter housing inlet and place it aside.
- 17.2.2 Remove the filters from the first and second filter holders using forceps. Place the filters into pre-labeled petri slides.
- 17.2.3 Clean all of the module parts and allow them to air dry completely. (See the cleaning instructions.)
- 17.2.4 Holding the module with the metal quick connect end down, place a screen in the bottom holder and place the appropriate filter on top of it.
- 17.2.5 Push on the first holder and ring, placing the appropriate filter on top of the screen.
- 17.2.6 Now push on the top with the male end. Make sure that both of the filters are flat on the screen and all three layers are securely pressed together. Screw on the sleeve and place in a plastic Ziplock bag.
- 17.2.7 URG 450 - Hold the module so that the metal quick connect end is down. Unscrew the Delrin screw sleeve, remove it and place it aside.
- 17.2.8 Pull off the top male end layer and remove the filter using forceps. Place the filter in a pre-labeled petri slide.
- 17.2.9 Remove the screen from the module.
- 17.2.10 Clean all of the module parts and allow to air dry completely. (See cleaning instructions.)

- 17.2.11 Place the screen in the filter holder with the appropriate filter flat on top. Push the male end down on top of the filter. Make sure all layers are pressed together securely.
- 17.2.12 Finally screw on the Delrin screw sleeve and place the module in a plastic Ziplock bag for storage.

18.0 R & P ChemComb Model 3500 Speciation Sampling Cartridge Disassembly/Assembly

18.1 Summary of Task

This procedure details the handling of R&P type modules in the SHAL.

18.2 Procedure

- 18.2.1 Place the sampling module on the work table in front of you. Inspect retaining clips and external condition of module.
- 18.2.2 Place filter pack end of module in jig.
- 18.2.3 Loosen filter pack retaining clips and remove cylinder and inlet assembly. Place cylinder on its side on the work table.
- 18.2.4 Inspect filter for damage, wrinkles, etc. Note any problems on the Level 0 Validation Form. Remove filter with tweezers. Place filter in petri slide holder.
- 18.2.5 Clean parts of the filter pack. Clean the rim of the cylinder which touched the filter. Allow all to air dry, then re-install parts in filter pack.
- 18.2.6 Loosen inlet retaining clips and remove inlet from cylinder. Set cylinder aside. Be careful! The cylinder may contain glass spacers and denuders.
- 18.2.7 Remove impactor plate from inlet. Set it aside, impactor side up. Clean inlet interior and allow to air dry.
- 18.2.8 Refurbish impactor plate with vacuum grease. Re-install impactor in inlet; be sure impactor surface faces the inlet jet. Change to a new pair of gloves when impactor has been re-installed.
- 18.2.9 Carefully remove any glassware and spacers from interior of cartridge for cleaning or re-use. Clean interior of empty cartridge.
- 18.2.10 Attach the inlet/impactor assembly to the cartridge. Secure by closing retaining clips. Load denuder components in cartridge as required for setup.

- 18.2.11 Place the filter pack into the jig. Install proper filter in the top-most filter holder. NOTE: Components of module vary with type of filter. See detailed instructions.
- 18.2.12 Insert the cylinder/inlet assembly into the filter pack assembly. Secure by closing retaining clips.
- 18.2.13 Remove the assembled module from the jig. Close both ends with plastic caps. Place the labeled module in a plastic bag and store until ready for shipment.

19.0 R&P FRM Module Disassembly/Assembly

19.1 Summary of Task

This procedure describes the handling of the R&P FRM modules in the SHAL.

19.2 Procedure

- 19.2.1 Remove the blue R&P FRM filter modules from the transport magazine cylinder. Place the modules on a clean work area for disassembly.
- 19.2.2 Separate the blue cassette rings and open the filter cassette. Remove the filter. Place the filter into a petri slide.
- 19.2.3 Clean the blue poly cassette rings and the support screens. Allow all parts to air dry completely. (See cleaning instructions.)
- 19.2.4 Place the appropriate filter on top of the screen in the bottom ring of the cassette. Close the cassette by replacing the top ring and pressing down into the bottom ring.
- 19.2.5 Place the filter modules back into the transport magazine.
- 19.2.6 Place the magazine in a clean Ziplock bag for storage prior to shipping back to the field sampling site.

20.0 URG 3000N Cartridge Disassembly/Assembly

20.1 Summary of Tasks

This procedure describes the handling of the URG 3000N modules in the SHAL.

20.2 Procedure

- 20.2.1 Place the URG 3000N on a clean work surface for disassembly.
- 20.2.2 Remove the red caps and open the filter cassette. Remove the filter using the cassette tool. Place the filter in a petri slide.

- 20.2.3 Clean the filter cassette and support screen. Allow all parts to air dry completely. (See cleaning instruction.) While the parts are drying, download the compact flash memory card data to the PM_{2.5} Speciation database.
- 20.2.4 Place the appropriate filter on the bottom ring of the cassette. Close the cassette using the cassette tool.
- 20.2.5 Place the filter cassette and compact flash card in a clean Ziplock bag for storage prior to shipping back to the field sampling site.



21.0 PM Coarse Filter Handling

21.1 Summary of Task

This procedure describes the handling of the coarse filter modules in the SHAL.

21.2 Procedure

- 21.2.1 Place the coarse filter module on a clean surface for disassembly.
- 21.2.2 Disassemble the coarse filter module following the manufacturers specifications.
- 21.2.3 Remove the sampled filters and place in petrislides.
- 21.2.4 Clean all of the module parts and allow to air dry completely.
- 21.2.5 Install new clean filters into the module in preparation for the next sampling event.
- 21.2.6 Place the filter module into a clean Ziplock bag for storage prior to shipping back to the field sampling site as described in Section 5.0

22.0 Denuders for Collection of Acidic, Basic, and Organic Gases

22.1 Summary of Task

This procedure describes the handling of denuders in the SHAL.

22.2 Procedure

- 22.2.1 Freshly prepared denuders for the collection of acidic and basic gases and organic vapors will be supplied to the SHAL by the Denuder Refurbishment Laboratory.
- 22.2.2 As directed by EPA, denuders will be installed in modules for the purposes of removing acidic, basic or organic gases from the air being sampled. Some denuders will only be employed to “scrub” gases from the sampled air. Other denuders will be used to collect the target gases for subsequent extraction followed by analysis to determine the concentration of the gases in the sampled air.
- 22.2.3 The use of appropriate denuders will be scheduled in the PM_{2.5} database. Based on this schedule, the SHAL will load the correct denuder type into sampling modules for subsequent shipment to the field sampling locations. The denuder will be identified by the unique inventory number of the filter module in which it is installed.
- 22.2.4 Denuders may be installed into modules containing filters, or they may be installed in modules that contain only a denuder or a series of denuders.
- 22.2.5 Upon their return to the SHAL from the field sampling location, the denuders will be removed from the modules.
- 22.2.6 For those denuders that are only used to “scrub” gases out of the airstream and will not be subsequently extracted, they may be reinstalled in the module for the next sampling event if it is determined that the denuder has remaining capacity to “scrub” out the target gas from the airstream.
- 22.2.7 The denuders that will be extracted will be assigned a unique laboratory identification number and returned to the denuder laboratory from the SHAL for extraction and subsequent analysis.

Standard Operating Procedure for Coating and Extracting Compact Parallel-Plate Denuders for Ammonia Determination

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

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

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Standard Operating Procedure for Coating and Extracting Compact Parallel-plate Denuders for Ammonia Determination

1.0 Purpose and Applicability

This document outlines procedures for coating a denuder with phosphorous acid and extracting the denuder for the collection and quantifying of gas-phase basic species in the ambient air, primarily ammonia. This standard operating procedure (SOP) applies to coating and extracting glass parallel-plate denuders of the type that could be used by the MetOne SASS chemical speciation sampler. The procedures may also be used, with some modifications, to process other types of denuders, such as glass annular denuders. Other uses of the parallel plate denuder, not covered in this SOP, involve coating the surfaces with basic substances (e.g., sodium carbonate) for use in capture and quantifying acidic gases (e.g., nitric acid vapor, sulfur dioxide) present in ambient air.

2.0 Safety Precautions

- 2.1 Always wear clean, dry, laboratory grade gloves when handling any components involved in these procedures and corrosive chemicals. Disposable nitrile gloves provide adequate protection against accidental hand contact with small quantities of most laboratory chemicals.
- 2.2 Always wear protective eyewear when conducting the laboratory procedures specified in this SOP.
- 2.3 Read, understand, and follow the Material Safety Data Sheets (MSDSs) for all chemicals involved in this procedure. Several chemicals are corrosive or should not contact the skin for other reasons.
- 2.3 Always keep open chemical containers in properly operating fume hoods and wear adequate protective clothing, as outlined in the MSDSs.
- 2.5 Always label secondary containers used in this procedure.
- 2.6 Disposal of waste materials should be in accordance with the appropriate MSDS.

3.0 Equipment and Materials

- 3.1 Laboratory nitrile gloves, appropriately sized. VWR Brand Cat. No. 40101.
- 3.2 Phosphorous acid, 99%. 100-200 g. Aldrich, Cat. No. 215112.
- 3.3 Citric acid, monohydrate. 500 g. J.T. Baker Brand, Cat. No. 0118-01
- 3.4 Methanol, 4 liters, reagent grade. VWR Brand Cat. No. VW4300-3.
- 3.5 Volumetric flask, 250 mL, Pyrex Class A. VWR Brand Cat. No. 29610-182.
- 3.6 Glove box or cabinet; heavy clear flexible plastic film. Fulcrum Inc., Model GC-2 with two chambers and four air valve assemblies.

- 3.7 Laboratory deionized/reverse osmosis water.
- 3.8 Source of ammonia-free nitrogen gas or clean air to purge glove box.
- 3.9 Sample bottles, narrow-mouth, high-density polyethylene, 15 mL capacity, VWR Brand Cat. No. 160570-007.
- 3.10 Graduated cylinders, 10 and 50 mL capacity, VWR Brand Cat. No. 24711-295 or equivalent.
- 3.11 Pyrex rectangular glass baking dishes, various sizes. (could be a local purchase).
- 3.12 Plastic powder funnels, sized to fit inside neck of volumetric flasks and sample bottles.
- 3.13 Antistatic, polystyrene, 3.4 oz. weigh boats. VWR Cat. No. 89106-766
- 3.14 Wristwatch or small electronic timer.
- 3.15 Denuder drying manifold or assembly as given in Section 6.3.6. (Must be custom-designed for the laboratory; at this time there are no commercially available drying manifolds. See References 1 and 2.).
- 3.16 Thermo Scientific Finnpiquette, 1-10 mL auto-pipette and pipette tips. Cat. No. EW-25013-24
- 3.17 BD Falcon lidded, sterile, 47 mm, disposable petri slides. WR Cat. No. 25373-085.
- 3.18 BD Falcon 16mL, round-bottom, capped, sterile, polystyrene test tubes. VWR Cat. No. 60819-422 (use as filter storage and extraction container).
- 3.19 Various laboratory supplies (fine-tipped plastic and/or stainless steel tweezers, beakers, watch glasses, plastic rinse bottles containing deionized water and methanol, laboratory tissue wipes, marking pen, labels, etc.). These items may be selected from general laboratory stock.
- 3.20 Laboratory notebook for recording data or an electronic database.

4.0 Preparation of 5% Coating Solution

Note: Minimal exposure of reagent chemicals and solvents to ambient air is required to keep ammonia values in the blank sample(s) low. *Exhaled breath contains ammonia.*

- 4.1 Record all information in a laboratory data notebook and directly to an electronic database. At a minimum, the labeling for bottles must show the date of preparation, content, initial volume, and the name of the person preparing the contents.
- 4.2 Use the following steps to prepare a 5% Phosphorous Acid Coating Solution.

Note: Solutions at other percentage concentrations are prepared by adjusting the amount of phosphorous acid weighed.

- 4.2.1 Using a laboratory balance readable to the nearest 10 mg, zero the balance and then tare a clean, dry, polystyrene weigh boat. Weigh out 12.5 g of phosphorous acid crystals. Do this quickly to avoid absorption of ammonia gas from the air.

- 4.2.2 Working in a fume hood, fold two sides of the weigh boat to almost meet and then transfer the phosphorous acid crystals directly into a pre-labeled, 250 mL glass volumetric flask. Use a graduated cylinder containing 25 mL of deionized water to rinse any residue remaining in the weigh boat into the volumetric flask.
- 4.2.3 Add methanol to the flask until the total volume reaches 250 mL. Cap the volumetric flask, swirl, and invert several times until phosphorous acid is dissolved. Set flask aside for use in coating denuders.

5.0 Preparation and Use of Glove Cabinet

- 5.1 Ensure interior surfaces of the glove cabinet are clean; wipe down with a clean sponge or paper towel that is moist with deionized water. Line the bottom of the cabinet with clean, dry, paper towels.
- 5.2 Pour citric acid crystals into 3 or 4 polystyrene weigh boats to a depth of about 0.25 inch. Place the dishes inside, along the back of the cabinet, at a point away from the area where you will be manipulating denuders during the coating and extraction processes. The dishes will stay inside the cabinet during use to absorb ammonia should any be present.
- 5.3 Determine what procedures you plan to conduct inside the glove cabinet and load needed equipment into the main section of the cabinet and into the side section of the cabinet. Equipment may include the following: clean denuders to be coated; a flask or bottle containing the coating solution; rinse bottles containing water or methanol; beakers and watch glasses for covering beakers, freshly-coated denuders; a box of laboratory wipes (KimWipes® or equivalent); a large glass beaker to serve as a “sink” for waste liquids; a plastic bag to contain discarded laboratory wipes; pre-labeled bottles to receive rinses from extracted denuders; pre-labeled plastic bags to contain coated denuders when they are dry and ready to be removed from the cabinet.
- 5.4 Connect a source of nitrogen (high purity house nitrogen or high purity compressed gas cylinder) via Teflon® or plastic tubing to an inlet on the glove cabinet. Slightly open the plastic zippers on the front, side, and interior of the cabinet so that a significant flow of nitrogen can pass freely through the cabinet interior and out the openings; do not over-pressurize the flexible plastic cabinet. After about 5 minutes, close one of the exterior zippers and allow a slow, excess flow of gas to continue while one is working inside the cabinet.

Note: Clean house air may be substituted for nitrogen.

- 5.5 Depending on personal preferences and convenience, hand access to the glove cabinet interior can occur in several ways:
- By way of the built-in plastic gloves that are laminated to the front plastic wall of the cabinet.
 - Since the built-in gloves are bulky and do not provide good tactile qualities, the hand ends of the built-in gloves can be cut off. The user then dons laboratory gloves and uses large rubber bands or stretchable Velcro to make a snug fit of the built-in glove

sleeves to the forearm. If this method is used, be sure to roll up and clamp or clip the sleeves of the built-in gloves when they are not in use to prevent entry of room air to the cabinet interior.

- So long as a noticeably positive flow of air or nitrogen from within the cabinet to the outside is maintained, the user may partially open the front zipper and insert a gloved hand (or both hands) in the opening to maneuver within the cabinet. Do not leave the zipper open any longer than necessary to coat a denuder, extract a denuder, etc.
- Close the zipper between distinct operations. Be sure the clean gas flow ceases or is lowered when the zipper is closed or nearly closed; this prevents over-pressurizing the chamber walls.

6.0 Cleaning, Coating, and Storage of Compact Parallel-plate Denuders

6.1 This procedure is written for use with quartz, parallel-plate denuders with dimensions that allow them to fit into the MetOne sampling module. Any changes in the size and design of the denuder will necessitate revisions to this section of the SOP. Each denuder comes with a set of “caps” which screw onto the ends of the denuder. These caps are used to protect the device from exposure to air and dust after it has been sampled, cleaned, or coated and stored. Figure 1a and Figure 1b, adopted from Reference 1, illustrate details of the parallel-plate denuder and show how it is mounted inside the MetOne SASS sampling module.

6.2 Wear gloves when conducting the steps in the following cleaning process. This cleaning process may be used to prepare the denuder when first received from the manufacturer or for removing an acidic coating from a previous sampling event.

- 6.2.1 Disassemble the denuder by removing the top and bottom caps. There is an o-ring in the top of the denuder and one in the bottom cap. Remove the o-rings from their grooves. The o-ring must be cleaned in the same manner as the denuder and the end caps.
- 6.2.2 Rinse the denuder, o-ring, and end caps in a running stream of hot tap water. Rinse all openings in the denuder, invert it and rinse from the other end as well. Rinse the exterior of the denuder and the interior and exterior of each end cap. Carefully shake out excess tap water. To help the water to drain from each piece, place them on a stack of laboratory paper towels.
- 6.2.3 Rinse the o-rings in a stream of running of DI water. Pat them dry with paper towels
- 6.2.4 Rinse the top and bottom caps by filling each with DI water, swishing, and discarding the rinse. Repeat three times. To help the water drain from the end caps turn each upside down on paper towels.

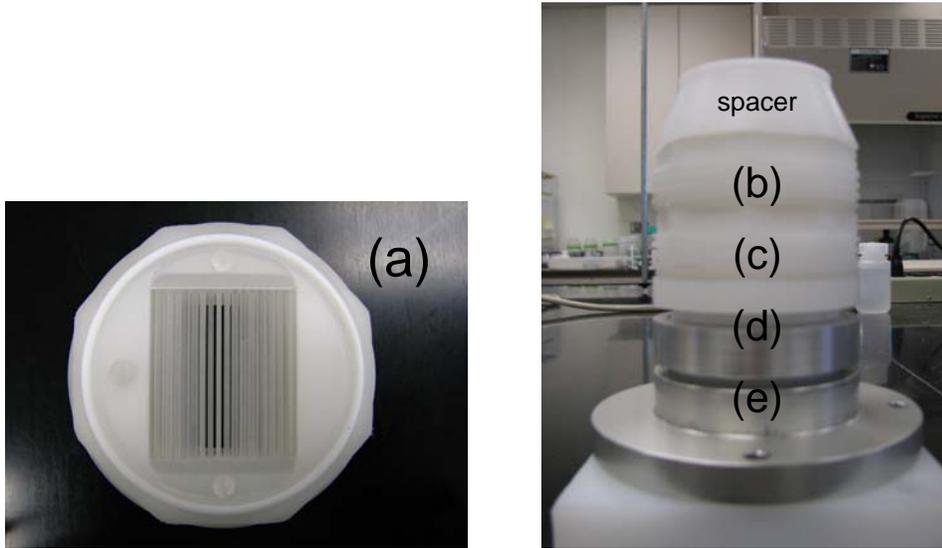


Figure 1a. SASS sampling canister featuring Prototype 2 denuders: (a) Prototype 2 integrated slide denuder; Prototype 2 sampling train assembled (b) Denuder A, (c) Denuder B, (d) Filter 1, and (e) Filter 2. This assembly is enclosed by the cover and spacer shown in Figure 1b.

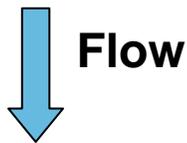


Figure 1b, SASS sampling mounted in plastic block for ease of handling. (f) sharp cut PM2.5 cyclone, (g) canister cover, (h) canister extender.

- 6.2.5 Rinse the denuder with DI water for approximately 10 seconds. Ensure that the water runs into the channels between the plates of the denuder and makes contact with each plate wall. Rinse the outside threads of the denuder.
 - 6.2.6 Place the denuder in the top cap and then fill the cap with DI water. Fill the bottom cap with DI water.
 - 6.2.7 Set the caps and denuder aside and allow them to soak for ~ 5 minutes.
 - 6.2.8 Repeat steps 6.2.3 through 6.2.6 three additional times. When repeating step 6.2.6 shake the denuder back and forth for thirty seconds, open the denuder and then discard the rinse. It is not necessary to repeat the 5-minute soaking in step 6.2.7.
 - 6.2.9 After the final rinse in Step 6.2.8, take care not to drop or bump the denuder, use relatively vigorous shaking to remove the excess water from the channels of the denuder and the caps.
 - 6.2.10 To speed the drying process, dislodge water droplets by holding the denuder in front of a moderately flowing stream of nitrogen. Repeat the nitrogen drying with each cap.
 - 6.2.11 Place the denuder, o-rings, and the caps inside the glove box on a bed of laboratory toweling. To ensure complete drying, set the nitrogen purge to allow excess gas to flow from one opening in the glove cabinet. Ensure that all other openings are closed.
- 6.3 The following coating process is used to apply a phosphorous acid solution to the parallel plates in the denuder. Be sure to prevent intrusion of room air by maintaining an excess flow (slight positive pressure) from the nitrogen purge while working inside the glove cabinet.
- 6.3.1 Ensure that the o-rings are properly seated in the grooves on the denuder and the bottom end cap. Then screw the denuder firmly into the lower storage cap.
 - 6.3.2 Transfer approximately 15 mL of the 5% phosphorous acid coating solution to a 25 mL beaker. Although the work is conducted inside the glove cabinet, care needs to be taken not to expose large volumes of the solution to the atmosphere.
 - 6.3.3 Use the Thermo Scientific Finnpiquette auto-pipette to deliver 6 mL of the coating solution into the denuder. Ensure that each channel between the plates receives some of the solution with this delivery.
- Note:** Deliver more solution if needed; however, ensure that the channels are not overfilled. The solution should not flow out onto the surface of the denuder.

- 6.3.4 Cover the denuder by threading the upper cap loosely onto the denuder. Allow the denuder to soak in the coating solution for 10 minutes.
 - 6.3.5 Remove the top cap and then unscrew the denuder from the bottom cap. Remove most of the coating solution from the denuder by tapping it gently against the bottom cap or shaking the denuder gently over the bottom cap.
 - 6.3.6 If a drying manifold is unavailable, place the denuder and caps on a bed of crumpled laboratory toweling and allow wicking to remove the excess coating solution from the denuder. Crumpling the tissues allows circulation of ammonia-free gases through the denuder channels. After a minute or two, grasp the denuder and turn it over. Leave the denuder in place in the cabinet for twenty minutes and then examine to determine if the solvents of the coating solution have evaporated.
 - 6.3.7 Verify evaporation of the coating solution by viewing the denuder from one end to determine if all channels are open to light and that no liquid is visible or present as evidenced by touching the denuder to a dry laboratory tissue. To prevent possible contamination from room air, ensure that there is an excess nitrogen flow. Continue the drying process as necessary.
 - 6.3.8 When the denuder is completely dry, it maybe installed directly into the sampling module or stored for later use.
- 6.4 If storing the denuder for future use, screw the top and bottom caps onto the denuder, place the assembly in zip-closing, plastic bag and store it in the refrigerator.
- Note:** It is recommended that the denuder and bag be placed in another larger plastic bag to ensure no room air enters. At this point, it is very important that the denuder be uniquely identifiable so that it can later be associated with a sampling event/location. Use an indelible pen to write this information on both of the denuder end caps and the zip-closing bag. Record all this information in a laboratory notebook or directly into an electronic database.
- 6.5 If the MetOne sampling module is to be loaded at this time, use the following steps to conduct the loading procedure while inside the glove cabinet. Determine which filters are to be used in the sampling event and insert the appropriate filter cassettes. If filters are not required, use Teflon[®] spacers as necessary
- 6.5.1 Place MetOne sampling module into a plastic block having holes to contain the module's attachment flanges. This holds the module in a level position and maintains stability during placement of the denuder and closure of the total module assembly. (Refer to Figure 1b).
 - 6.5.2 Loosen all of the module bolts before attempting to remove them completely. Remove module cover exposing the interior of the module.
 - 6.5.3 Determine which filters will be used during sampling and insert the filters into the appropriate filter cassettes. Record the identification numbers for each filter being used. If using Teflon[®] filters, record the pre-weights for each filter as well as the filter ID numbers.

- 6.5.4 *Nylon filter*: insert the filter cassette into the “outlet” section of the sampling module. Place a stainless steel filter spacer on top of the nylon filter cassette. If the nylon filter is not used, insert a Teflon[®] spacer as a place holder for the filter in the assembly.
- 6.5.5 *Teflon[®] filter*: place the Teflon[®] filter cassette on top of the stainless steel (or Teflon[®]) filter spacer.
- 6.5.6 Place a plastic spacer on top of the Teflon[®] filter cassette. This spacer is used to separate the Teflon[®] filter and the parallel-plate denuder.
- 6.5.7 Place a coated parallel-plate denuder onto the spacer. To ensure a secure fit, align the spacer pins with the denuder pins. Ensure that the black o-ring is properly seated in the groove on top of the denuder
- 6.5.8 Place the conical spacer on top of the denuder. To ensure a tight seal against the conical spacer, the denuder’s o-ring must face upwards in the assembly.
- 6.5.9 Place an o-ring on the top of the conical spacer. This o-ring will ensure a tight seal against the “inlet” section of the sampling module.
- 6.5.10 Without disturbing the alignment of the filter cassettes, spacers, and denuder, carefully place the “inlet” section of the sampling module over the assembly.
- 6.5.11 Insert the module bolts and tighten each bolt one half turn in sequence to ensure the sampling module seals evenly.

Note: It is important that the data records link the identity of the denuder to the identifying information assigned to the sampling module.

7.0 Quantitative Extraction of Compact Parallel-Plate Denuders

In order to avoid exposure to room air, the module containing the sampled denuder must be opened while inside the nitrogen-purged glove cabinet. It is okay to loosen the bolts on the module before placing it inside the cabinet. Wear laboratory gloves when conducting the extraction. Proceed as shown below to extract an exposed denuder for subsequent analysis:

- 7.1 Disassemble the module, remove the denuder, ensure that the o-ring is in place, and then screw the denuder firmly onto its bottom cap.
- 7.2 Use the auto-pipette to deliver 6 mL DI water (extracting solution) into the denuder and then screw the top cap on firmly.
- 7.3 Shake the denuder to move the extracting solution back and forth through the channels for a minute or two. Rotate the denuder top to bottom a few times while shaking it.
- 7.4 Place the denuder inside the glove cabinet and then unscrew the top cap and set it aside.
Note: Use caution when unscrewing the top cap because the denuder could unscrew from the bottom cap at the same time.
- 7.5 While holding the bottom cap firmly against the bench top, slowly and gently unscrew the denuder from the bottom cap.

- 7.6 When the denuder detaches from the bottom cap gently tap it against the bottom cap or shake it gently over the bottom cap to dislodge any solution trapped between the denuder plates.
- 7.7 Carefully decant the extract from the bottom cap into an appropriately labeled, 15 mL sample bottle.
- 7.8 Attach a label with the appropriate sample information to a 15 mL sample bottle. Prepare a blank sample by pipetting 6 mL of DI water into the bottle.
- 7.9 Submit the blank and the denuder's extract to the laboratory for analysis of ammonium or refrigerate the samples while awaiting analysis. Ensure that the denuder's extract is analyzed within the established holding time.

Note: Sampling could be conducted using two parallel-plate denuders in a single sampling module. To process the second denuder, repeat the steps in this section. It is important to label the bottles to receive the extracts to ensure one knows which denuder's extract is in the bottle.

8.0 Storage and Handling of Denuder Extract and Handling in the Ions Laboratory

- 8.1 Store the extract in a labeled sample bottle. Store the sample bottle in a chemical free refrigeration unit capable of maintaining temperatures between 1 and 5 degrees C until it is time to transfer custody of the solution to the analytical laboratory.
- 8.2 Alert the analytical laboratory that it will be necessary to take precautions to limit exposing the samples to room air when pouring the extract from the 15 mL bottle into analysis vials for use with the ion chromatograph or automated colorimeter. The analyst should seal the analysis vials securely to prevent intrusion of air that may contain ammonia while the vials await their turn for analysis.

9.0 Corrective Action

- 9.1 High laboratory or field blank values are the usual causes for concern. If this occurs, repeat the cleaning procedure for the denuder, evaluate the ammonium content of the coating solution, and conduct a peer evaluation the processes used to clean, coat, install, and check the laboratory and field blank samples. Repeat the coating and recheck the blank extract solutions for acceptable values. Past experience (Reference 2) has shown a blank laboratory value of 1.0 $\mu\text{g NH}_4^+$ per denuder can be achieved.

10.0 References

1. Schurman, Misha Iris, Fall 2009. Master of Science Thesis: “Developing and Testing Prototype Compact Denuders for Ambient Air Sampling Applications.” Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado.
2. Eaton, W. Cary, Wall, Constance V., and Walters, Steven J., October 2009. “Refinement and Field Testing of Denuder Technology for Quantification of Basic and Acidic Gases to Support EPA PM_{2.5} and CASTNET Ambient Air Monitoring Network Research.” RTI International Institutional Research and Development Final Report.

Standard Operating Procedure for Shipping Filters to and from an Off-Site Laboratory

Environmental and Industrial Sciences Division
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Date: 2/18/2009

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Date: 2/19/09



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

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Standard Operating Procedure for Shipping Filters to and from an Off-Site Laboratory

1.0 Purpose

This procedure describes the required process for storing, packaging, and shipping filters between RTI and off-site laboratories.

2.0 Scope

This procedure applies to all filters being shipped between an offsite laboratory and RTI.

3.0 Responsibility

This procedure is for RTI staff members who send filters to an off-site analytical laboratory and staff members at off-site analytical laboratories who handle and return the filters to RTI.

4.0 Procedure

4.1 Materials

- Blue Ice packs (2 $\frac{5}{8}$ " x 5 $\frac{1}{8}$ " x 1 $\frac{1}{4}$ ")
- Small cardboard boxes (7" x 3 $\frac{1}{2}$ " x 3 $\frac{1}{2}$ ")
- Filters in Millipore petri slides, labeled with unique identification numbers
- Resealable bags (12" x 12")
- Small hand-held cooler
- Carton sealing tape.

4.2 Pre-Packaging Activities

1. Place Blue Ice packs in a freezer at -15 to -20 degrees Centigrade at least 48 hours prior to the shipping date
2. Assemble cardboard boxes to be used in packaging
3. From the freezer, retrieve the necessary number of filters contained in plastic Millipore petri slides labeled with unique identification numbers

4.3 Preparation of Laboratory Chain-of-Custody Forms (RTI only)

1. In the Speciation Database section "Find/Create Aliquot Batch to Lab," create the batch of filters to be sent to the off-site laboratory.

2. Generate a Laboratory Chain-of-Custody (LCOC) Form for the batch of filters.
3. Print the LCOC onto three-part carbonless copy paper. A sample LCOC is shown in **Figure 1**.
4. Sign and date the LCOC at the bottom of each page in the section entitled “RTI SHAL, Out.”
5. In the “RTI SHAL, Out” field, enter the date of shipment from RTI.
6. Remove the bottom copy of the multi-part form and retain it in the shipment records in the Sample Handling and Archiving Laboratory (SHAL) as a record of the shipment.
7. Send the top two copies of the LCOC with the filters to the off-site laboratory.

4.4 Packaging the Filters for Shipment

1. Place petri slides containing filters into a small cardboard box
2. Insert the small cardboard box into a resealable bag and seal the bag

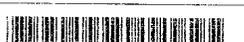
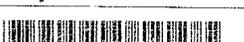
 H26176F		Page 1 of 2 RTI PM 2.5 Laboratory Chain of Custody Form (LCOF) DRI	
Bar Code	Identification Number	Filter Type	Analysis Requested
Delivery Order: 0019		RTI Task: 08858	
	A5152814	IMPROVE Quartz	IMPROVE_A
	A525043X	IMPROVE Quartz	IMPROVE_A
	A525044Y	IMPROVE Quartz	IMPROVE_A
	A5275990	IMPROVE Quartz	IMPROVE_A
Delivery Order: 0020		RTI Task: 08858	
	A5153500	IMPROVE Quartz	IMPROVE_A
	A5154718	IMPROVE Quartz	IMPROVE_A
	A5154729	IMPROVE Quartz	IMPROVE_A
	A515476D	IMPROVE Quartz	IMPROVE_A
	A515477E	IMPROVE Quartz	IMPROVE_A
	A515486F	IMPROVE Quartz	IMPROVE_A
	A523649D	IMPROVE Quartz	IMPROVE_A
Delivery Order: 0021		RTI Task: 08858	
	A5236448	IMPROVE Quartz	IMPROVE_A
	A5236459	IMPROVE Quartz	IMPROVE_A
Delivery Order: 0022		RTI Task: 08858	
	A5153453	IMPROVE Quartz	IMPROVE_A
Custody Record (Name, Date)			
1. RTI SHAL, Out	<i>Jim Rowke</i>	<i>5/17/07</i>	Laboratory, In
2. Laboratory, Out			RTI SHAL, In
Comments			

Figure 1. Sample Laboratory Chain-of-Custody Form.

4. Place one or more sealed bags that contain boxes of filters, into a small insulated cooler
5. Place the previously frozen Blue Ice packs around the boxes of filters inside the cooler. Fill the cooler completely with the Blue Ice packs so that the contents are maintained at or below 4 degrees Centigrade during transit.
6. Put the top two pages of the LCOC Form for the filters in a separate resealable bag along with a cover letter for the shipment. The cover letter must specify:
 - a. The numbers of filters in the shipment.
 - b. The expected date analytical results should be received at RTI.
 - c. The date the unused portions of filters and packaging materials from the off-site laboratory must be shipped back to RTI.
7. Retain a copy of the cover letter at RTI.
8. Place the resealable bag containing the cover letter and the LCOC Form directly on top of the items in the cooler.
9. Close the cooler and seal the cooler securely with tape.
10. Prepare an airbill for overnight delivery service and affix it to the cooler.
11. Retain a copy of the airbill at RTI.
12. Ship the cooler via overnight service to the off-site laboratory. Only send shipments on Monday through Thursday and never on Friday through Sunday or on the day before a holiday.
13. Send an e-mail notification to the RTI Project Manager, who will inform the intended package recipient of the:
 - a. Date of shipment.
 - b. Identity of the shipment contents.
 - c. Carrier.
 - d. Airbill number used for the shipment.
 - e. Expected delivery date of the cooler.

4.5 Storage and Handling of Filter Samples By an Off-Site Laboratory

1. When a cooler is received, immediately remove the resealable bags containing the cardboard boxes of filters from the cooler.

2. Immediately place the resealable bags containing the cardboard boxes of filters into a freezer or refrigerator.
 - a. Teflon and nylon filters must be kept in a refrigerator at 4 degrees Centigrade.
 - b. Quartz filters must be kept in a freezer at or below minus 15 degrees Centigrade before and after analysis, but individual boxes of filters are to be kept in a refrigerator or cooler during working hours on the day (or days) they are to be analyzed.
3. Immediately after analysis, reseal each remaining filter in its original labeled petri slide to protect the integrity of the filters for potential future analyses and place it back into the refrigerator or freezer.
6. When analysis of the filters in the box or tray is complete, or at the end of day, whichever comes first, reseal the refrigerated box or tray of filters in its resealable bag and place it back in the freezer or refrigerator.

4.6 Return Shipment of Filters from an Off-Site Laboratory

1. Each shipment of filters sent from RTI must be shipped back to RTI after analysis unless by previous agreement the offsite laboratory will retain or archive the filters.
2. Place Blue Ice packs in a freezer at minus 15 to minus 20 degrees Centigrade for at least 48 hours prior to being used for shipping filters.
3. Make sure that:
 - a. The petri slides that contain the filters are all in the same cardboard boxes in which they were received.
 - b. Each box of filters is in a separate resealable bag.
 - c. All resealable bags are sealed.
4. Place the resealable bags containing the filters in a small insulated cooler.
5. Place all of the frozen Blue Ice packs that were received in the original shipment of filters around the packaged filters to fill the cooler and to keep the filters at or below 4 degrees Centigrade during transit.
6. Sign and date the original LCOC Form for these filters in the "Laboratory Out" section, indicating the date of shipment back to RTI.
7. Keep the second page of the multipart LCOC Form as part of the records of the analyses.

8. Place the original top page of the LCOC Form into a separate resealable bag.
9. If the off-site laboratory prepares a cover letter, place it in the resealable bag containing the LCOC Form.
10. Close the cooler and seal it securely with tape.
11. Prepare an airbill for overnight delivery service and attach it securely to the cooler.
12. Ship the cooler only via overnight service back to RTI. Only send shipments on Monday through Thursday and never Friday through Sunday or on the day before a holiday.
13. E-mail a notification to the contact at RTI on the date of shipment identifying the shipment contents, the carrier, the airbill number used for the shipment, and the expected delivery date of the cooler.

Standard Operating Procedure for Cleaning Nylon Filters Used for the Collection of PM_{2.5} Material

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

Prepared by: Em D. Handison

Date: 8/26/09

Reviewed by: Jane B Flayn

Date: 8/26/09

Approved by: RKM Jayant

Date: 8/26/09



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

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Standard Operating Procedure for Cleaning Nylon Filters Used for the Collection of PM_{2.5} Material

1.0 Procedural Section

1.1 Purpose and Applicability

Nylon filters are used for the collection of PM_{2.5} material in the chemical speciation particulate samplers. These filters are analyzed for the following ions: nitrate, sulfate, ammonium, sodium, and potassium. The filters, as purchased and received from different manufacturers, show unacceptable levels of these ions, often exceeding the maximum level of 1 μg per filter for a particular ion. This has prompted the development of a procedure for cleaning the nylon filters prior to their use for field sampling; this procedure is described in this standard operating procedure (SOP).

1.2 Summary of Method

Fifty nylon filters are placed in a 2 L polypropylene jar with approximately 1000 mL of polished deionized water (18.2 M Ω -cm; water that has been passed through a secondary deionization system). The filters are shaken in the water for approximately 2 minutes, and the water is decanted and discarded. This process is repeated. The jar is then filled with polished deionized water and placed on a Toxicity Characteristic Leaching Procedure (TCLP) apparatus (TLCP, EPA SW-846 Method 1311). The jar is rotated for 7 to 8 hours, and the water is replaced with fresh polished deionized water. The jar is then rotated overnight for 14 to 16 hours before the water is replaced again. After another 24 hours of washing, the water is drained from the filters and the filters are dried. (The order of extended washing may vary; that is the sequence may be 24 hours, 7 to 8 hours, and then 12 to 14 hours rather than 7 to 8 hours, 12 to 14 hours, and 24 hours.) The filters are dried on glass racks in a convection oven set at 45°C. One filter out of 50 is desorbed and analyzed by IC to test for residual contamination, prior to being approved for later use.

1.3 Health and Safety Warnings

The PM_{2.5} filter-preparation operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of gloves rinsed with deionized water is required for all steps of the filter cleaning process because this will minimize the potential for laboratory contamination.

2.0 Apparatus and Reagents

The nylon filters used are Whatman 47 mm nylon membrane filters, 1.0 µm pore size (Whatman catalog number 7410-004).

The only reagent needed is polished deionized water (18.2 MΩ-cm; water that has been passed through a secondary deionization system).

Several pieces of equipment are used for cleaning the nylon filters. Included are:

1. 2-L polypropylene wide-mouth Mason jars (VWR Catalog Number 16128-660 or equivalent)
2. TCLP apparatus (TLCP, EPA SW-846 Method 1311) that holds six 2-L jars.
3. Programmable timer (VWR Lab Controller or equivalent)
4. Convection drying oven (VWR Model 1320 or equivalent)
5. 11" x 11" glass drying rack (custom made from 1/4" glass rods in parallel rows attached to 3/8" glass rods serving as a frame; center-to-center distance for the 1/4" parallel glass rods is 1/2")
6. Plastic colander approximately 8" in diameter from a kitchen appliance store.

3.0 Filter Cleaning

3.1 Cleaning Procedure

The nylon filters are cleaned using the following procedure, which should be started at the beginning of a work day. The date when the cleaning is started is entered into the log book and the batch is identified by this date.

1. Fifty 47-mm nylon filters are carefully removed from the manufacturer's filter container using either gloves or forceps. Each filter is separated with a blue tissue which is removed prior to placing the 50 filters into a 2-L polypropylene jar that contains approximately 1000 mL of polished deionized water. The lid is attached, and the jar is shaken gently for approximately 2 minutes. The water is then carefully poured out of the jar without losing any filters. This rinse step is repeated. The two-step rinse procedure is then duplicated with five additional 2-L jars each loaded with 50 filters. Each jar is labeled with a letter (i.e., A, B, C), using a marker.
2. Each jar is carefully filled with polished deionized water until it is overflowing; it is then capped tightly and placed on the TCLP apparatus. The apparatus is turned on and mixes the filters and polished water by rotating the jars end-over-end. It cycles until the end of the day (i.e., 7 to 8 hours). The water is carefully poured out of each jar, and the jars are again filled to overflowing. The jars are placed on the TCLP apparatus, turned on, and allowed to run overnight, or for 14 to 16

hours. At the beginning of the next work day, the water is poured out again and replaced, and the jar is placed back on the apparatus for approximately 24 hours, or until the beginning of the next work day. Depending on a person's work schedule, the order of the extended washing may be varied; that is, the sequence may be 24 hours, 7 to 8 hours, and then 12 to 14 hours rather than 7 to 8 hours, 12 to 14 hours, and 24 hours.

Note: Because the filters tend to stick to the sides of the jars during rotation, the TCLP apparatus is connected to a timer that is programmed to rotate the jars for 15 minutes, and then allow them to sit at rest for 2 minutes. During this rest period, the filters that were stuck to the sides of the jar slip away and fall to the lower part of the jar of water. This timed cycle of rotation, followed by resting, continues through each cleaning period. The procedure for programming the time is given in Attachment A.

3. The jars are removed from the TCLP apparatus after the final wash and are taken to a Class 100 clean room for drying of the filters. The lid of a jar is removed and the water and filters are gently poured into a pre-rinsed plastic colander placed in a sink in the clean room. It may be necessary to add polished deionized water to the jar several times to remove all of the filters. The excess water is allowed to drain from the filters and the colander for several minutes. Any filters that fall into the sink during this process will be discarded.
4. With gloves and a clean forceps, the filters are removed from the colander one by one and placed separately on the drying rack, which has been thoroughly pre-rinsed with polished deionized water shortly before use. The loaded rack is carefully placed in the oven, which is set at 45°C. The filters are allowed to dry completely. The filters sometimes curl slightly during the drying process. A large amount of curling indicates that the oven temperature is too high. If so, slightly reduce the temperature so the filters dry without curling.

Note: The drying oven must be kept free of any dust or particulate material and should only be operated in a clean environment. The oven should be visually inspected for any contamination prior to each use. A dedicated oven used only for drying PM_{2.5} nylon filters is used.

5. The dried filters are removed from the drying rack using clean forceps and are placed back into the original manufacturer's plastic containers. These containers are washed with deionized water and are dried before reuse. Filters will be inspected for pinholes and tears; any damaged filter will be discarded. Twenty-five filters are placed in each container. Each container is labeled with the batch number (i.e., start date for cleaning) and the jar identifier (i.e., A, B, C).

3.2 Filter Acceptance Testing

One filter from each set of dried filters is selected at random for analysis. Blank filters are analyzed according to the analytical procedure described elsewhere in the SOPs for Anion (Hardison, 2008) and Cation (Hardison, 2008) analysis contained in the laboratory Quality Assurance Project Plan. For lot acceptance, the filter loadings of the ions of interest (i.e., sodium, potassium, ammonium, nitrate, and sulfate) must each be less than 1.0 μg per filter. If any ion exceeds the limit, the entire lot must be rejected. Rejected lots may be re-cleaned using the same procedure.

Each accepted batch of filters is assigned a unique number. Each filter's batch number is recorded in the PM_{2.5} database when it is loaded into a sample module in the Sample Handling and Archiving Laboratory. The lot number can be used to trace the acceptance test results in case there is a question about any filter.

Note: Several different cleaning procedures were used during the course of the PM_{2.5} Speciation Trends Network contract, which began in early 2000. This note summarizes the procedures used for cleaning nylon filters prior to finalization of the method described in this SOP.

Prior to March 28, 2000, filters were soaked three times for 30 minutes in deionized water without shaking or ultrasonication. Drying and acceptance procedures were identical to those previously described.

Prior to December 1, 2001, filters were cleaned using a shaker for the final 24-hour wash in deionized water. In fall 2001, some batches of filters received from the supplier were noted to be partially disintegrating in the shaker. It was concluded that the filter's durability was somewhat variable, and that shaking for 24 hours was too forceful for the less durable filters; therefore, the more gently rolling method was adopted.

Prior to December 1, 2002, filters were placed in a polypropylene jar of sodium carbonate/sodium bicarbonate solution (the eluent used for anion analysis). The jar containing the filters was placed in an ultrasonic bath for 1 hour. The filters were then rinsed three times with deionized water, rinsed gently using a jar roller mill in deionized water for about 1 hour, rinsed again manually three or four times, and then rinsed gently in fresh deionized water for 24 hours using the jar roller mill. This procedure was abandoned for the following reasons: the ultrasonic bath sometimes caused partial disintegration of the filters, sodium from the eluent solution was sometimes still present on the filters, and the TCLP apparatus was better than a roller because it provides end-over-end mixing. The method described in this SOP was subsequently adopted.

4.0 Quality Control

The quality control activities include the following:

1. Perform ion analyses of the polished deionized water whenever the deionizer beds are changed to determine that the ions of interest are below their maximum allowable concentration, as presented in Table 1. Replace the ion exchange beds in the water deionization system if these limits are exceeded.

Table 1. Maximum Allowable Concentration (MAC) for Ions of Interest

Ion of Interest	MAC, $\mu\text{g/mL}$
Nitrate	0.01
Sulfate	0.01
Ammonium	0.01
Sodium	0.01
Potassium	0.02

2. Keep all jars closed and stored in a clean environment when not in use.
3. Periodically wipe down the inside of the drying oven with wet, lint-free tissues.

5.0 References

Hardison, E. 2008. *Standard Operating Procedure for PM_{2.5} Anion Analysis*. Quality Assurance Project Plan Chemical Speciation of Particulate Matter, Volume II, Appendix A-5.1, revision 6.

Hardison, E. 2008. *Standard Operating Procedure for PM_{2.5} Cation Analysis*. Quality Assurance Project Plan Chemical Speciation of Particulate Matter, Volume II, Appendix A-5.2, revision 6.

Attachment A

Method for Programming the VWR Lab Controller

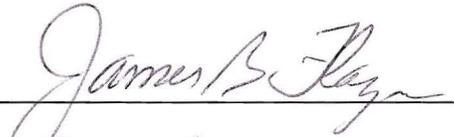
The device is programmed for the repeat mode, which permits repeatedly turning equipment on or off at one or two unique time intervals.

1. Press the CHANNEL SELECT key until the OUTLET channel is selected.
2. Delete all time-of-day program times by pressing the C key, and then the REPEAT key.
3. Press the OUTLET ON/OFF key to ON.
4. Press the 1, 5, 0, and 0 keys to program 15 minutes (15.00) power on.
5. Press the REPEAT key.
6. Press the 2, 0, and 0 keys to program 2 minutes power off.
7. Turn on the toggle switch on the TCLP apparatus (if it is not already on) and press the START/STOP key to begin counting down.
8. At zero, the outlet switches to OFF, the alarm sounds for 2 seconds, the display automatically returns to the programmed 2 minutes, and the timer begins counting down. At the next zero, it switches, alarms, displays 15.00, and begins counting down. This process will repeat until the C key is pressed, or the toggle switch is turned off.

Standard Operating Procedure for Long-Term Archiving of PM Filters and Extracts

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

Prepared by:  Date: 8/26/09

Reviewed by:  Date: 8/26/09

Approved by:  Date: 8/26/09



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

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Standard Operating Procedure for Long-Term Archiving of PM Filters and Extracts

1.0 Scope and Application

This standard operating procedure (SOP) describes the procedures to be used in the archiving of samples (Teflon and quartz filters and extracts of nylon filters) collected under the U.S. Environmental Protection Agency's (EPA's) laboratory support contract for Chemical Speciation of PM Filter Samples. All mention of a database in this SOP refers to RTI's Speciation Program Information Management System (SPIMS).

2.0 Archiving Conditions

2.1 Quartz Filters

Quartz filters will be archived for up to 10.5 years in petri-slide holders, sorted by state into petri-slide trays, and sorted by sampling date within a tray. Full trays of quartz filters will be placed in heavy-duty plastic zippered bags and placed in plastic bins in a freezer maintained at or below -15°C . Individual filters will be located by Archive Bin ID, Tray ID, and Aliquot ID.

2.2 Teflon Filters

Teflon filters will be archived for up to 10.5 years in petri-slide holders, sorted by state into petri-slide trays, and sorted by sampling date within a tray. Full trays of Teflon filters will be 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 will be located by Archive Bin ID, Tray ID, and Aliquot ID.

2.3 Filter Extracts

Filter extracts (nylon or Teflon) will be archived for 6 months in extraction vials and they will be grouped in laboratory batches, which will be 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 will be located by Archive Bin ID, Batch ID, and Aliquot ID.

3.0 Procedure for Archiving Quartz and Teflon Filters

3.1 Print Labels for Archiving

Labels for individual samples (Section 3.1.1) are printed on demand at the beginning of the archiving process; labels for trays and bins (Sections 3.1.2 and 3.1.3) can be printed in batches in advance and used as needed.

- 3.1.1 Filter Sample Labels: Print in human-readable form on a 1.875" x 0.75" label for each filter sample containing (at a minimum) the following information:

- 1.01_ State ID of the sampler,
- 1.02_ Location ID of the sampler,
- 1.03_ Sampling Date of the sample, and
- 1.04_ Aliquot ID of the filter.

3.1.2 Tray Labels: Print in human-readable and barcode form a series of unique Tray ID numbers on 1.875" x 0.75" (or larger) labels.

3.1.3 Archive Bin Labels: Each bin is labeled with a large printed label that gives the year the filters were sampled and the State ID.

3.2 Sort Filters by State ID and by Sampling Date

3.2.1 Scan (into a text file or a database application) the Aliquot ID bar code on each petri-slide holder in a lab batch of filters to be archived.

3.2.2 Print (via a database software application) labels (in the order the Aliquot IDs were scanned) for all of the filters in the lab batch.

3.2.3 Affix each label (printed in the same order as the petri-slide holders in the batch) to the appropriate petri-slide holder by visually verifying that the Aliquot ID on the label matches the Aliquot ID on the petri-slide holder.

3.2.4 Manually sort the filters by state and then by date (both in human-readable form per Section 3.1.1).

3.3 File Filters in Petri-slide Trays by State ID and Scheduled Sampling Date

3.3.1 Place a Tray ID label and write the State ID on a petri-slide tray for each state for which filters are to be archived.

3.3.1.1 Each tray will have a unique Tray ID and will be used to archive filters from only one state.

3.3.1.2 Frequently more than one tray will be required to archive all of the filters from a single state.

3.3.1.3 As the original trays are filled and moved to archive bins or as new states are added, new trays are made.

3.4 Log Full Trays of Filters into Archive Bins

3.4.1 Once a tray is full, the Tray ID is associated with the Archive Bin ID. This is done by scanning into the database the barcode for each State ID and then for each tray.

3.4.2 When a tray has been filled with filters from a given state, log the tray into the archive bin set aside for or already containing filters from that state.

3.4.2.1 All of the trays for a State ID will be grouped in one or more archive bins.

- 3.4.3 Filters will remain in trays in the archive bins until they are either logged out (individually) and returned to the requesting state or turned over (en masse) to EPA's sample custodian at the end of the contract.

4.0 Procedure for Archiving Filter Extracts

4.1 Print Labels for Archiving

Labels for individual samples are already on the vials as received from the laboratory; labels for tube trays and bins (Sections 3.1.1 and 3.1.2) can be printed in batches in advance and used as needed.

- 4.1.1 Tube Tray Labels: Print in human-readable and barcode form a series of unique Tray ID numbers on 1.875" x 0.75" (or larger) labels.
- 4.1.2 Archive Bin Labels: Print in human-readable and barcode form a series of unique Archive Bin ID numbers on 1.875" x 0.75" (or larger) labels.

4.2 Log extracts into Tube Tray by Aliquot ID

- 4.2.1 Place a Tray ID label on a tube tray in which extracts are to be archived.
- 4.2.2 Log each extract into the tube tray by associating the Aliquot ID of the extract with the Tube Tray ID.

4.3 Log Full Tube Trays of Extracts into Archive Bins

- 4.3.1 When a tray has been filled with extracts, log the tube tray into an archive bin by associating the Tube Tray ID with the Archive Bin ID.
- 4.3.2 Tube Tray IDs are associated with Archive Bin IDs as tube trays are filled with extracts.
- 4.3.3 Extracts will remain in tube trays in archive bins until they are either logged out (individually) and returned to the requesting state or discarded at the end of the 6-month archiving period.

5.0 Procedure for Removing Samples from Archiving

5.1 Identify Samples

- 5.1.1 Search the database to identify the Aliquot IDs of the filters or extracts to be found.
- 5.1.2 Extract from the database the Archive Bin ID, Tray ID, State ID, sampling date, and any other useful information for each aliquot to be found.

5.2 Locate Samples

- 5.2.1 Locate the archive bin(s) containing the sample(s).
- 5.2.2 Within the archive bin, locate the tray containing the sample(s).

5.2.3 Within the tray, locate and remove the individual samples to be removed.

5.3 Log Out Samples

5.3.1 Verify each sample by scanning the Aliquot ID barcode.

5.3.2 Compare the State ID, sampling date, and any other useful information with the information expected from Section 4.1.2.

5.3.3 Change the status of the sample in the database from Archived to Returned or Destroyed, as appropriate.

5.4 Exceptions

5.4.1 Extracts are to be destroyed at the end of a 6-month archiving period.

5.4.1.1 Search the database for Tube Tray IDs that contain no extracts less than 6 months old.

5.4.1.2 Locate all tube trays (as in Section 4.2) that meet the criteria in Section 4.4.1.1.

5.4.1.3 Identify and pull from the tube trays any extracts that are to be returned to a state.

5.4.1.4 Change the status of the pulled samples in the database from Archived to Returned, and ship the samples to the appropriate addresses.

5.4.1.5 Change the status of all remaining samples in the tube trays from Archived to Destroyed.

5.4.2 Change the status of all remaining samples at the end of the contract from Archived to Returned when they are transferred to EPA's designated sample custodian.

Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

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Reviewed by: Jan C. Flanagan Date: 7/11/08

Approved by: RKM Jayaram Date: 7-10-08



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

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Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis

1.0 Procedural Section

1.1 Scope and Applicability

This standard operating procedure (SOP) describes filter preparation and gravimetric analysis operations in the RTI International (RTI) Environmental and Industrial Sciences Division (EISD) Gravimetry Laboratory (Grav Lab). This SOP applies to particulate matter (PM) samples collected on Teflon[®] filters and includes the performance of the Federal Reference Method (FRM) for the determination of PM_{2.5} in ambient air. Filter conditioning and weighing currently take place in a dedicated laboratory for weighing PM filters. The laboratory consists of two weighing chambers, which have computer-controlled temperature and relative humidity (RH) that meet the requirements of 40 CFR Part 50, Appendix L, and the U.S. Environmental Protection Agency's (EPA's) *Quality Assurance Guidance Document 2.12*.

- **Analyte:** PM, including PM_{2.5} and PM_{10-2.5}
- **Matrix:** Ambient air
- **Analytical Method:** Reference Method for the Determination of Fine PM as PM_{2.5} in the Atmosphere, 40 CFR 50, Appendix L, July 1997
- **Calculated Laboratory MDL:** 7 µg per 46.2 mm Teflon[®] filter.

1.2 Summary of Method

This SOP describes the processes used by RTI for performing PM filter gravimetric analyses by the PM_{2.5} FRM (Reference Method for the Determination of Fine PM as PM_{2.5} in the Atmosphere), 40 CFR 50, Appendix L. The major steps in the process for handling the filters are as follows:

- Obtaining filters from the manufacturer and characterizing each lot
- Conditioning and pre-weighing each filter
- Packaging and sending the filters to the client for use in their PM monitoring program
- Receiving, conditioning, and post-weighing each filter
- Calculating and reporting results
- Archiving the filters.

The individual procedures are described in this SOP and related SOPs. This SOP concentrates on filter weighing operations, and other SOPs are referenced as necessary.

1.3 Definitions

- Gravimetric Analysis—Determination of particulate concentration based on weight difference
- PM_{2.5} — PM with an aerodynamic diameter less than or equal to 2.5 microns
- PM_{10-2.5} — PM with an aerodynamic diameter between 10 and 2.5 microns, also known as PM_{Coarse}
- Filter Lot — Units of filters from a single type, grade, class, size, and composition, manufactured under essentially the same conditions and time by the same manufacturer
- Filter Batch — Units of unsampled filters inspected and equilibrated under essentially the same conditions and time in the RTI EISD Grav Lab for use in one given shipment (or hand delivery, if appropriate) of tared filters to the client
- Weighing Session — Period of time in which filters for one client are weighed by one Laboratory Analyst on one balance on one date, interrupted only by brief breaks of no more than 15 minutes' duration.

1.4 Health and Safety Warnings

The PM weighing operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions must be followed.

RTI personnel must exercise caution when using antistatic devices containing radioactive polonium sources, must keep an inventory of the location and size of antistatic devices, and must dispose of the devices in accordance with manufacturers' specifications, RTI safety and health guidelines, and state and local regulations.

1.5 Cautions

Laboratory personnel will always wear clean clothes and wash thoroughly all parts of their bodies that are exposed during weighing, especially their hands, arms, face, and hair, using adequate soap and water to remove loose skin and hair, as close as possible in time to the weighing activity. Laboratory coats and gloves are required and will minimize the potential for laboratory contamination. Laboratory coats must be taken off before leaving the weighing facility to minimize contamination from the external environment.

RH is a particularly difficult parameter to control; even if total moisture content stays constant, if temperature changes, RH will also change. Gravimetric laboratory personnel must be aware of the potential for unacceptable RH excursions during seasonal extremes (e.g., high heat and humidity in the summer). Corrective measures must be taken whenever environmental controls are out of specification.

1.6 Interferences

PM gravimetric results are highly sensitive to certain interfering factors and conditions. The following list describes common precautions to be taken against interferences:

- Ensure proper handling procedures humidity and temperature control of the filter and particulate sample during weighing, and promptness in, and consistency of, the weighing method prior to and following collection to control weighing artifacts due to environmental conditions.
- Minimize or standardize weight losses by keeping the filters cool during transport to the weighing laboratory and by conditioning and weighing the filters promptly after their receipt in the laboratory. Weight losses can occur due to thermal or chemical decomposition or evaporation of compounds like ammonium nitrate (NH_4NO_3), which releases ammonia and nitric acid as gases. Semivolatile organic compounds (SVOCs) may be part of the PM on the filters; if so, they may evaporate and cause sample weight losses.
- Check for weight loss in any new lot of filters that is received. Filters must not be used until their weights have stabilized. Some new blank Teflon[®] filters have been found to exhibit a weight loss of up to 150 micrograms (μg) over a period of time up to 6 weeks after being removed from their original shipping containers.
- Minimize weight loss due to mechanical removal of particles and/or filter material by careful handling during removal of the filter from its cassette, filter conditioning, neutralization of electrostatic charge buildup on the filter, and all other filter-handling tasks before weighing.
- Neutralize electrostatic to prevent biases due to electrostatic attraction or repulsion during the weighing process.

1.7 Personnel Qualifications

Personnel employed to perform weighing operations must have a minimum of a high school diploma with at least 6 months' experience in computer applications, including spreadsheet and word processing software and laboratory sample handling and record-keeping practices. Lead analysts must have a minimum of a bachelor's degree in a laboratory science and at least 6 months' additional experience in the RTI EISD Grav Lab. All personnel employed to perform weighing operations will be trained by a supervisor before being allowed to process client samples for the PM program. RTI Laboratory Supervisors helped to devise the written examination and the hands-on practical examination for the laboratory component of EPA's PM_{2.5} FRM Performance Evaluation (PE) program. All RTI analysts will be trained to a competency level that is equivalent to the FRM PE certification before they are allowed to perform weighing operations.

1.8 Apparatus and Materials

Mention of specific suppliers or trade names does not constitute endorsement by RTI.

- Mettler Toledo UMT2 or UMX2 balance
- U-electrode (ionizer)
- Marble balance table
- Filters, 46.2 mm, Teflon[®]
- Millipore Petrislides[®], appropriately sized for 46.2 mm filters
- Filter cassettes of the correct type and make
- Filter cassette holders, protective containers
- Nonmetallic forceps to handle weights
- Nonmetallic forceps to handle filters
- Staticide[®]
- Kimwipes[®]
- Three sets of National Institute of Standards and Technology (NIST)–traceable standards used for working mass reference standards
- At least one set of NIST–traceable standards used for primary mass reference standards
- Millipore Petrislides[®]
- Powderfree gloves
- Labcoats
- Shoecovers
- Sticky floor mats
- Computer
- Balance Link[®] or equivalent data acquisition software
- Laboratory notebook or database.

1.9 Calibration

The microbalance will be certified upon initial set-up by an authorized microbalance service representative. Thereafter, the microbalance will be serviced at least annually, and on an as needed basis, by an authorized microbalance service representative. Records kept by RTI will include service dates and calibration results. NIST–traceable standards will be tracked by a control chart to determine if any bias is entering into the system. These standards will be recertified annually.

Temperature and RH sensors will be calibrated annually.

The microbalance will be internally calibrated using its internal standards and “Autocalibrate” function each time it is brought up from “Standby” mode.

If the microbalance is found to be out of calibration during routine weighing operations, it must be recalibrated by the analyst using the microbalance’s internal standards and “Autocalibrate” function. If the microbalance cannot be autocalibrated, it must be serviced only by an authorized microbalance service representative.

1.10 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the state or federal agencies responsible for exposing the filters.

1.11 Sample Handling

Note: The information in this section pertains to EISD Grav Lab handling of both speciation and compliance samples. Additional information on this topic that is specific to the speciation network can be found in the SOP, *Standard Operating Procedure for the Sample Handling and Archiving Laboratory (SHAL)*, Research Triangle Institute, 2005. The SHAL SOP is the default SOP for the handling of speciation samples.

RTI will provide Chain-of-Custody documentation with all sample shipments to track and ensure the following: 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 written 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 client.

Upon initial receipt of new filters, RTI will prepare a “Filter Inventory and Inspection” spreadsheet containing the manufacturer’s lot number, box numbers, filter identification numbers, and date received by the RTI EISD Grav Lab. This form will allow laboratory personnel to select and use the filter boxes in the proper sequence.

If the filters are from a manufacturer’s lot that has not previously been used in the RTI EISD Grav Lab, then an Initial Lot Stability Test must be performed on randomly selected filters to determine and document the minimum length of time required to condition filters from that lot. The Initial Lot Stability Test is explained fully in Section 1.12.1 (Initial Lot Stability Test).

Filters must be inspected and conditioned before use. Inspection and conditioning must be performed in the weighing environment. The inspection date, analyst’s initials, number of filters rejected, and reasons for rejection must be noted on the hard copy “Pre-sampling Batch Inspection and Stability Form” in the RTI EISD Grav Lab and will be entered into the “Filter Inventory and Inspection” spreadsheet as soon as is practicable. Conditioned filters must be sequentially weighed and packaged for shipment to the designated receiving address(es) in order

of filter identification number. Additional information on this topic can be found in Section 1.12.3 (Filter Inspection and Conditioning).

Filters will be shipped to the designated address(es) or hand delivered to the designated SHAL contact within 5 days of preweighing to ensure that the 30-day window for using the filters is met. If a filter expires without being used, the filter will be returned to RTI to be reconditioned and weighed again only if a system for the return of unsampled filters to RTI has been established with the client. The decision to recondition filters will be made on a case-by-case basis by the Laboratory Supervisor in coordination with the Project Manager and client.

Chain-of-Custody forms will accompany each sample shipment and will contain the filter identification numbers, accompanying cassettes' identification, pre-sampling weighing date, and date shipped to the designated site operator. Chain-of-Custody forms will be completed by site operators to provide tracking information from receipt in the field, through sample collection, to return sample shipment to RTI.

Upon receipt of loaded filters, RTI will complete the receipt portion of the "Chain-of-Custody" form, including the date and maximum temperature, if specified.

RTI will implement, as a matter of standard practice, a sample turnaround time of 10 calendar days from the date of receipt from the field. Shipping and maintaining the filters at or below 4°C provides a 30-day window from sampling for RTI to condition and weigh filters. The designated site operators are responsible for shipping filters and cassettes, and cassette containers, to RTI at a temperature at or below 4°C. All custody information will be entered into and maintained in the project database.

Once the filters have been weighed and the appropriate internal quality control (QC) procedures have been completed, the filters must be returned to their Petrislides[®] and the lids must be securely replaced. The Petrislides[®] must be placed in numerical order in the Millipore[®] slide tray. Each tray must be labeled with the client's name and the range of filter ID numbers archived in that tray and then sealed in a plastic bag. Two sealed trays will be placed in each outer cardboard Millipore[®] box. The outer box must then be labeled with the appropriate archival information, including the client's name, RTI contact name and telephone extension, filter ID range, and archival date. The box must be placed in a cold storage facility to be maintained at or below 4°C. The archival date must be entered into the appropriate Microsoft (MS) Excel[®] spreadsheet beside each filter ID number.

1.12 Sample Preparation and Analysis

Note: Additional information on this topic for the laboratory's support of the Speciation Trends Network is found in the SOP, *Standard Operating Procedures for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters*, Research Triangle Institute, 2005.

1.12.1 Initial Lot Stability Test

Information derived from the Lot Stability Test must be used to determine the average length of time required to equilibrate filters from a given lot. All Lot Stability Test information must be recorded in the laboratory notebook. The Lot Stability Test must be performed as follows:

1. Randomly select six filter boxes from the same filter lot.
2. Randomly select 2 filters from each box.
3. Weigh the 12 filters and then place the filters in Petrislides®.
4. Allow the filters to equilibrate for at least 24 hours in the weighing environment.
5. Weigh the 12 filters, return them to their Petrislides®, allow them to equilibrate for another 24 hours in the weighing environment, and reweigh the filters.
6. Continue the 24-hour equilibration and weighing process for up to 7 days (5 days minimum) and plot the trend of weight loss. If the trend is still decreasing after 5 days, continue the 24-hour schedule of equilibration and weighing.
7. The filters are considered equilibrated when they no longer exhibit a consistent downward weight trend.
8. Record the length of time it took the filters to equilibrate. This will be the minimum time that all filters from this lot must equilibrate prior to performing a Batch Stability Test. (described in Section 1.12.4).

1.12.2 Filter Storage

After successful completion of the Initial Lot Stability Test, the numbered boxes of unused filters will be stored until needed. After the manufacturer's lot number, box numbers, filter identification numbers, and date received by the RTI EISD Grav Lab are recorded in the "Filter Inventory and Inspection" spreadsheet, the numbered boxes will be placed on the designated laboratory shelf in numerical order so that the next box to be used can be easily obtained. The boxes must be used in numerical order, with the lowest number being used first.

1.12.3 Filter Inspection and Conditioning

An initial screening inspection of each lot of filters must be performed prior to their use for the program. Randomly select 10% of the total quantity of filters received from the vendor. Transport these filters to the Optical Microscopy Laboratory and examine each filter with the aid of a stereo microscope and enhanced lighting (e.g., fiberoptic illuminators, tensor lamps). Record observations of filter appearance, including, but not limited to, extraneous debris or loose pieces of extra filter membrane, filter damage, uniformity of color, clarity of identification number, overspray of filter identification number, or crimping or irregularities in the thickness of the reinforcing ring. Provide the appropriate Task Leader and the program's Quality Assurance Officer (QAO) with a copy of the inspection notes. The lot will be rejected and returned to the manufacturer for replacement if more than 1/4 of the filters inspected (2.5% of the total lot) exhibit defects that are judged by the Task Leader and QAO to adversely impact sample collection or data quality.

In addition to the initial screening, filters must be individually inspected in groups of 25 before they are conditioned for taring. A filter must be rejected if it exhibits any of the following defects:

- Pinhole
- Separation of ring
- Chaff or flashing
- Loose material
- Discoloration
- Filter nonuniformity
- Others: see Laboratory Supervisor.

If a filter is rejected, the analyst must make a note of the rejection on the hard copy “Pre-sampling Batch Inspection and Stability Form” and in the MS Excel “Filter Inventory and Inspection” spreadsheet and must discard the filter. If the filter is accepted, the analyst must place it in a Petrislide for equilibration. The analyst must place the Petrislide lid slightly ajar over the well so that it covers approximately 3/4 of the filter surface. This placement of the lid allows for outgassing of the filter and offers some protection from particle deposition. The analyst must inspect and equilibrate a sufficient number of filters to allow for unforeseen filter problems or rejection during weighing. The number of filters equilibrated will consist, at a minimum, of the number of filters required for shipment to the client plus an additional 5 filters. Filters must equilibrate for at least the period of time determined in the Initial Lot Stability Test.

1.12.4 Pre-sampling Batch Stability Test

The Batch Stability Test is used to verify that filters from a particular batch have achieved weight stability and are not losing weight due to outgassing or another process. The Batch Stability Test must be performed after the filters have equilibrated for at least the period of time determined in the Initial Lot Stability Test. Only stable filter batches will be used for PM sampling. The following procedure must be performed each time a batch of filters that has been equilibrated in the RTI EISD Grav Lab for less than 60 hours is prepared for analysis:

1. Randomly select 3 filters from the batch of equilibrated filters.
2. Weigh each of the 3 filters and record their weights in the laboratory notebook.
3. Allow the filters to equilibrate overnight and reweigh.
4. If the average weight loss for the 3 filters is less than 5 μg , they are ready to be weighed for shipment to the client.
5. If the average weight loss for the 3 filters exceeds 5 μg , repeat the 24-hour schedule of equilibration and weighing until the average weight loss for the 3 filters is less than 5 μg .

1.12.5 Pre-sampling Weighing Procedure

The following procedure must be performed each time PM filters are tare-weighed in the RTI EISD Grav Lab:

1. The laboratory's Dickson[®] RH and temperature data logger is routinely set to collect 5-minute grab samples. Twenty-four hours prior to a weighing session, verify that this logger setting has not been changed.
2. The microbalance must be left plugged in and turned on at all times to avoid lengthy warm-up periods. If the microbalance has been left in "Standby" mode, the LCD screen display must be turned on by pressing the tare (Zero) button once.
Note: Do not press the On/Off button.
3. Verify that the microbalance is level by observing the level indicator bubble at the rear of the sample chamber. If the microbalance is level, the air bubble will be positioned in the center of the indicator circle. If the air bubble is not centered, level the microbalance by turning the two leveling feet at the rear of the sample chamber until the bubble is in the middle of the indicator circle. **Note:** The microbalance must be releveled each time it is moved. Releveling will not normally be necessary because the microbalance is not routinely moved. If observation of the level bubble indicates that the microbalance has been moved, notify the Laboratory Supervisor immediately. Always calibrate the microbalance after releveling.
4. Internally calibrate the microbalance with its "Autocalibrate" function. The microbalance must be internally calibrated each time it is brought up from "Standby" mode. **Note:** Do not lean on or place weight on the stone balance table or open the laboratory door while the internal calibration is in progress. Minimize movement in the laboratory during the internal calibration.
5. Turn on the computer, if necessary, and download the humidity and temperature data from the data logger to the computer.
6. Pull the data into an MS Excel spreadsheet and calculate the 24-hour mean and standard deviation for temperature and RH. Report temperature to 3 significant digits.
7. Verify that the weighing chamber's mean temperature and RH for the previous 24 hours have met the following specifications: temperature maintained between 20–23 °C with a standard deviation less than 2, and 24-hour mean RH maintained between 30–40% with a standard deviation less than 5.
8. Lightly spray a low-lint disposable cloth (Kimwipe[®]) with Staticide[®]. Do not direct the spray toward the data logger, microbalance, reference weights, filters, or area around the microbalance and computer. Use the moistened cloth to wipe both sets of forceps and the work area around the microbalance and computer. Allow the forceps and work area to air-dry before proceeding. The computer and monitor will be routinely cleaned with products designed for that purpose.

9. Open the weighing template spreadsheet in the client's folder or the Grav Lab speciation database application, each where appropriate, and create a filename or initial weighing session consisting of the first and last filter ID numbers in the range to be weighed (e.g., 9021884_9021920).
10. Complete the QC data worksheet or initial weighing session setup form with analyst initials, weigh date, start time, client/RTI project number, filter lot, initial RH (%), and initial temperature ($^{\circ}\text{C}$, to 3 significant digits).
11. Complete the database worksheet or Grav database initial weighings form with filter ID number, weighing type, and any other specified information.
12. Begin the weighing session by weighing reference standards that bracket the typical weight of a filter. Using nonmetallic forceps, place either the 100 mg or 200 mg working mass standard on the microbalance weigh pan and close the microbalance door. Take care not to drop, bend, or otherwise mar the standard.
13. Wait for the microbalance to display a stable reading for at least 20 seconds.
14. Press either the "print" button on the microbalance or the "print screen" button on the computer keyboard to enter the displayed weight directly to the cursor position in the spreadsheet or database form.
15. Repeat this process with a second working mass standard to bracket the weight of a typical Teflon[®] PM filter.
16. Compare the weights of the working mass standards to the QC weight acceptance limits posted near the microbalance. If a mass standard varies from its verified weight by more than 3 μg , autocalibrate the microbalance and reweigh the working mass standard. If the mass standard still varies by more than 3 μg , contact the Laboratory Supervisor.
17. Reposition the cursor (if necessary) in the first filter weight cell. Using the filter handling forceps, pick up the first filter to be weighed and pass it through the U-electrode to neutralize static charge and place the filter on the weigh pan and close the microbalance door. Wait for the microbalance to display a stable reading for at least 20 seconds.
18. Press the "print" or "print screen" button to enter the weight directly into the database worksheet or data entry form.
19. Open the automatic microbalance door, remove the filter from the weigh pan, and reclose the microbalance door. The microbalance must return to zero on its own. If, after 20 seconds, the microbalance has not returned to zero, press the "tare" key. It should not be necessary to press the "tare" key after every filter. If it proves necessary to press the "tare" key after every filter, troubleshoot the system as outlined in this procedure.
20. Repeat the process for all the filters. After every tenth filter, reweigh working mass standards that bracket the weight of a typical filter (e.g., 100 mg and 200 mg) and record the weight in the QC data worksheet. Compare the weights of the working mass standards to the QC weight acceptance limits for the working mass standards.

21. If the number of tared filters needed for shipment or hand delivery to the client can be weighed in one weighing session, then weigh the number of filters needed for shipment or delivery plus 1 additional filter to be used as a laboratory (lab) blank. If the client requires a quantity of filters too large to be weighed in one weighing session, then weigh the number of filters that can be safely weighed in the time available and select 1 filter to be used as a lab blank for that weighing session. In each case, the lab blank must be placed in a Petrislide[®] and labeled with the client name, RTI project number, weigh date, and the filter ID range that it represents. In each case, the lab blank must also be identified as a lab blank in the weighing spreadsheet.
22. Reweigh every filter and record the initial and final weights in the appropriate spaces on the database or Excel form used for the weighing session. If replicate filter weights vary by more than 5 μg , weigh the filter a third time to confirm the weight. If replicate filter weights vary by more than 15 μg , contact the Laboratory Supervisor. The Laboratory Supervisor will troubleshoot the system and direct the analyst to troubleshoot the microbalance system and/or to allow the filters to equilibrate an additional length of time before reweighing all the filters in the batch.
23. If replicate filter weights are within 15 μg , then reweigh the 100 mg and 200 mg working mass standards. If the working mass standards are within 3 μg of their verified weight, then the weighing session is complete. All changes to the spreadsheet or weighing session must be saved.
24. If the purpose of the weighing session is to tare filters to complete the batch started previously, then a lab blank must be included in the weighing session. This practice will result in multiple lab blanks covering all weighing sessions for the batch of filters shipped or delivered to the client.

1.12.6 Preparing the Filters for Shipment

Shipping and receiving of filters for the PM Chemical Speciation Program will be performed in the SHAL. These procedures are discussed in the SOPs for the SHAL.

1.12.7 Receipt of Filters from the Field

Shipping and receiving of filters for the PM Chemical Speciation Program will be performed in the SHAL. These procedures are discussed in the SOPs for the SHAL.

1.12.8 Receipt of Filters from the SHAL and Post-sampling Batch Stability Test

The following procedure must be performed each time PM filters are received from the SHAL:

1. Review and complete all Chain-of-Custody forms submitted with the filters. Return one completed carbonless copy of the form to SHAL and retain the other copies.

2. Log the filter identification information in the PM Sample Receipt Notebook. Include filter ID numbers, date received from the SHAL, receiver's initials, pertinent information concerning shipment integrity communicated by the SHAL, and any observations about obvious filter damage.
3. Transfer the copies of the "Chain of Custody" form(s) with the filters to the weighing chamber in RTI Building 11. If the filters are not received from the SHAL in Petrislides[®], place each filter in a clean Petrislide[®]. Label each Petrislide[®] with client name, date received from the SHAL, and filter ID number.
4. Place the Petrislides[®] containing the filters in numerical order on a tray. Verify the filter ID numbers against the ID numbers recorded on the "Chain of Custody" form(s).
5. Place the filter tray on the appropriate shelves in the weighing chamber to equilibrate. Place the Petrislide[®] lid slightly ajar over the slide well so that it covers approximately 3/4 of the filter surface.
6. Allow the filters to equilibrate in the weighing chamber for at least 24 hours.
7. Randomly select 3 of the sampled filters, weigh them, and then replace them on the shelf to equilibrate at least 24 additional hours.
8. Reweigh the 3 sampled filters. If the average weight loss for the 3 filters is less than 5 μg , the batch of filters can be weighed. If the average weight loss for the 3 filters exceeds 5 μg , repeat the 24-hour equilibration and weighing process.

1.12.9 Post-sampling Filter Weighing

Open the appropriate MS Excel[®] spreadsheet(s) or database final weighing session forms to perform post-sampling weighing of PM filters. Post-sampling weighing is performed as outlined in the pre-sampling weighing section (see 1.12.5). All internal QC procedures described in the pre-sampling filter weighing section must be followed during post-sampling weighing. Different or additional QC data that must be recorded are as follows:

1. Perform replicate weighing of post-sampling filters at a frequency of every third filter rather than reweighing every filter. In addition to incremental reweighing, reweigh any filter for which a negative net mass is noted. Reweigh any field or trip blank for which a negative net mass or a net mass greater than 30 μg is noted.
2. Identify field or trip blanks, if known, in the "Blanks" column of each spreadsheet.
3. Reweigh the lab blank for each tare session with filters in the post-sampling batch and enter these weights in the appropriate field of the QC data worksheet or database final weighings form. It is imperative that all lab blanks for the batch be reweighed in each post-sampling weighing session. Initial and final lab blank weights must not differ by more than 15 μg . A weight gain of more than 15 μg (positive weight change) indicates potential contamination in the weighing chamber. A weight loss of more than 15 μg (negative weight change) indicates either that the filters were not adequately equilibrated before shipment to the sampling sites or that the filters were contaminated before shipment with

particulate that was dislodged prior to post-sampling weighing. If the lab blank does not meet the appropriate criterion, notify the Laboratory Supervisor and QAO immediately. Anomalies that cannot be traced to issues in the laboratory will be noted as such by the Laboratory Supervisor.

4. Record field and trip blank weighings in the appropriate section of the QC data worksheet or database final weighings form. The initial and final field blank weights must not differ by more than 30 μg . A weight gain of more than 30 μg indicates possible field contamination of the filters or that tare or post-sampling weights were not correctly recorded. A weight loss of more than 30 μg indicates possible inadequate equilibration of the filters before shipment to the sampling sites, or that tare weights were not correctly recorded. If initial and final field blank weights differ by more than 30 μg , notify the Laboratory Supervisor so that the issue can be investigated in the laboratory and the client can be notified of possible field-related problems.
5. All post-sampling filter weights must be recorded. Note any problems observed during post-sampling filter weighing (e.g., filter damage, incomplete documentation) in the “Comments” field of the database worksheet or database final weighings form. Data flags will notify quality assurance (QA) and SHAL personnel, and, if necessary, the client, that these data must be reviewed to be deemed valid or invalid.

1.12.10 Filter Archival

After post-sampling weighing, filters must be archived according to the procedure outlined in Section 1.11 (Sample Handling). The “Archival Date” column must be completed in the appropriate MS Excel[®] spreadsheet.

1.12.11 Troubleshooting

Problems in meeting the various QC requirements during a pre-sampling or post-sampling weighing session can be related to the filter conditioning environment, a malfunctioning microbalance, or the filters themselves (e.g., exposed filters). Analysts must take the appropriate corrective action or call the matter to the attention of the Laboratory Supervisor if serious problems are observed. All problems that affect reportable data must be brought to the attention of the Laboratory Supervisor and must be documented for use during data validation. Serious, systematic, or chronic problems must be dealt with using the Corrective Action Procedures described in the laboratory's QA Project Plan (QAPP).

The following list describes common troubleshooting situations and recommended solutions:

- If filter weights are unstable, ensure that temperature and RH are within the acceptance criteria and that levels do not fluctuate excessively. Also, check temperature and RH monitoring devices with independent devices.

- If unexplained weight gains are observed on laboratory blanks, or if visual contamination is observed, laboratory contamination is present. In this case, more frequent cleaning is required.
- If there are measurement uncertainties and fluctuations associated with electrical charge, samples must be charge-neutralized prior to weighing using Polonium 210 alpha sources or an ionizing electrode. Since the radioactive half-life of Polonium 210 is approximately 6 months, Polonium charge neutralizers, if used in the lab, must be replaced at least annually.
- If a power failure has occurred, the user must manually reset the microbalance's electronics and run the internal recalibration procedure. Recovery time may be required for the microbalance to stabilize after a power outage. Refer to the instrument's operating manual for recommendations.
- If blank or working standard weighing discrepancies are observed between sessions, recertify the working standards against the laboratory primary standards and/or calibrate the microbalance using an external laboratory primary standard.
- If microbalance repairs or significant internal adjustments are necessary, a qualified service technician must be called. Unqualified personnel must not attempt to adjust or repair the microbalance. **Note:** Additional information on this topic can be found in Section 2.2.2 (Removing a Microbalance from Service).
- If certain exposed filters appear to be losing weight systematically over time, the PM may be composed of nitrates or other semivolatile species. Notify the QAO and expedite final weighing as much as possible within the confines of the reference method.
- If any unused filter is found to have a weight outside the normal range (i.e., 110 to 160 mg), an investigation is warranted. Examine other filters from the same lot for defects.
- If there is a consistent negative replication ($>15 \mu\text{g}$) for laboratory blank filters, it is a sign that the filters have not equilibrated long enough and are off-gassing semivolatiles from the manufacturing process. Monitor other filters from the same lot; additional conditioning time is required before filters from that lot can be used for sampling.

1.13 Data Acquisition Hardware and Software

Note: See the SOP, *Data Handling Procedures for the Speciation Analysis Program*, for detailed procedures on this topic. The referenced SOP will provide details about the data acquisition software to be used in the chemical speciation program.

The three major programs currently used to process RTI EISD Grav Lab data are MS Access[®], MS Excel[®], and Mettler BalanceLink[®]. Spreadsheets used for managing state client compliance data are created in MS Excel[®]. Speciation data are managed with custom RTI-written MS

Access[®] routines to facilitate compliance with Good Automated Laboratory Practices requirements. Speciation data are recorded on the program's dedicated server maintained by RTI's Ragland Computer Center staff.

IBM-PC compatible computers will be used in the weighing laboratory. These will be networked via RTI's internal computer network. Password security will be used to validate users. Full or incremental backups of the data will be performed daily.

1.14 Calculations and Data Reduction

The calculations relevant to the gravimetric procedures are listed in the following table.

Parameter	Units	Type of Conversion	Equation
Filter Volume (V_a)	m^3	Calculated from average flow rate (Q_{ave}) in L/min, and total elapsed time (t) in minutes	$V_a = Q_{ave} \times t \times 10^{-3}$
Mass on Filter (M_{PM})	μg	Calculated from the filter post-weight (M_f) in mg and filter pre-weight (M_i) in mg, multiplied by the unit conversion ($\mu g/mg$)	$M_{PM} = (M_f - M_i) \times 10^3$
PM Concentration (C_{PM})	$\mu g/m^3$	Calculated from laboratory data and sampler volume	$PM = M_{PM} / V_a$

1.15 Records Management

Note: See the SOP, *Data Handling Procedures for the Speciation Analysis Program*, for detailed procedures on this topic. The following discussion outlines the records management procedures to be implemented for the gravimetric filters. The referenced SOP will provide the detailed records management protocols for all filter and sample types that are used on the chemical speciation program.

As outlined in Section 1.11 (Sample Handling), RTI will prepare a "Filter Inventory and Inspection" spreadsheet upon initial receipt of new filters. This form will be completed with filter ID numbers, box numbers, date received, date inspected, number of filters rejected, and reason(s) for rejection. The form will allow laboratory personnel to select and use the filter boxes in the proper sequence.

RTI will provide Chain-of-Custody documentation with all sample shipments to track and ensure the following:

- Samples are collected, transferred, stored, and analyzed by authorized personnel.
- Sample integrity is maintained during all phases of sample handling and analysis.

- An accurate written 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 client.

Chain-of-Custody forms will include filter ID numbers, accompanying cassette identification, pre-sampling weighing date, and date shipped to the designated site operator. One copy of the Chain-of-Custody form will be retained by the site operator. A second copy of the form will accompany return shipments to RTI. Upon receipt of loaded filters from the field, RTI will complete the final portion of the Chain-of-Custody form, including date received at RTI and maximum temperature during shipment. The designated site operators are responsible for shipping filters and cassettes, and cassette containers to RTI at a temperature at or below 4°C.

The filter database will be completed with the information described above and with filter archiving information. Filters will be archived, following the procedures outlined in Sections 1.11 (Sample Handling) and 1.12.8 (Filter Archival), until 1 year after termination of the contract or until the client requests return of such materials. Boxes of archived filters will be labeled with the appropriate archiving information, including client name, RTI contact name and telephone extension, filter ID range, and archive date, and the boxes will be placed in a secure cold storage facility. The archival date for each filter ID number will be completed in all pertinent MS Excel® spreadsheets.

2.0 Quality Control and Quality Assurance

2.1 Determination of Working Standard QC Weight

The following procedure must be performed each time the working mass reference standards are recertified by the North Carolina Department of Agriculture Standards Laboratory, or a similar NIST-traceable standards laboratory, and each time the working mass reference standards exceed the PM acceptance limits.

1. Using clean weight forceps, weigh the working mass reference standard daily for five days.
2. Record the weights and calculate the mean (i.e., The mean will be the weight used for comparison during each subsequent weighing session).

If the mean weight determined for the working mass reference standard differs from the certified value by more than 20 µg, verify the primary standards and then either call the microbalance manufacturer's service representative to calibrate the microbalance or return the working mass standard for recertification.

2.2 Monitoring Microbalance Performance

2.2.1 Quality Control Checks of the Microbalance

Routine checks of the microbalance using certified mass standards must be performed to detect any appreciable changes in instrument response over time. Since fine particulate mass concentrations are calculated based on the measured difference between loaded filters and clean filters, the absolute response of the microbalance is less critical than long-term stability and repeatability. Internal QC checks are recorded during each weighing session on the session's QC data worksheet. The following internal QC checks designed to monitor appreciable changes in microbalance response are performed at the beginning and end of every weighing session:

1. Measure and record the temperature, RH, operator's initials, date, and time on the weighing session's QC data worksheet.
2. Zero and autocalibrate the microbalance.
3. Weigh the NIST Class 1 100 mg mass standard. Record the weight on the QC data worksheet for that weighing session and compare this weight to those previously determined for the 100 mg standard.
4. Weigh the NIST Class 1 200 mg calibration weight. Record the weight on the QC data worksheet for that weighing session and compare this weight to those previously determined for the 200 mg standard.

2.2.2 Removing a Microbalance from Service

If the weights recorded for the certified mass standards used to perform systematic checks of the microbalance differ by more than 20 μg from their certified value or by more than 5 μg from their last recorded weight, the microbalance must be examined to verify that it is level, that the weigh pan and sample chamber are free of visible contamination, and that the chamber door mechanism is free of visible contamination that would prevent the door from sealing properly. These conditions must be corrected, if necessary. The microbalance must be internally calibrated and the certified mass standards must be weighed again. If the weights recorded for the certified mass standards still differ by more than 20 μg from their certified value or by more than 5 μg from their last recorded weight, 3 laboratory blanks must be randomly selected from the laboratory blanks exposed in the laboratory. The 3 laboratory blanks will be weighed and their weights will be recorded on the QC data worksheet for the weighing session. If the weight recorded for any 1 of the laboratory blanks differs by more than 15 μg from its initial weight, the microbalance will be removed from service pending repair and calibration by an authorized microbalance service representative.

The procedure for removing a microbalance from service in the RTI EISD Grav Lab is as follows:

1. Leave the microbalance in "Standby" mode.
2. Notify the Laboratory Supervisor that a routine check of the microbalance as described above has indicated that the microbalance is out of compliance.
3. Place a clearly written notice on the stone weighing table that states, "THIS

MICROBALANCE WAS REMOVED FROM SERVICE ON (MM/DD/YY) PENDING REPAIR AND CALIBRATION BY AN AUTHORIZED MICROBALANCE SERVICE REPRESENTATIVE.” Sign and date the notice.

4. Print the pertinent weighing session QC data worksheet. Paste this worksheet into the microbalance log. Write a brief summary of the microbalance checks and corrective actions in the microbalance log and initial and date the summary.
5. The Laboratory Supervisor will contact Mettler Toledo to schedule a service appointment, notify the QAO, and contact clients and the SHAL, as deemed necessary and appropriate, to discuss rescheduled delivery of tared filters.
6. If sampled filters must be weighed to avoid expiration in the RTI EISD Grav Lab, notify the Laboratory Supervisor. Weigh the sampled filters on the laboratory’s second microbalance. Flag any filter with an explanatory comment where the post-sampling weighing is performed on a microbalance other than the microbalance on which its initial (tare) weighing was performed.
7. After the microbalance has been repaired, calibrated, and certified by an authorized microbalance service representative, remove the written notice from the stone weighing table. Write a brief summary of the microbalance repair in the microbalance log and initial and date the summary.
8. Verify the microbalance performance with the certified working mass standards as described in Section 2.2.1 and document this verification in the microbalance log.

2.3 QC Filter Samples

The following table summarizes the recommended frequency of QC filters for the PM program:

Type of QC Filter	Description	Acceptance Criteria
Lot Stability Test Filters	Twelve (12) filters are repeatedly weighed to determine the minimum necessary equilibration time for filters from the same manufacturing lot.	Weight trend approaches zero
Batch Stability Test Filters	Three (3) filters from a batch are repeatedly weighed during equilibration to verify the stability of the filter shipment batch.	Weight loss < 5 µg
Laboratory Blank Filters	One (1) laboratory blank filter is weighed for every weighing session.	Weight loss < 15 µg
Field Blank Filters	Unexposed filters from each shipment batch are designated as field blanks by the client.	Weight difference < 30 µg
Replicate Filter Weighings	Every filter (pre-weighing) or every third filter (post-weighing) is reweighed.	Weight difference < 15 µg

2.4 Cleaning the Laboratory

The laboratory will be cleaned monthly or as needed to minimize contamination in the weighing environment. The laboratory will be cleaned after any renovation, maintenance, or repair activity in the vicinity of the weighing chambers (RTI Bldg 11, Bay 6). Cleaning will be performed by Laboratory Analysts who are familiar with the laboratory equipment, systems, and gravimetric analysis operations. Ultraviolet (UV) fluorescent inspection of surfaces in the weighing chambers will be performed annually to detect particulate microcontamination in the controlled environment to aid the analysts in identifying problem areas and refining their cleaning strategy. In this inspection, a UV hand lamp will be used to highlight contamination on surfaces in the illumination area. At a minimum, the following procedure will be followed when cleaning the laboratory:

1. Don shoe covers, disposable lab coats, and powder-free gloves prior to cleaning the laboratory.
2. After donning protective garments and gloves, replace all Petrislide[®] lids securely on open Petrislides[®] in which unsampled and sampled filters are conditioning. Closing the Petrislides[®] protects filter surfaces from contamination due to fall-out of settled particulate that is resuspended during cleaning.
3. Place all balances in “Standby” mode.
4. Verify that all working mass standards (reference weights) are stored in tightly closed boxes to protect them from contamination during cleaning.
5. Shut down all computers.
6. Remove all auxiliary supplies (e.g., unopened boxes of filters, FRM magazines and cassettes, mouse pads) from the chamber.
7. Invert all ionizing units and tap them gently on a table top to dislodge particulates. **Note:** Do not tamper with or touch the foil-covered Polonium strips if any are in use.
8. Damp-wipe all vertical and horizontal surfaces with a low-lint disposable cloth moistened with deionized (DI) water. Disposable cloths should be damp, not wet. Add a small amount (approximately 50 μ L) of Staticide[®] to the DI water used to wipe items, including walls, shelves, table tops, and network junction boxes. **Note:** Do not wipe the floor with a Staticide[®] solution; Staticide[®] may make the floor slippery. Discard disposable cloths after use.
9. When damp-wiping vertical and horizontal surfaces, pay particular attention to cables and cords, corners, ledges, network/telephone junction boxes, telephones, computer components, computer mouse, the shelf racks on which trays of filters are placed, the work area around the balances, and the balances themselves. Gently wipe the top of the balance’s power supply, data acquisition component, and chamber component. Do not place pressure on the microbalance.
10. Gently clean the balance’s sample chamber and weigh the pan with the brush provided by the manufacturer. The brush is located in a small drawer on the side of the chamber component. Pay particular attention to the groove in which the automatic chamber door moves as it opens and closes.

11. Using a low-lint sponge mop, damp-mop the floor with DI water. Rinse the mop frequently and change the water frequently. Use a textured scrubber as needed to remove visible staining. As noted previously, Staticide[®] must not be added to the water used to mop the floor.
12. Exit the chamber, changing the adhesive mats inside and outside the chamber door.
13. Allow surfaces to air dry. Wait at least 1 hour for the chamber's air circulation system to pull air through the plenum's coarse filters.
14. Pre-clean auxiliary supplies before returning them to the chamber.
15. After donning protective garments and gloves, remove Petrislide[®] lids from the Petrislides[®] that were closed prior to cleaning and place each lid slightly ajar over the Petrislide[®] well so that it covers approximately 3/4 of the filter surface. As noted previously in this SOP, such a placement of the lid allows for outgassing of the filter and offers some protection from particle deposition.
16. Reboot computers.
17. Bring balances up from "Standby" mode and internally calibrate them using the "Autocalibrate" function.

3.0 References

40 Code of Federal Regulations, Parts 50 (Appendix L), 53, and 58. *Revised Requirements for Designation of Reference and Equivalent Methods for PM_{2.5} and Ambient Air Quality Surveillance for Particulate; Final Rule* (referred to herein as 40 CFR Parts 50/53/58) as published in the *Federal Register*, Volume 62, Number 138, Friday, July 18, 1997.

U.S. EPA (Environmental Protection Agency) *The U.S. EPA Quality Assurance Handbook. Monitoring PM_{2.5} in ambient air using designated reference or class 1 equivalent methods.* Volume II, Part II, Section 2.12., November 1998

Mettler UMT2/UMX2 Microbalance Operations Manuals

Related SOPs:

- *Sample Receiving, Shipping, and Archiving Procedures for the PM_{2.5} Chemical Speciation Program*, RTI, 2005.
- *Standard Operating Procedures for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters*, RTI, 2005.
- *Data Handling Procedures for the Speciation Analysis Program*, RTI, 2005.

Standard Operating Procedure for PM_{2.5} Anion Analysis

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

Prepared by: Em D. Harrison Date: 8/26/09
Reviewed by: Jan B. Flayn Date: 8/26/09
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* RTI International is a trade name of Research Triangle Institute.

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Standard Operating Procedure for PM_{2.5} Anion Analysis

1.0 Procedural Section

1.1 Purpose and Applicability

This document outlines procedures for the extraction and subsequent determination of anions in filter extracts. Analytical procedures outlined are specific to the ion chromatographs used in RTI's Ion Analysis Laboratory.

1.2 Summary of Method

Collected aerosol filter samples are extracted by a method appropriate for the analyte of interest. Sample extracts are passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. Anion separation is due to the different affinities of the anions for the active resin sites. Following separation, the anions pass through a suppressor column, which exchanges all cations for H⁺ ions. An eluent that yields a low-conducting acid is used. Species are detected and quantified as their acids by use of a conductivity meter.

In a laboratory evaluation of the accuracy of the method, spiked PM_{2.5} filter extracts and quality assurance/quality control (QA/QC) samples were analyzed for sulfate and nitrate ions. The accuracy (expressed as % recovery) achieved using the subject method is presented in Table 1.

To test the precision of the method, PM_{2.5} filter extracts were analyzed in duplicate, and the blank extracting solution and a low-level QC sample were analyzed seven times each. The results are summarized in Table 2.

Table 1. Accuracy Values for QA/QC Samples and Spiked PM_{2.5} Filter Extracts

Analyte	QA/QC Sample Average % Recovery* (range)	Spiked Extract Average % Recovery* (range)
SO ₄	100.5 (97.5–104.2) n = 187	99.9 (98.2–100.7) n = 61
NO ₃ ⁻	99.6 (96.9–103.0) n = 187	99.3 (97.5–103.3) n = 61

* % Recovery = (concentration found/concentration expected) × 100

Table 2. Precision Values for PM_{2.5} Filter Extracts, Extracting Solution, and QC Samples

Analyte	Sample Type		
	PM _{2.5} Filter Extracts Average RSD** (range)	Blank Extracting Solution Average (Standard Deviation), n = 7	QC Sample (0.600 ppm NO ₃ , 1.200 ppm SO ₄) RSD, n = 7
SO ₄ ⁼	0.2 (0.0–1.4)	0.000 (0.000)	0.3
NO ₃ ⁻	0.3 (0.0–1.7) for 86 duplicates for 86 duplicates	0.000 (0.000)	0.2

** RSD = relative standard deviation (the standard deviation divided by the average value and expressed as a percentage)

1.3 Health and Safety Warnings

The PM_{2.5} ion analysis operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of gloves is required and will minimize the potential for laboratory contamination.

1.5 Interferences

Large amounts of anions eluting close to the ions of interest will result in an interference. No interferences have been observed in nylon filters samples or Teflon filter samples analyzed to date. If interferences are observed, several steps to increase separation can be taken, such as reducing eluent strength and/or flow rate or replacing the guard and/or separator column.

1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least an associate's degree in a laboratory science and will be trained by a supervisor before being allowed to process client samples for the PM_{2.5} program.

1.7 Apparatus and Materials

1. Disposable centrifuge tubes with screw caps, 50 mL (polypropylene).
2. Calibrated Rainin electronic pipette (10 mL capacity) and adjustable Eppendorf pipette (10–100 μ L).
3. Tweezers.
4. Ultrasonic bath fitted with epoxy-coated test-tube rack to hold centrifuge tubes.

5. Mechanical shaker.
6. Ion chromatograph complete with workstation (see Table 3).
7. Pressurized eluent and regenerant reservoirs.
8. Volumetric flasks (an assortment of sizes).
9. Dionex autosampler vials with filter caps.
10. Coldroom at $\leq 4^{\circ}\text{C}$.
11. Refrigerators.

Table 3. Configurations of Ion Chromatographs Used for Anion Analysis

Instrument ID	A1	A2	A3	A4	A5	A6
Dionex Model	DX-500	DX-500	DX-500	DX-600	DX-600	ICS-2000
Chromatography Module	LC20	LC20	LC20	LC30	LC30	None
Pump	GP50	IP25	IP20	IP25	IS25	IS2000
Conductivity Detector	CD20 DS3 Cell	CD20 DS3 Cell	CD20 DS1A Cell	CD20 DS3 Cell	CD25 DS3 Cell	Built-in DS6
Autosampler	AS40	AS40	AS40	AS40	AS40	AS40
Software	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex Chromeleon	Windows XP Dionex Chromeleon			
Guard Column	AG12A	AG12A	AG12A	AG12A	AG12A	AG12A
Separator Column	AS12A	AS12A	AS12A	AS12A	AS12A	AS12A
Suppressor Column	AMMSIII	AMMSIII	AMMSIII	AMMSIII	ASRS Ultra Auto-regen mode	ASRS Ultra Auto-regen mode
Other	—	—	—	—	—	Built-in eluent generator (not used)

1.8 Ion Chromatography Reagents

Use ACS reagent-grade chemicals and 18.2M Ω -cm deionized water for the preparation of all solutions.

1. Concentrated eluent (100X), 30mM NaHCO₃/270mM Na₂CO₃: Dissolve 2.5209 g NaHCO₃ and 28.6178 g Na₂CO₃ in 1 L of deionized water (Note: Do NOT dry the salts that are used to prepare the eluent).

- Working eluent, 0.3mM NaHCO₃/2.7mM Na₂CO₃: Dilute 200 mL concentrated eluent to 20 L with deionized water.
- Regenerant, 0.025N H₂SO₄: Dilute 100 mL 5.0N H₂SO₄ to 20 L with deionized water (Note: This reagent is not used for an IC system equipped with a self-regenerating suppressor.).

1.9 Calibration Standards

Use ACS reagent-grade chemicals and 18.2MΩ-cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105 °C for 2 hours and cool in a desiccator immediately before use.

- Mixed Stock Solution, 1000 mg/L NO₂⁻, NO₃⁻, and SO₄²⁻, and 200 mg/L Cl⁻: Dissolve 1.4998 g NaNO₂, 1.3708 g NaNO₃, 1.8142 g K₂SO₄, and 0.3297 g NaCl in 1 L of deionized water (Note: These are the four anions typically analyzed in the Ion Analysis Laboratory. PM_{2.5} filter extracts will be analyzed using standards prepared from this mixed-stock solution.).
- Standard Solution A (100 mg/L NO₂⁻, NO₃⁻, SO₄²⁻, and 20 mg/L Cl⁻): Dilute 10 mL mixed-stock solution to 100 mL with deionized water.
- Standard Solution B (10 mg/L NO₂⁻, NO₃⁻, and SO₄²⁻, and 2 mg/L Cl⁻): Dilute 10 mL Standard Solution A to 100 mL with deionized water.
- Calibration Standards: Using Standard Solutions A and B, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 4. Prepare fresh calibration standards weekly.

Table 4. Preparation of Anion Calibration Standards

Standard	NO ₃ ⁻ , SO ₄ ²⁻ (mg/L)	mL of Standard Solution/100 mL
Standard Solution A		
1	25.0	25.0
2	10.0	10.0*
3	3.0	3.0
Standard Solution B		
4	1.0	10.0*
6	0.5	5.0
7	0.2	2.0
1 mg/L STANDARD (Standard 4)		
8	0.1	10.0*
9	0.05	5.0*

Note: Higher concentration standards can be prepared from Standard A or from the mixed-stock solution if needed.

*For these solutions, use two times the stated mL of standard solution in a 200 L flask.

1.10 Quality Control Solutions

Use ACS reagent-grade chemicals and 18.2MΩ-cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105 °C for 2 hours and cool in a desiccator immediately before use. Quality control solutions must be prepared independent of the calibration solutions.

1. Chloride Stock Solution, 1000 mg/L Cl⁻: Dissolve 0.8243 g NaCl in 500 mL of deionized water.
2. Nitrite Stock Solution, 1000 mg/L NO₂⁻: Dissolve 0.7499 g NaNO₂ in 500 mL of deionized water.
3. Nitrate Stock Solution, 1000 mg/L NO₃⁻: Dissolve 0.6854 g NaNO₃ in 500 mL of deionized water.
4. Sulfate Stock Solution, 1000 mg/L SO₄²⁻: Dissolve 0.9071 g K₂SO₄, in 500 mL of deionized water.
5. QC-Intermediate Solution, 10 mg/L Cl⁻, 20 mg/L NO₂⁻, 30 mg/L NO₃⁻, and 60 mg/L SO₄²⁻: Pipette 1 mL of 1000 mg/L Cl⁻, 2 mL of 1000 mg/L NO₂⁻, 3 mL of 1000 mg/L NO₃⁻, and 6 mL of 1000 mg/L SO₄²⁻ into a 100 mL volumetric flask and dilute to the mark with deionized water.
6. QC Samples: Using the QC-intermediate solution, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 5. Prepare fresh calibration standards weekly.

Table 5. Preparation of Anion Quality Control Samples

QC Sample ID	mL QC-Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	NO ₃ ⁻ Conc (mg/L)	SO ₄ ²⁻ Conc (mg/L)
QC-LOW	2.0	100	0.6	1.2
QC-MED	5.0	100	1.5	3.0
QC-HIGH	10.0	50	6.0	12.0

1.11 Quality Assurance Solutions

Use commercially prepared, NIST-traceable solutions to prepare an intermediate quality assurance solution known concentrations of Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻. Solutions can be purchased from CPI (www.cpichem.com) or GFS Chemicals (www.gfschemicals.com).

1. QA-Intermediate Solution, 10 mg/L Cl⁻, 20 mg/L NO₂⁻, 30 mg/L NO₃⁻, and 60 mg/L SO₄²⁻: Pipette 1 mL of 1000 mg/L Cl⁻, 2 mL of 1000 mg/L NO₂⁻, 3 mL of 1000 mg/L NO₃⁻, and 6 mL of 1000 mg/L SO₄²⁻ into a 100 mL volumetric flask and dilute to the mark with deionized water.

2. Using the QA-intermediate solution, prepare calibration standards with deionized water in 100 mL volumetric flasks as shown in Table 6. Prepare fresh quality assurance samples as needed.

Table 6. Preparation of Anion Quality Assurance Samples

QC Sample ID	mL QA-Intermediate Solution	Final Volume, mL (Volumetric Flask Size)	NO ₃ - Conc (mg/L)	SO ₄ ²⁻ - Conc (mg/L)
QA-CPI_LOW	2.0	100	0.6	1.2
QA-CPI_MED-HI	10.0	100	3.0	6.0

1.12 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the state agency responsible for exposing the filters.

1.13 Sample Handling

Note: Additional information on this topic can be found in the *Standard Operating Procedure for the Sample Handling and Archiving Laboratory (SHAL)*, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, 2001.

RTI will provide chain-of-custody documentation with all sample shipments to track and ensure that samples are collected, transferred, stored, and analyzed by authorized personnel; sample integrity will be maintained during all phases of sample handling and analysis; and an accurate written record will be 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 client.

Upon initial receipt of filters, RTI will prepare a Filter Inventory Sheet containing the filter identification numbers, box numbers, date received, date inspected, and the number of filters rejected. This sheet will allow laboratory personnel to select and use the filter boxes in the proper sequence.

1.14 Filter Extraction Procedure

1.14.1 Nylon Filters

Note: Nylon filters to be analyzed for nitrate only will be extracted with the eluent used for IC analysis, a dilute sodium carbonate/sodium bicarbonate buffer. Filters to be analyzed for anions and cations will be extracted with 18.2MΩ-cm deionized water. The anion eluent produces a large sodium peak in the cation chromatogram that precludes quantitation of the sodium ion in the filter extract and interferes with the quantitation of ammonium ion.

To extract the filters, the analyst will do the following:

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
2. Using gloved hands and tweezers, place each filter in a polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label two 50-mL extraction tubes as Reagent Blank DI H₂O and Reagent Blank Eluent. The eluent blank will not be prepared if there are no “nitrate only” samples to be analyzed with the batch.
4. Add 25.0 mL of extraction solution (2.7 mM Na₂CO₃/0.3 mM NaHCO₃ for subsequent anion analysis or deionized water for subsequent anion and cation analysis) using a calibrated automatic pipette.
5. Screw the cap tightly on the centrifuge tube.
6. Ensure that the filter is completely submerged in the extraction solution.
7. Place the batch of centrifuge tubes in an epoxy-coated wire test-tube rack and place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level but below the screw cap. Sonicate for 60 minutes.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Install the extraction racks on the mechanical shaker and shake overnight in a cold room ($\leq 4^{\circ}\text{C}$) at approximately 60 cycles per minute.
9. Record the date of extraction on the RTI Sample Log Form.
10. Store the extracts in a refrigerator until analysis.

1.14.2 Teflon Filters

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
2. Using gloved hands and tweezers, place each filter in a polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label one 50-mL extraction tube as "Reagent Blank DI H₂O." Remove the caps from all 50-mL extraction tubes. To prevent contamination place the caps in an upside-down position.
4. Using an Eppendorf 100- μ L pipette, wet the entire surface of each Teflon filter with 100 μ L of nanopure ethanol. This is done by very slowly pipetting the ethanol on the center of the filter. Capillary action will distribute the ethanol over the entire surface. The "reagent blank" tube will not contain a filter. Add the 100 μ L of ethanol directly to the bottom of the tube.

Note: Before proceeding, visually inspect each filter to be sure that the entire filter surface is wet.

5. Using a calibrated automatic pipette, add 25.0 mL of deionized water to each extraction tube. The deionized water must have a resistance of at least 18.2M Ω -cm.
6. Recap all extraction tubes tightly to prevent leakage during the extraction procedure. Be sure that the exposed area of the filter is completely immersed in the extraction solution.
7. Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level but below the screw cap.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Install the extraction racks on the mechanical shaker and shake overnight in a cold room ($\leq 4^{\circ}\text{C}$) at approximately 60 cycles per minute.
9. Record the date of extraction on the RTI Sample Log Form.
10. Store the extracted filters in the refrigerator prior to analysis.

1.15 IC Procedure

1. Fill the eluent reservoirs with the eluent and the regenerant reservoirs with regenerant and pressurize the reservoirs.
2. Start the eluent flow at 1.5 mL/min, and if using a self-regenerating suppressor, activate it. Allow the baseline to stabilize.
3. Inject two deionized water blanks to flush the system and to ensure that the system is operating properly.
4. Using the calibration schedule, perform the daily multipoint calibration over the range 0.05 to 25.0 ppm NO₃⁻ and SO₄²⁻ followed by QA/QC samples listed below.
 - A QC sample containing concentrations of NO₃⁻ and SO₄²⁻ typical of those found in the mid-range of actual filter extract concentrations (QC-MED).
 - A QC sample containing concentrations of NO₃⁻ and SO₄²⁻ typical of those found at the lower end of actual filter extract concentrations (QC-LOW).
 - A commercially prepared, NIST-traceable QA sample containing known concentrations of NO₃⁻ and SO₄²⁻ (QA-CPI_LOW).

If the observed value for nitrate or sulfate differs by more than 10% from the known values, identify and correct the problem before analyzing samples.

5. Remove sample extracts from the refrigerator and allow to equilibrate to room temperature (Note: This should be performed while the system is stabilizing and the calibration is being conducted.)
6. Load the sample extracts into the autosampler vials according to the schedule prepared for that day. Typically, 50 field samples are analyzed per day. The daily schedule includes, at a minimum, 3 duplicate samples, 2 spiked samples, and 5 QA/QC samples.
7. Begin the analysis run, occasionally checking to ensure that the system is operating properly.
8. Examine the data at the end of the run. If the concentration of any ion exceeds the upper end of the calibration curve, dilute the sample appropriately and include with the samples to be analyzed the following day.

1.16 Calculations and Data Reduction

Peak areas are entered into the computer where calculations are performed using a quadratic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^2 + bx_i + c$$

where:

- y = the calculated anion concentration, µg/L
- x = the instrument response

Initially, the calibration curve from 0.05 to 10.0 ppm is used for the calculation of the extract nitrate and sulfate concentrations. All sulfate and/or nitrate concentrations that exceed 10 ppm are recalculated with the 25.0 ppm standard added to the calibration curve. If a recalculated nitrate or sulfate concentration exceeds 25 ppm, the extract is diluted appropriately (usually 5-fold) to bring the ion concentration into the calibration range and reanalyzed.

2.0 Quality Assurance and Quality Control

Compare the regression parameters (a, b, c, and correlation coefficient) for the standard curves with those obtained in the past. If they exceed the control limits, stop the analysis and identify the problem.

Analyze QA/QC samples (see Sections 1.10 and 1.11) at the beginning of every analytical run. Compare the results with those obtained during previous QA/QC tests. If the observed concentration of any ion differs from the known value by greater than 10%, stop the analysis until the problem is identified and corrected. Analyze a duplicate sample, a QA/QC sample, and a spiked sample after at least every 20 field samples.

Standard Operating Procedure for PM_{2.5} Cation Analysis

Environmental and Industrial Sciences Division
RTI International*
Research Triangle Park, North Carolina

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

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Standard Operating Procedure for PM_{2.5} Cation Analysis

1.0 Procedural Section

1.1 Purpose and Applicability

This document outlines procedures for the extraction and subsequent determination of ammonium, sodium, and potassium ions in filter extracts. Analytical procedures outlined are specific to the ion chromatographs used in RTI's ion analysis laboratories.

1.2 Summary of Method

Cations in solution are separated when passed through a surface-sulfonated ion-exchange resin due to the differing affinities of the cations for the active sites on the resin. After separation, the cations pass through a suppressor column, which exchanges all anions for OH⁻ ions. Species are detected and quantified as their hydroxides by a conductivity meter. The eluent is sulfuric acid, which yields deionized water when passed through the suppressor column.

In a laboratory evaluation of the accuracy of the method, spiked PM_{2.5} filter extracts and quality assurance/quality control (QA/QC) samples were analyzed for sodium, ammonium, and potassium ions. The accuracy (expressed as % recovery) achieved using the subject method is presented in Table 1.

To test the precision of the method, PM_{2.5} filter extracts were analyzed in duplicate, and the blank extracting solution and a low-level QC sample were analyzed seven times each. The results are summarized in Table 2.

Table 1. Accuracy Values for QA/QC Samples and Spiked Pm_{2.5} Filter Extracts

Analyte	QA/QC Sample Average % Recovery* (range)	Spiked Extract Average % Recovery* (range)
NH ₄ ⁺	99.0 (91.0 - 108.0) n = 59	99.4 (96.4 - 105.9) n = 14
Na ⁺	104.2 (100.0 - 107.7) n = 20	101.8 (97.0 - 105.1) n = 5
K ⁺	103.0 (96.6 - 106.3) n = 20	99.2 (97.0 - 102.7) n = 5

*% Recovery = (concentration found/concentration expected) × 100.

Table 2. Precision Values for PM_{2.5} Filter Extracts, Extracting Solution, and QC Samples

Analyte	Sample Type		
	PM _{2.5} Filter Extracts Average RSD** (range)	Blank Extracting Solution Average (Std Dev), n = 7	0.05 ppm QC Sample RSD, n = 7
NH ₄ ⁺	0.6 (0.1 - 1.6) for 13 duplicates	0.000 (0.000)	2.0
Na ⁺	8.0 (0.6 - 19.8) for 17 duplicates	0.001 (0.003)	13.3
K ⁺	1.1 (0.1 - 3.1) for 17 duplicates	0.000 (0.000)	2.0

** RSD = relative standard deviation (the standard deviation divided by the average value and expressed as a percentage)

1.3 Health and Safety Warnings

The PM_{2.5} ion analysis operations do not involve unusual risks from electrical equipment or chemical exposures. Standard RTI laboratory health and safety precautions will be followed.

1.4 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of gloves is required and will minimize the potential for laboratory contamination.

1.5 Interferences

Large amounts of cations eluting close to the ions of interest will result in an interference. No interferences have been observed in extracts analyzed by RTI to date. If interferences are observed, several steps to increase separation can be taken, such as reducing eluent strength and/or flow rate, or replacing the guard and/or separator column.

1.6 Personnel Qualifications

Personnel employed to perform ion analysis operations will have at least an associate's degree in a laboratory science and will be trained by a supervisor before being allowed to process client samples for the PM_{2.5} program.

1.7 Apparatus and Materials

- Disposable centrifuge tubes with screw caps, 50 mL (polypropylene)
- Calibrated Rainin electronic pipette (10-mL capacity) and adjustable Eppendorf pipette (10-100µ)
- Tweezers

- Ultrasonic bath fitted with epoxy-coated test tube rack to hold centrifuge tubes
- Mechanical shaker
- Ion chromatograph complete with workstation (See Table 3.)
- Pressurized eluent reservoirs
- Volumetric flasks in an assortment of sizes
- Dionex autosampler vials with filter caps
- Coldroom at $\leq 4^{\circ}$ C
- Refrigerators.

Table 3. Configurations of Ion Chromatographs Used for Cation Analysis

Instrument ID	C1	C2	C3	C4
Dionex Model	DX-500	DX-600	ICS-2000	DX-600
Chromatography Module	LC20 (no temperature unit)	LC30	None (built in temperature unit)	LC30
Pump	IP20	IP25	IS2000	IS25
Conductivity Detector	CD20 DS1A Cell	CD20 DS3 Cell	Built-in DS6 cell	CD25 DS3 Cell
Autosampler	AS40	AS40	AS40	AS40
Software	Windows 2000 Dionex PeakNet 5.2	Windows 2000 Dionex PeakNet 5.2	Windows XP Dionex Chromeleon	Windows 2000 Dionex Chromeleon
Guard Column	none	none	none	none
Separator Column	CS12A	CS12A	CS12A	CS12A
Suppressor Column	CSRS-300 auto regenerator	CSRS-ultra auto regenerator	CSRS-ultra auto regenerator	CSRS-ultra auto regenerator
Other	-	-	Built-in eluent regenerator (not used)	EG50 eluent generator (not used)

1.8 Ion Chromatography Reagents

Use ACS reagent grade chemicals and 18.2M Ω -cm deionized water for the preparation of all solutions.

1. Concentrated Eluent Stock Solution: 5N H₂SO₄, purchased from VWR Scientific
2. Working Eluent, 22mN Sulfuric Acid: Dilute 4.4 mL 5N H₂SO₄ to 1 liter using deionized water. Sonicate for 15 minutes just prior to use to de-gas the solution.

1.9 Calibration Standards

Use ACS reagent-grade chemicals and 18.2M Ω -cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105°C for 2 hours and cool in a desiccator immediately before use.

1. Calibration Standard Stock Solution, 1000 mg/L each NH₄⁺, Na⁺, and K⁺: Dissolve 2.9654 g NH₄Cl, 2.5422 g NaCl, and 2.2284 g K₂SO₄ in 1 liter deionized water.
2. Standard Solution A: Dilute 10 mL stock solution to 100 mL with deionized water (100 mg/L NH₄⁺, Na⁺, K⁺).
3. Standard Solution B: Dilute 10 mL Standard Solution A to 100 mL with deionized water (10 mg/L NH₄⁺, Na⁺, K⁺).
4. Using Standard Solutions A and B, prepare calibration standards with deionized water in 100-mL volumetric flasks, as shown in Table 4. Prepare fresh calibration standards weekly.

1.10 Quality Control Solutions

Use ACS reagent-grade chemicals and 18.2M Ω -cm deionized water for the preparation of all solutions. Dry the salts used for the preparation of calibration standards at 105°C for 2 hours and cool in a desiccator immediately before use. Quality control (QC) solutions must be prepared independent of the calibration solutions.

1. Sodium QC Stock Solution, 1000 mg/L Na⁺: Dissolve 1.2711 g NaCl in 500 mL of deionized water
2. Ammonium QC Stock Solution, 1000 mg/L NH₄⁺: Dissolve 1.4827 g NH₄Cl in 500 mL of deionized water
3. Potassium QC Stock Solution, 1000 mg/L K⁺: Dissolve 1.1142 g K₂SO₄ in 500 mL of deionized water
4. QC-Intermediate Solution, 100 mg/L each Na⁺, NH₄⁺, and K⁺: Pipette 10 mL of 1000 mg/L Na⁺, 10 mL of 1000 mg/L NH₄⁺, and 10 mL of 1000 mg/L K⁺ into a 100-mL volumetric flask and dilute to the mark with deionized water.
5. QC Samples: Using the QC-intermediate solution, prepare QC samples with deionized water in 100-mL volumetric flasks, as shown in Table 5. Prepare fresh QC samples as needed.

Table 4. Preparation of Cation Calibration Standards

Standard	NH ₄ ⁺ , Na ⁺ , K ⁺ (mg/L each)	mL of Standard Solution/100 mL
STANDARD SOLUTION A		
1	25.0	25.0
2	10.0	10.0
3	3.0	3.0
STANDARD SOLUTION B		
4	1.0	10.0
5	0.3	3.0
1 mg/L STANDARD (Standard 4)		
6	0.1	10.0
7	0.05	5.0

1.11 Quality Assurance Solutions

Use commercially prepared, NIST-traceable solutions to prepare an intermediate QA solution with known concentrations of Na⁺, NH₄⁺, and K⁺. Solutions can be purchased from CPI (www.cpichem.com) or GFS Chemicals (www.gfschemicals.com).

1. QA-Intermediate Solution, 100 mg/L each Na⁺, NH₄⁺, and K⁺: Pipette 10 mL of 1000 mg/L Na⁺, 10 mL of 1000 mg/L NH₄⁺, and 10 mL of 1000 mg/L K⁺ into a 100-mL volumetric flask and dilute to the mark with deionized water
2. Prepare QA samples with deionized water in 100-mL volumetric flasks, as shown in Table 6. Prepare fresh QA samples as needed.

Table 5. Preparation of Anion Quality Control Samples

QC Sample ID	mL QC-Intermediate	Final Volume, mL (volumetric flask size)	Na ⁺ , NH ₄ ⁺ , and K ⁺ Conc (mg/L)
RTI 2 ppm QC	2.0	100	2.0
RTI 5 ppm QC	5.0	100	5.0

Table 6. Preparation of Anion Quality Assurance Samples

QA Sample ID	Dilute	Final Volume, mL (volumetric flask size)	Na ⁺ , NH ₄ ⁺ , and K ⁺ Conc (mg/L)
GFS 4.0 ppm QA	4.0 mL QA-Intermediate	100	4.0
GFS 0.4 ppm QA	10 mL GFS 4.0 ppm QA	100	0.4

1.12 Sample Collection

Sample collection is not applicable to this SOP because samples are acquired by the state agency responsible for exposing the filters.

1.13 Sample Handling

Note: Additional information on this topic can be found in the SOP *Sample Receiving, Shipping, and Archiving Procedures for the PM_{2.5} Chemical Speciation Program*, RTI International, Center for Environmental Measurements and Quality Assurance, 1999.

RTI will provide chain-of-custody 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 written 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 client.

Upon initial receipt of filters, RTI will prepare a Filter Inventory Sheet containing the filter identification numbers, box numbers, date received, date inspected, and number of filters rejected. This form will allow laboratory personnel to select and use the filter boxes in the proper sequence.

1.14 Filter Extraction Procedure

1.14.1 Nylon Filters

Note: Filters to be analyzed for anions and cations or for cations only will be extracted with deionized water.

To extract the filters, the analyst will do the following:

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
2. Using gloved hands and tweezers, place each filter in a polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label a 50-ml extraction tube as "Reagent Blank DI H₂O."
4. Add 25.0 mL of deionized water to each tube using a calibrated automatic pipette.
5. Screw the cap tightly on the centrifuge tube.
5. Ensure that the filter is completely submerged in the extraction solution.
6. Place the batch of centrifuge tubes in an epoxy-coated wire test tube rack and place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level but below the screw cap. Sonicate for 60 minutes.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature and add ice as necessary during the sonication to maintain an acceptable temperature.

7. Install the extraction racks on the mechanical shaker and shake overnight in a cold room ($\leq 4^{\circ}\text{C}$) at approximately 60 cycles per minute.
8. Record the date of extraction on the RTI Sample Log Form.
9. Store the extracts in a refrigerator until analysis.

1.14.2 Teflon Filters

1. Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
2. Using gloved hands and tweezers, place each filter in polypropylene centrifuge tube that has been labeled with the sample ID printed on a durable (water-resistant) label.
3. Label a 50-ml extraction tube as "Reagent Blank DI H₂O."
4. Remove the caps from all 50-ml extraction tubes. To prevent contamination, place the caps in an upside-down position.
5. Using an Eppendorf 100- μl pipette, wet the entire surface of each Teflon filter with 100 μl of nanopure ethanol. This is done by very slowly pipetting the ethanol on the center of the filter. Capillary action will distribute the ethanol over the entire surface. The "Reagent Blank DI H₂O" tube will not contain a filter. Add the 100 μl of ethanol directly to the bottom of the tube.
Note: Before proceeding, visually inspect each filter to be sure that the entire filter surface is wet.
6. Using a calibrated automatic pipette, add 25.0 ml of deionized water to each extraction tube. The deionized water must have a resistance of at least 18.2M Ω -cm.

7. Recap all extraction tubes tightly to prevent leakage during the extraction procedure. Be sure that the exposed area of the filter is completely immersed in the extraction solution.

CAUTION: Monitor the bath temperature during sonication. The temperature should not exceed 27°C. Add ice initially to lower the temperature, and add ice as necessary during the sonication to maintain an acceptable temperature.

8. Place the extraction rack in the ultrasonic bath. Make sure that the water level of the ultrasonic bath is higher than the extraction solution level, but below the screw cap. Sonicate for 60 minutes.
9. Install the extraction racks on the mechanical shaker and shake overnight in a cold room ($\leq 4^{\circ}\text{C}$) at approximately 60 cycles per minute.
10. Record the date of extraction on the RTI Sample Log Form.
11. Store the extracted filters in the refrigerator prior to analysis.

1.15 IC Procedure

1. Fill the eluent reservoirs with eluent.
2. Start the eluent flow, activate the self-regenerating suppressor, and allow the baseline to stabilize.
3. Inject four eluent blanks to flush the system and to ensure that the system is operating properly.
4. Using the calibration schedule, perform the daily multipoint calibration over the appropriate range followed by the GFS 4.0 ppm QA sample. If the observed value for any cation differs by more than 10% from the known value, identify and correct the problem before analyzing samples.
5. Load the filter extracts into the autosampler vials according to the schedule prepared for that day. The daily schedule includes duplicate samples, spiked samples, and QA/QC samples.
6. Begin the analysis run, occasionally checking to ensure that the system is operating properly.
7. Examine the data at the end of the run. If the NH_4^+ , Na^+ , or K^+ concentration of any extract exceeds the upper end of its calibration curve, dilute the extract appropriately and analyze that day or include with the samples to be analyzed the following day.

1.16 Calculations and Data Reduction

For ion chromatographs using Dionex PeakNet® software, peak areas are automatically entered into the computer where calculations are performed using a quadratic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^2 + bx_i + c$$

where

y = the calculated cation concentration, µg/L
x = the instrument response

For ion chromatographs using Chromeleon® software, NH₄⁺ peak areas are automatically entered into the computer where calculations are performed using a cubic fit to the calibration data. The quadratic fit yields the following:

$$y_i = ax_i^3 + bx_i^2 + cx_i + d$$

where

y = the calculated NH₄⁺ concentration, µg/L
x = the instrument response

The cubic fit for NH₄⁺ is used at the recommendation of Dionex. Na⁺ and K⁺ concentrations are calculated using a quadratic fit as described above.

The calibration curve from 0.05 to 10.0 ppm is used for the calculation of the extract NH₄⁺, Na⁺, and K⁺ concentrations. If a cation concentration exceeds 10 ppm, the extract is diluted appropriately (usually 5-fold) to bring the cation concentration into the calibration range and reanalyzed.

2.0 Quality Control and Quality Assurance

Compare the regression parameters (a, b, c, and correlation coefficient) for the standard curves with those obtained in the past. If they exceed the control limits, stop the analysis and identify the problem.

Analyze QC samples (see Section 1.13) at the beginning of every analytical run. Compare the results with those obtained during previous QC tests. If the observed concentration of any ion differs from the known value by greater than 10%, stop the analysis until the problem is identified and corrected. Analyze a duplicate sample, a QA/QC sample, and a spiked sample after at least every 20 field samples.

3.0 Reference

DRI Document No. 8068.1F4, Appendix D, Section 4.2.

Standard Operating Procedure for the X-Ray Fluorescence Analysis of Particulate Matter Deposits on Teflon Filters

Environmental and Industrial Measurements Division
RTI International*
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* RTI International is a trade name of Research Triangle Institute.

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Standard Operating Procedure for the X-ray Fluorescence Analysis of PM Deposits on Teflon Filters

1.0 Scope and Application

This standard operating procedure addresses the application of energy dispersive X-ray fluorescence (EDXRF) spectrometry to the determination of trace elements in particulate matter (PM) deposits on Teflon filters. This technique is capable of quantitative analysis of elements with atomic numbers 11 (sodium) through 92 (uranium). The 33 elements specific to this project are listed in Table 1.

Table 1. Project-Specific Elements Analyzed for the PM Speciation Program

Element	Element	Element	Element
Sodium (Na)	Titanium (Ti)	Arsenic (As)	Indium (In)
Magnesium (Mg)	Vanadium (V)	Selenium (Se)	Antimony (Sb)
Aluminum (Al)	Chromium (Cr)	Bromine (Br)	Cesium (Cs)
Silicon (Si)	Manganese (Mn)	Rubidium (Rb)	Barium (Ba)
Phosphorus (P)	Iron (Fe)	Strontium (Sr)	Cerium (Ce)
Sulfur (S)	Cobalt (Co)	Zirconium (Zr)	Lead (Pb)
Chlorine (Cl)	Nickel (Ni)	Silver (Ag)	
Potassium (K)	Copper (Cu)	Cadmium (Cd)	
Calcium (Ca)	Zinc (Zn)	Tin (Sn)	

1.1 Principle

The basis of X-ray fluorescence (XRF) spectrometry is the interaction of X-ray photons from a separate excitation source with atoms of the elements of interest found in the sample (filter deposit). When these excitation photons interact with the atoms in the sample, the photons cause the ejection of inner shell electrons. Outer shell electrons then fall into these vacancies. These transitions result in the emission of X-rays that are characteristic of the element. The energy of the characteristic X-ray is equal to the difference in the electron-binding energies of the two electron shells involved in the transition. Because the electron-binding energies are a function of the atomic number, the energy of the X-ray is characteristic of the element. The number or intensity of X-rays produced at a given energy provides a measure of the amount of the element present by comparisons with standards.

The X-rays are detected with a semiconductor material, lithium-drifted silicon. The X-ray passing into the detector produces a pulse of electrical current; the more energetic the X-ray, the larger the pulse of electrical current. The electrical pulses are measured and counted with appropriate electronics. These analyzer electronics further process the signals and display the X-ray energy spectrum (numbers of X-rays versus energy) on a personal computer (PC). The computer software determines the energy and intensity of the characteristic X-ray peaks, and then calculates the elemental concentrations through comparison to calibration parameters. The analysis of PM filter deposits is based on the assumption that the thickness of the deposit is small with respect to the analyte characteristic X-ray transmission thickness. It is assumed that the overall production of fluorescence X-rays is equivalent for PM samples and thin film, elemental standards. Therefore, the concentration of analytes in an unknown sample is determined by first calibrating the spectrometer with thin-film standards to determine sensitivity factors, and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration factors.

1.2 Method Overview

The first step is to check the energy calibration to ensure that peak energies are accurately tied to specific elements. Energy adjustment is performed using a ThermoNoran copper (Cu) calibration standard. This procedure is run every day before any analysis is performed. The energy adjustment involves measuring the Cu K α line (8041), and then determining the difference between the measured peak energy value and the ideal value and if any adjustments are required, the instrument software performs it automatically.

Filter samples are removed from cold storage and are loaded into the sample cups. Sample information is entered into the instrument logbook. The filters (in their sample cups) are loaded into the XRF sample tray in the same order as they are written into the instrument logbook. The instrument is then prepared for analysis by entering each filter aliquot number into the Method Tray List within the WinTrace software. The PM filter deposit analysis is then initiated.

This analysis protocol consists of each filter being analyzed five separate times using five different excitation conditions (See Section 6.2, *Method Setup*). The specific excitation conditions have been optimized for specific groups of elements listed in Table 1. The different excitation conditions are used to maximize the sensitivity of the measurement of the different groups of elements, which fluoresce over a wide range of excitation energies. Each analytical run, which includes nine samples, has a multi-element thin film standard to verify overall method and instrumentation performance.

Quantitative calibration for the elements is based on the use of thin film, elemental standards available from Micromatter, Inc. Recalibration of the instrument is required when the quality control samples or the National Institute of Standards and Technology standard falls outside their acceptance limits, when the detector or tube is replaced, or when the instrument undergoes significant repair or other changes in the hardware. Typical recalibration frequency is on the order of once every 6 to 12 months.

2.0 Safety

Operating the ThermoNoran QuanX XRF analyzer under normal operations and following Good Laboratory Practices to provide a safe working environment, but the following cautions should be noted.

ThermoNoran QuanX XRF analyzer operators are protected from accidental exposure to X-rays by a lid lock and front and back door interlocks when the instrument is in operation. Monthly the RTI Radiation Safety Officer performs area monitoring around each instrument to check for any leaking radiation. Also, the operator wears one to monitor his or her exposure. If any problems arise with the "X-RAYS ON" indicator light on the sample chamber lid or the interlock system, contact the instrument service engineer.

A beryllium (Be) window is present to separate the sample chamber from the X-ray tube and detector. Because this window is fragile and brittle, do not allow sample or debris to fall onto the window and avoid using compressed air to clean the window because it will cause the window to rupture. If the window should rupture, it is important to note that Be metal is poisonous. Use extreme caution when collecting pieces of Be and consult the instrument service engineer for advice on cleaning up the broken window and replacing it.

3.0 Filter Sample Considerations

It is assumed that the PM material is uniformly deposited on the filter and that the position of the PM filter and the standards in the instrument is the same. It is important that care be taken when loading filters into the sample cups so that the deposit is not scraped, smudged, or smeared in any way. Care also needs to be taken to assure that the filters are placed flat in the sample cups and that these cups rest flat on the instrument sample-positioning wheel.

4.0 Interferences and Intensity Corrections

The following sections describe potential sources of error in the procedure:

4.1 Spectral Interferences

Spectral interferences with analyte line intensity determination include elemental peak overlap, escape peak, and sum peak interferences. These interferences are automatically corrected within the method program. No action is required by the XRF operator once these interferences have been addressed within the method.

4.2 Background Correction

The laboratory background correction is determined using 10 blank, unused Teflon filters. These filters are analyzed on the XRF instrument for the 33 elements. Only those elements for which the average laboratory blanks values is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for each of the select elements with a background above three times the uncertainty, and this median value is subtracted from the measured value for each of these elements to make the corrections. The correction values are entered into the software for automatic correction of field sample data.

4.3 Particle Size Effects

The X-ray production efficiency is affected by particle size for the lightest elements, such as aluminum; however, PM particle size effects are substantially less than 1 percent for most elements. Because the true particle size distribution cannot be determined for any given filter without microscopic analysis of that filter, no correction for particle size is performed.

4.4 Attenuation Correction

X-ray attenuation occurs when incoming (excitation) x-ray photons are absorbed by the sample before causing the desired fluorescence and when outgoing (fluorescent) photons are absorbed by the sample before escaping the sample. The net effect is that the instrument detects less signal from an element than would be expected if there is no attenuation correction; smaller values indicate a greater attenuation effect. RTI Attenuation correction software accounts for the excitation energies used in the RTI ThermoNoran QuanX XRF instruments. The software, which is a modification of a routine used by EPA, determines attenuations and their uncertainties for both thin, homogeneous deposits principally from aerosol condensation and also from deposits that contain particles with diameters in the high end of the PM_{2.5} size range. The software is applied to RTI's XRF data post measurement to correct for the attenuation before that data is posted in the AQS.

5.0 Instruments

Three ThermoNoran QuanX XRF analyzers (i.e., bench top, laboratory grade, EDXRF spectrometers) are used for this procedure. Each instrument uses a high flux rhodium anode X-ray tube, which is positioned to direct excitation X-rays through one of five preselected filters onto the sample. Standard equipment for each instrument includes an electronically cooled lithium-drifted silicon (Si[Li]) solid-state X-ray detector, a 10-position sample filter wheel, and pulse-processing electronics that communicate spectral data to a PC, which displays and processes spectral information and outputs elemental concentration data. Each analyzer contains the following major components:

- ThermoNoran QuanX cabinet that contains the detector, X-ray tube, and sample changer and electronics for system control and signal processing.

- PC with the ThermoNoran WinTrace software.
- Vacuum pump.
- Printer for analysis reports.
- Uninterruptible power supply, which supplies the instrument, PC, and the vacuum pump with 6 hours of uninterruptible power.

6.0 Instrument Calibration

6.1 Standards

Standards used for calibration consist of single or two non-interfering elements deposited as thin film standards from Micromatter, Inc; the standards are prepared by vacuum deposition resulting in highly uniform deposits. The 31 Micromatter standards used for calibration at RTI are listed in Table 2.

Table 2. Micromatter Calibration Standards

Analyte	Analyte	Analyte	Analyte
Sodium or chlorine as NaCl	Titanium as Ti metal	Zinc as ZnTe	Indium as In metal
Magnesium as Mg metal	Vanadium as V metal	Arsenic as GaAs	Tin as Sn metal
Aluminum as Al metal	Chromium as Cr metal	Selenium as Se metal	Antimony as Sb metal
Silicon as SiO	Manganese as Mn metal	Bromine or cesium as CsBr	Cesium as CsF ₂
Phosphorus or gallium as GaP	Iron as Fe metal	Rubidium as RbI	Barium as Ba F ₂
Sulfur as CuSx	Cobalt as Co metal	Strontium as Sr F ₂	Cerium as CeF ₃
Potassium as KI	Nickel as Ni metal	Silver or mercury as Ag-Hg Amalgam	Lead as Pb metal
Calcium as Ca F ₂	Copper as Cu metal	Cadmium or selenium as CdSe	

6.2 Method Setup

The standardization procedure consists of following steps:

- Set up reference peak spectra: Acquisition of reference spectra is required when performing calibration. As long as no processing methods have changed, these peak shape references remain valid. The procedure of acquiring reference spectra consists of analyzing thin film standards or pure element material (as listed in Table 2) and acquiring individual elemental spectra that are stored in the Method File with each of the analytical conditions. The reference spectra must be interference free, and the peak count for the

reference spectra must be greater than 30,000 counts. These reference spectra are used in the standard deconvolution and mathematical separation of overlapping peaks of the unknown spectra.

- Select acquisition conditions and analysis technique: Five different excitation conditions are performed during the analysis, as shown in Table 3. The specific excitation conditions have been optimized for specific groups of elements listed in Table 1. The different excitation conditions are used to maximize the sensitivity of the measurement of the different groups of elements, which fluoresce over a wide range of energies. When creating the excitation conditions, there are two operational parameters that are typically used and need to be considered (as shown in Table 4). These are determination of live time and atmospheric conditions, which will depend on the elements of concern and the detection limits that need to be achieved. Typically, for the lighter the elements, the live time is set to 300, and the atmospheric condition is set to vacuum.

Table 3. Excitation Conditions

Condition	Filter	Atmospheric Conditions	Voltage (kV)	Current (mA)	Analytes*	
1	Low Za	None	Vacuum	4	1.98	Na and Mg
2	Low Zb	Graphite	Vacuum	10	1.98	Al, Si, P, S Cl, K, and Ca
3	Mid Za	Pd thin	Vacuum	30	1.66	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cs, Ba, and Ce
4	Mid Zc	Pd thick	Vacuum	50	1.00	As, Se, Br, Rb, Sr, and Pb
5	High Za	Cu thin	Vacuum	50	1.00	Zr, Ag, Cd, In, Sn, and Sb

Cs, Ba, Ce, Pb, are quantified from L-lines; all other elements are quantified from the K-lines.

Table 4. Operational Parameters

Parameter	Description
Live time	This is pre-set in the Method File; for the unknown samples, each excitation condition is set to between 200 and 300 seconds live time
Atmosphere	This is pre-set in the Method File; for the unknown samples, each excitation condition will operate under vacuum

- Set up standards file: The Micromatter standards listed in Table 2 are manually entered into a Standards Library and imported into the Method File. The information provided in the Standards Library is the standard name, identification number, and certified concentration of the particular standard. The software will not allow the measurement of

the standards until the standard file is imported into the Method File.

- Measurement of standards: After the Standards Library is imported into the Method File, the analyst proceeds with calibration by clicking the calibrate icon. The software will prompt to acquire all spectra for the standards. Verify that the standards are placed in the sample tray correctly, then start the acquisition. The software will acquire all the necessary spectra to perform the calibration. Because the method is quantifying for 33 elements and the sample tray is for 10 samples, the software will prompt for the next tray to be loaded after finishing the first 10 standards.
- Determine background correction: Laboratory background correction is determined using 10 blank, unused Teflon filters. These filters are analyzed for the 33 elements. Only the elements for which the average laboratory blank value is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for the select elements with background levels above three times the uncertainty, and this median value is subtracted from the measured value for each of these elements to make the correction. The correction is manually added into the software under the Coefficients view, for automatic correction of the data.
- Validate calibration: After the standards and reference spectra have been acquired and the background correction has been applied, the round-robin samples (See Section 12 regarding the round-robin program) and the NIST 1832, along with Micromatter standards (as unknowns) are analyzed to verify calibration and check recoveries for each element of concern. A typical adjustment to the calibration is due to the +/- 5% error with the Micromatter standards. If an element's recovery is too high or low when the standard has been analyzed as an unknown, then an adjustment is made within the Coefficients view of the Method File to accurately correct for the error with the standard.
- Run unknowns: After the instrument has successfully performed calibration, quantitative analysis can be performed on real-world samples.

6.3 Calibration Frequency

Calibration is performed only when the quality assurance/quality control (QA/QC) limits are exceeded or if there is a change in the excitation and/or detection conditions, such as a change in the tube, detector, X-ray filters, or signal processor. Calibrations are typically valid for 6 months to 1 year.

7.0 Filter Handling

Teflon filters are received from RTI's Gravimetric Laboratory after being weighed to determine the mass (loading) of the filter. Custody of the Teflon filters is transferred to RTI's XRF Laboratory by signing the appropriate chain-of-custody forms. The filters are placed in cold storage (refrigerator in Building 6) until they are scheduled for analysis. Note that the filters are analyzed at room temperature and under vacuum conditions.

8.0 Filter Preparation and Analysis

8.1 Preparation

Filters scheduled for analysis are removed from cold storage and are allowed to come to room temperature. With a 10-tray autosampler, the QA standard will always be loaded into position 10, and the unknowns will start out with position 1 and will continue to position 9. The analyst will wear powder-free gloves when working with the filters and samples holders. Before any filters are loaded into the sample cups, the cups must be wiped with a Kimwipe to remove any residue left behind from the previous filters. This will eliminate potential cross-contamination. To load a filter into a sample cup, first remove the top of the Petri slide. Next, turn over the Petri slide into the sample cup with the exposed area of the filter now face down in the cup and ready for analysis. The filter will gently fall from the Petri slide into the cup. If a filter is stuck in the Petri slide, cleaned forceps are used to gently grab the filter by the outer ring and to place it face down into the sample cup. Place the sample cup in the next available tray position and write down the filter aliquot number in the instrument's logbook. Recording the tray position and filter aliquot number in the logbook will allow the operator to cross check the information when entering the filter information into the WinTrace software for analysis. No other preparation of the samples is required.

8.2 Analysis

After the filters are loaded into the sample cups and loaded into the sample tray, a Method Tray List is created in Acquisition Manager within the WinTrace software. The Method Tray List will allow for automated quantitative analysis in conjunction with a Method File. The Method Tray List is created by entering the first sample identification and choosing the Method File from the directory. After the Method File is opened by Acquisition Manager and the sample position is verified in the tray as being correct, then proceed to enter the next sample on the next line. The program automatically fills in the Method File specified for the previous sample.

After the Method Tray List is set up, click the spectrum icon on the toolbar to start the acquisition. The chamber lid will latch and the "X-RAYS ON" warning light will illuminate and the vacuum pump will click on. After a 300-second warm up, acquisition will begin starting with the lowest power condition.

9.0 Data Acquisition and Calculations

After all the spectra have all been acquired (they are saved in the respective Method File), Method Explorer will process the spectrums and display the analytical results in a specific format. The instrumental analysis report details the analyte, concentration, uncertainty, peak counts per second (cps), and background cps.

To obtain the analytical results of the unknowns, go into Method Explorer and open the respective Method File. Under sample lists, identify the samples needed, and then click on the analysis report item to obtain the results in an rtf format. Save the report onto the hard drive. The

results file must be converted from the rtf format to a csv format to be able to upload to the RTI XRF database. ThermoNoran provided RTI with an external program to complete the conversion. After the data has been converted, it is an acceptable format to upload into the RTI XRF database for report generation, uncertainty determinations, attenuation correction through EPA provided software, and perform QC analysis. During report generation, the unit concentration $\mu\text{g}/\text{cm}^2$ is multiplied by the sample area, 11.3 cm^2 , to obtain the value for $\mu\text{g}/\text{filter}$.

The WinTrace XRF software does not calculate uncertainty values when the peak and concentration result is zero (i.e., peak area \leq background area). To obtain the uncertainty values for when the result is zero, a calculation is performed during the import into the RTI XRF database. The calculation is

$$\text{Uncertainty} = \text{Slope} * A * \text{sqrt}(3 * \text{sqrt}(B * t) + B * t)/t$$

Where:

Slope is the response slope calculated in the method

B = Background count rate (cps)

A = Scaling factor for converting to $\mu\text{g}/\text{cm}^2$

t = Live time

10.0 Quality Control

Several different QC activities are performed as part of the analysis procedure. These activities, their frequency, the measures of acceptable performance, and action if the item fails performance standards are provided in Table 5.

Table 5. Quality Control Procedures

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 the instrument's run logbook
Calibration verification	Monthly	Percentage of recovery of seven elements on thin-film National Institutes of Standards and Technology reference materials	Adjust instrument calibration factors	Document in the instrument's run logbook; results stored in the XRF database
	Monthly	90% to 110% recovery analyzing the PM2.5 calibration standards as unknowns		Results stored in instrument's method file
Ongoing calibration verification	Run with every tray of samples	90% to 110% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10 μ g/cm ²	Re-check instrument calibration and adjust if necessary; re-analyze samples	Document in the instrument's run log book
Background Determination	Monthly	Analysis of 10 blank, unused Teflon filters. All elements below three times the uncertainty	Adjust instrument background values	Documented in instruments run logbook

11.0 Data Review and Validation

The analytical dataset undergoes Level 0 and Level 1 validations. These levels of validation will ensure that the dataset being reported will be of good quality.

11.1 Level 0 Validation

A Level 0 validation begins with the analyst, who identifies any problems related to the chain-of-custody, the filter, or any mechanical or software problems that might have occurred during the analysis of the filters. If such items are identified, the analyst notes any problems in the instrument logbook, which is reviewed by the Technical Area Supervisor.

11.2 Level 1 Validation

A Level 1 validation is a more technical review of the analytical data. This review starts with the analyst, but it will primarily be performed by the Technical Area Supervisor. Using the review criteria developed by the QA Manager, the responsibilities of the analyst and the Technical Area Supervisor are provided in Table 6.

If any discrepancies are noted by the analyst or the Technical Area Supervisor, they will be reported on their respective checklist (Figure 1 and Figure 2).

Table 6. Level 1 Validation Responsibilities

Analyst	Technical Area Supervisor
Verify proper custody documentation is provided in batch folder	Ensure analytical dataset is complete and the proper procedures were followed to analyze the filters
Check sample identifications against COC forms and proper number of samples match given COC	Check that proper paperwork is provided in the batch folder and for any notations regarding the analysis of the batch or flaws with the filters that were analyzed
Confirm mass values for each sample are present on final report	Review precision, accuracy, and replicate data for acceptable limits
Make sure sample identifications are consistent between final report versus pre-attenuation report	Check data for any inconsistencies or trends and report to QA Manager
Review pre and post attenuation reports for disparity with attenuated data	Apply flags to data , if applicable

After two levels of review have been performed on the analytical dataset, it is ready to be submitted for upload into the CSN database.

Batch Creation Date: _____

Batch ID Number: _____

Number of Samples: _____

(circle one, if no leave comment why)

Item #1: Custody Documentation

Chain-of-Custody form present

Yes No

Signed By: _____

Dated: _____

Sample Identification

No. of samples matches number on COC form

Yes No

ID#s on COC match Id #s on samples

Yes No

Item #2: Attenuation Correction

Sample IDs consistent with pre-attenuation report

Yes No

Mass values present on report

Yes No

Item #3: Data Comparison Pre-attenuation vs Attenuated Data

Results consistent between pre and post attenuation

Yes No

Comments Regarding Data: _____

Reviewer Signature: _____

Date Signed: _____

Figure 1. EDXRF Analysis Analyst Checklist.

COC Form No. _____ Report Date: _____

Data Review:

Sample Filter No. _____ Comments: _____

Quality Control Review:

Precision Data Acceptable? Yes _____ No _____ Notes: _____

Accuracy Data Acceptable? Yes _____ No _____ Notes: _____

Replicate Data Acceptable? Yes _____ No _____ Notes: _____

Chain-of-Custody Data Cover Letter Yes _____ No _____ Notes: _____

Filter-Loading Masses: Yes _____ No _____ Notes: _____

Reviewed by: _____ Date _____

Figure 2. EDXRF Analysis Technical Area Supervisor Checklist.

12.0 XRF Round-Robin Comparison Program

The XRF Round-Robin Filter Exchange Program is intended to provide an ongoing comparison of analysis results generated by the two laboratories that analyze XRF samples for the Chemical Speciation Network (CSN) Program. Exposed (real-world) filters obtained from the CSN archive are used to provide the most realistic samples possible. According to the contract with EPA, filters and aliquots must be kept for 5 years in case the state monitoring agencies want to re-analyze them or have them returned to the respective agency.

12.1 Selection of Filters

To find filters that are likely to yield the most useful data, the database is periodically searched for filter samples that have the following characteristics:

- Represents a range of different elements at levels above the analytical uncertainties (queries have been designed to select filter sets that maximize the number of different measurable elements)
- Represents a range of different concentrations, from low to high (but above the uncertainty levels)
- No data validity flags or codes
- In good condition by visual inspection.

12.2 Distribution of Filters, Data Tracking, and Reporting

The selected filters in their Petri slides are in the CSN archive based on their box numbers, which can be obtained from the CSN database. Filters are already in Petri slides and are marked by their original aliquot numbers (assigned when the filter was received from the field). Filters are visually inspected before further processing, and any defective filters are not used as round robins. Filters are assigned a new aliquot number and are transferred into new Petri slides labeled with new barcode stickers. This is conducted to make the sample partially blind to the laboratories when they are re-analyzed; however, filters are identified as round-robin samples so that laboratories operating two or more XRF instruments for the CSN Program can analyze them on all of their instruments before sending them back to RTI.

The aliquot number is linked in the database to measurement request ID number R28598T. Using a special measurement request ID allows data to be easily retrieved after the round-robin filters have been analyzed.

The filters are incorporated into normal shipments to the participating XRF laboratories, including RTI. On average, at least two round-robin filters per month are analyzed by each laboratory. Laboratories with multiple XRF instruments analyze the round-robin filters on each instrument

Each round-robin filter should be analyzed at least once by every participating laboratory (and instrument). Analysis of the same filter multiple times by the same laboratory is not considered

to be a problem; however, filters are rotated out of use after approximately 6 months of use and are replaced by new round-robin filters selected as described in Section 12.1 above.

Data are reported back from the participating XRF laboratories, including RTI, along with all the regular data. The round-robin data are uploaded into the CSN database, along with all the regular data. Round-robin results are ignored by the data-processing routines used for validating and reporting routine and blank filter data. The round-robin data are accessible in the CSN database using the unique measurement request number assigned to the Round-Robin Program.

Database queries have been developed that extract the round-robin XRF data, as well as the original values reported for the filter, and report them in a tabular format suitable for importing into Microsoft Excel or another data management and analysis tool.

12.3 Interpretation of Results and Corrective Actions

The most effective means of interpreting the results has been found to be plots of individual round-robin results versus the median of results for all reporting laboratories and instruments. The original result is usually included in the dataset from which the median is determined.

Systematic problems are defined as particular element/laboratory/instrument combinations that are consistently above the median by a significant amount. This amount is assessed relative to the uncertainty values that are reported along with the concentration data. Identification of problems is similar to the technique used with control charts: a potential problem would be indicated under the following conditions, where “1-sigma” is the uncertainty value for the element reported by the laboratory:

- One sample beyond 3-sigma.
- Two samples beyond 2-sigma (both in the same direction).
- Five samples beyond 1-sigma (all in the same direction).

Whenever an element or a set of elements appears to be systematically high or low relative to the median results as previously described, the laboratory with the bias (same procedures for all participating XRF laboratories, including RTI) is contacted and is asked to recalibrate the instrument and/or to review its QC data for the time period during which the questioned round-robin samples were analyzed. If the laboratory identifies a problem that requires recalibration, it will recalculate all data for the affected elements during the questioned time period and will resubmit the data to RTI, where it will be uploaded into the CSN database, replacing the previous data.

Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer

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1.0 Scope and Application

This method covers the determination of organic carbon (OC), elemental carbon (EC), carbonate carbon (CC), and total carbon (TC) in particulate matter collected on quartz-fiber filters. This method can also be used to estimate the quantities of OC evolved from the filter during each of four non-oxidizing heat ramps (Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC) and the quantity of OC that was pyrolyzed (Pyrol C) during those heat ramps.

2.0 Summary of Method

This is a thermal/optical-transmittance (TOT) method that speciates carbon in particulate matter collected on a quartz-fiber filter into OC, EC, and CC. In the first (or non-oxidizing) heating stage, organic and carbonate carbon are thermally desorbed from the filter under a flow of helium with controlled temperature ramps. The oven is then partially cooled, and the original flow of helium is switched to an oxidizing carrier gas (He/O₂). In the second (or oxidizing) heating stage, the original elemental carbon component plus pyrolyzed organic carbon formed during the first heating stage are oxidized/desorbed from the filter with another series of controlled temperature ramps. All carbon evolved from the sample is converted to CO₂ in an oxidizing oven immediately downstream from the desorption oven, and the CO₂ is converted to methane (CH₄) by a methanator oven before being measured with a flame ionization detector (FID).

NOTE: The FID response for organic carbon can be divided into five separate measurements. These measurements correspond to the carbon evolved during each of the four separate heating ramps in the first (or non-oxidizing) heating stage of the analysis (Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC) and to the carbon evolved during the second (or oxidizing) heating stage that is counted as organic carbon to correct for pyrolytically-produced elemental carbon (Pyrol C, see Section 3.1).

3.0 Interferences

3.1 Pyrolytically-Produced Elemental Carbon (Pyrol C)

Laser transmittance is used to optically correct for pyrolytically-produced elemental carbon (or char or Pyrol C) formed from organic compounds during the first (non-oxidizing) part of the analysis. Formation of Pyrol C decreases the transmittance of the laser beam through the system. During the second (oxidizing) part of the analysis, all EC (including Pyrol C) is burned off the filter. The split between OC and EC is assigned by the calculation software as the time during the analysis when the transmittance of the laser beam rises back to its initial value at the beginning of the analysis. Total FID response to the left of the split is assigned to OC, and total FID response to the right of the split (but before the internal standard peak) is assigned to EC. Pyrol C is defined as carbon evolved between the addition of oxygen and the OC-EC split. If the OC-EC split occurs before the addition of oxygen, Pyrol C is zero and Pk4 OC ends at the split time.

3.2 Carbonate Carbon

Carbonate carbon (from calcium carbonate) is volatilized near the end of the first (or non-oxidizing) heating cycle and is therefore initially included with organic carbon. The FID response for the distinctive carbonate peak can be integrated separately and subtracted from the total area assigned to organic carbon, which allows calculation of separate values for organic and carbonate carbon. Alternatively, a separate filter punch can be exposed to hydrogen chloride vapors (which reacts with carbonate to form gaseous carbon dioxide and remove carbonate carbon from the filter) and organic and elemental carbon can be measured (in the absence of carbonate carbon) in a second analysis. The first method is usually adequate for PM_{2.5} samples and can be accomplished with a single analysis.

NOTE: Carbonate carbon is not generally present in PM_{2.5} at quantities above the absolute uncertainty of the method.

4.0 Apparatus

4.1 Thermal/Optical-Transmittance Carbon Aerosol Analyzer (Sunset Laboratory Inc.)

- 4.1.1 Computer system that meets Sunset Laboratory's specifications for running the analyzer, storing the analysis data, and performing calculations
- 4.1.2 Color printer (for printing thermograms)
- 4.1.3 Sunset Laboratory instrument operation software version 220 (OCECInst220.exe) or higher
- 4.1.4 Sunset Laboratory calculation software version 130 (OCECCalc130.exe) or higher

4.2 Precision Punch (for removal of filter sample portion, nominal 1.5 cm²; punch areas are calculated using inside width and depth measurements--made with a micrometer caliper--of the rectangular punch; measured areas of the punches currently used for each instrument are: Retrofit, 1.48 cm²; Second, 1.49 cm²; and third, 1.49 cm²)

NOTE: Each punch is inspected regularly for any unevenness around the sharp edges, and punches with one or more significant notches in the sharp edges are replaced.

NOTE: The punch is cleaned between samples by rubbing the cutting edges with a piece of clean quartz filter.

4.3 Syringes or Automatic Pipettors, calibrated; capable of accurately pipetting standard solutions

4.4 Forceps, silicone-coated forceps for manipulation of the quartz boat during sample loading; uncoated forceps for manipulation of quartz filter samples and punches.

NOTE: The uncoated forceps are cleaned between samples by rubbing the gripping edges with a piece of clean quartz filter.

4.5 Clean Quartz-Fiber Filters

Quartz fiber filters (Whatman Catalog No. 1851047, Grade QMA, or equivalent) are cleaned by placing a batch (typically 100) of the filters in a large crucible, placing the crucible in a muffle furnace (Lindberg/Blue M No. BF51732PBC Box Furnace, or equivalent), heating the filters at 900 °C for at least 3 hours under a low flow of air, turning the furnace off, and allowing the filters to cool for at least 2 hours in the furnace under a low flow of nitrogen. Either 2% or a minimum of 2, whichever is more, of the filters are randomly selected from the cleaned batch and analyzed as detailed in Section 7.3. If any filter analyzed gives a measured blank value that exceeds 1 $\mu\text{g}/\text{cm}^2$ for total carbon, the filters from that batch will either be rejected or re-cleaned and tested again.

Batches of filters that pass the acceptance-testing criterion ($\leq 1 \mu\text{g}/\text{cm}^2$ 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 $\leq -15^\circ\text{C}$ until the filters are used.

4.6 Volumetric Flasks, Class A

4.7 Analytical Balance, capable of weighing to ± 0.0001 g

Check the Balance Lab Notebook to make sure balance has been certified within the past one year. Check balance with Class 1 weight(s) before using. Record all weights in the appropriate Lab Notebook.

4.8 Class 1 Weights

5.0 Reagents

5.1 Helium, ultra-high purity (UHP)

NOTE: Only copper and NO-OX™ tubing are used as transfer lines for helium. Helium gas is passed through both a non-indicating, high-capacity oxygen trap (Scott Specialty Gases, Catalog Number 53-43L, or equivalent) and an indicating, low-capacity oxygen trap (Scott Specialty Gases, Catalog Number 53-43T, or equivalent) before it reaches the carbon analyzer.

5.2 Hydrogen, ultra-high purity (UHP)

5.3 Oxygen (10%) in helium, premixed, purified

5.4 Methane (5%) in helium, premixed, certified

5.5 Carbon Dioxide (5%) in helium, premixed, certified

NOTE: CO₂ in helium is used to test methanator performance.

5.6 Air, Ultra Zero

5.7 Sucrose, 99.9% reagent grade

5.8 Potassium Hydrogen Phthalate, assay 99.95%-100.05%, Acidimetric Standard, EM Science PX1476-3 or equivalent.

5.9 Calcium Carbonate, 99.95% ACS Reagent Grade or equivalent

5.10 Hydrochloric Acid, 37%, ACS Reagent Grade or equivalent

5.11 Organic-Free Water, generated in-house by passage of tap water through a Millipore reverse-osmosis unit (Milli-RO Plus) with added filtration through a Milli-Q Plus unit.

6.0 Standards Preparation and Analysis

A set of external liquid calibration standards containing sucrose in organic-free water is used to establish the linearity of the FID response and to calibrate the gaseous internal standard (5% methane in helium) that is injected at the end of each analysis. A potassium hydrogen phthalate (KHP) standard is used to verify the carbon concentration of the sucrose standards.

NOTE: During TOT analysis of sucrose, some OC (the only kind of carbon in sucrose) is volatilized and some OC is pyrolyzed during all four of the non-oxidizing heat ramps. As a result, all OC fractions (Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C) show up in the thermogram. KHP, which also contains only OC, does not form significant char (Pyrol C), and it volatilizes from the filter over a fairly narrow temperature range.

6.1 Preparation of Standards

6.1.1 Sucrose Stock Solution--Prepare a sucrose stock solution by weighing 10.000 ± 0.010 g sucrose (verify balance accuracy using NIST-traceable Class 1 10-g check weight before weighing out sucrose) into a 1000-mL volumetric flask and diluting to the mark with organic-free water.

NOTE: 10.000 g of sucrose (C₁₂H₂₂O₁₁, MW 342.31) in 1,000.00 mL of solution has a carbon (C, AW 12.01) concentration of 4.210 µgC/µL.

$$\left(\frac{10.000 \text{ g sucrose}}{1,000 \text{ mL soln}} \right) \left(\frac{(12)(12.01 \text{ g C})}{342.31 \text{ g sucrose}} \right) \left(\frac{1 \text{ mL}}{10^3 \mu\text{L}} \right) \left(\frac{10^6 \mu\text{g}}{1 \text{ g}} \right) = 4.210 \frac{\mu\text{g C}}{\mu\text{L soln}}$$

6.1.2 Calibration Standards--Prepare at least three calibration standards that span the measurement range of the samples. Calibration standards are prepared either (1) by weighing appropriate masses of sucrose into a volumetric flask and diluting to the mark with organic-free water, or (2) by diluting aliquots of the

sucrose stock solution (Section 6.1.1) with organic-free water in a volumetric flask.

NOTE: A typical set of calibration standards includes the sucrose stock solution (nominally 4.2 µgC/µL) and two dilutions of the sucrose stock solution (to 2.1 µgC/µL and to 0.42 µgC/µL). Normally, 10.0 µL of each standard is used in a calibration analysis, but a larger volume of the sucrose stock solution could be used to extend the measurement range.

- 6.1.3 KHP Verification Standard--Prepare a potassium hydrogen phthalate (KHP) standard solution by drying KHP at 110°C for two hours, allowing the dried KHP to equilibrate to room temperature, weighing out 0.5000 ± 0.010 g of KHP (verify balance accuracy using NIST-traceable Class 1 0.5-g check weight before weighing out KHP), dissolving the KHP in reagent grade water with 0.4 mL concentrated HCl, and diluting the solution to volume in a 100-mL volumetric flask

NOTE: 0.5000 g of dry KHP (KHC₈H₄O₄, FW 204.22) in 100.00 mL of solution has a carbon (C, AW 12.01) concentration of 2.352 ugC/uL.

$$\left(\frac{0.5000 \text{ g KHP}}{100.00 \text{ mL soln}}\right)\left(\frac{(8)(12.01 \text{ g C})}{204.23 \text{ g KHP}}\right)\left(\frac{1 \text{ mL}}{10^3 \mu\text{L}}\right)\left(\frac{10^6 \mu\text{g}}{1 \text{ g}}\right) = 2.352 \frac{\mu\text{gC}}{\mu\text{L soln}}$$

- 6.1.4 Store sucrose stock solution, KHP verification standard solution, and sucrose calibration standards in a refrigerator at ≤4°C.
- 6.1.5 Prepare new stock solution, verification standard, and calibration standards at least every 6 months.

6.2 Calibration with External Standards

External standards are used to establish linearity of FID response and to calibrate the 5% methane in helium internal standard loop. Prepare and spike filter punches with external standards for calibration and analyze them according to the following instructions:

- 6.2.1 Punch out a new, clean section of a quartz filter and place the section on the quartz filter boat in the analysis oven.

NOTE: The filter punch section remaining in the oven from the last analysis can be used instead of a new section of filter.

- 6.2.2 Run an "Oven Clean" cycle to completely clean the filter section; then run an "Instrument Blank."
- 6.2.3 Open the quartz door to the oven and pull the quartz filter boat containing the cleaned filter punch to the front of the analyzer oven.
-

- 6.2.4 Use a precision syringe or a calibrated Eppendorf pipettor (or equivalent) to deliver 10.0 μL (or other appropriate volume) of a standard sucrose solution (Section 6.1.2) to the clean filter punch without removing the punch from the filter boat.

NOTE: Deposit the standard at the location on the punch that will be directly in the path of the laser during analysis.

- 6.2.5 Push the filter boat into the oven, close the quartz door of the oven, and allow the filter to dry completely (20-30 minutes) inside the cool oven before clicking the Start Analysis button.
- 6.2.6 Analyze the filter punch as described in Section 7.2.
- 6.2.7 Repeat Sections 6.2.3 through 6.2.6 until all three standards have been analyzed and all of the following criteria have been met:
- The 3-point calibration has an $R^2 \geq 0.998$ (linear least-squares fit forced through the origin of a plot of total FID area counts vs. mass of carbon spiked);
 - Each of the three analyses shows a percent recovery of 93% to 107% of theoretical (μgC measured/ μgC spiked);
 - Each of the three analyses gives an FID response to the internal standard within 90% to 110% of the average FID response to the internal standard for the three calibration analyses; and
 - Each of the three analyses gives a response factor (counts/ μgC) for the calibration standard that is within 90% to 110% of the average response factor for the three calibration analyses.
- 6.2.8 If necessary, change the calibration constant to a value that gives an average percent recovery of 99.95% to 100.05% when the new calibration constant is used to recalculate results from the 3-point calibration analyses.

6.3 Internal Standard

The internal standard is 5% methane in helium, an aliquot of which is injected through a fixed-volume loop near the end of the analysis. The mass of carbon in an aliquot injected from the loop must be determined using the external standards described above. The response factor from the 3-point calibration is used to determine the mass of carbon in the internal standard loop.

7.0 TOT Carbon Analyzer Procedure

7.1 Work Area Preparation

- 7.1.1 In a designated area near the OC/EC instrument, clear an area which can be maintained free of clutter, dust and chemicals. Cover the area with 5-6 layers of clean aluminum foil. Tape the edges down so that the foil is secured.
-

- 7.1.2 At the beginning of each analytical session, get a new, clean section of quartz filter and roll it around the forceps. Use this to scrub an area about 2 inches in diameter on the aluminum foil to be used for cutting filter punches.

7.2 Startup

- 7.2.1 From standby press CONTINUE button (if program has been exited double clicking on the "OCECINST" icon will start the analyzer).

- 7.2.2 Set gas flow rates as follows:

He-1 set to 54 - 58 cc/min

He-2 set to 12 - 15 cc/min

He-3 set to 67 - 70 cc/min

He/O₂ set to 12 - 15 cc/min

Air set to 280 - 300 cc/min

Cal set to 10 - 14 cc/min

Hydrogen - when ready to ignite the flame in the FID, set the Hydrogen flow to 80-100 cc/min. Once the flame has been lit (usually signaled by a small pop), return the flow rate to 40-59 cc/min.

NOTE: Use the recommended gas flow ranges displayed by the vendor-supplied software unless specifically directed by the vendor's technical support staff to use a different range.

NOTE: Check the pressure (PSIG). In the off-line mode it should be in the range of 0.15-1 psi. While analyzing on-line it should increase by about 1-2 psi. This oven pressure will change, depending upon flow rates and resistance of the MnO₂ oxidizer bed and methanator oven.

- 7.2.3 Fill in the Analyst field and the Punch Area field on the OCECInst form.
- 7.2.4 Select the RTIQuartz.par Parameter file and either select the instrument and current date data file or enter the name of it into the Raw Data file text box.

NOTE: The temperature profile (RTIQuartz.par) used for all OC-EC Analyzers at RTI beginning March 15, 2001, is given below.

```
' RTIQuartz.par
' Heating profile used on all RTI instruments beginning 15 March 2001
'
' modified quartz to run with true target temps
' added 28 July 1999 by David Smith
' sample carbon analyzer Parameter file for Sunset Lab;
' analyzes for organic and elemental carbon .
```

```
' by Robert A. Cary.  
' 1995 Feb 15: added calibration O2 mode.  
' mode <comma> time <comma> temperature  
' @ regimen must end 'Offline' mode.  
'  
'  
' purge for 10 sec with blower off.  
'  
  
Helium, 10, 1  
' start ramping the temperature  
Helium, 60, 310  
Helium, 60, 480  
Helium, 60, 615  
Helium, 90, 900  
' let the oven cool before starting elemental  
Helium, 30, 0  
' elemental  
Oxygen, 10, 0  
Oxygen, 35, 600  
Oxygen, 45, 675  
Oxygen, 45, 750  
Oxygen, 45, 825  
Oxygen, 120, 920  
CalibrationOx, 30, 1  
CalibrationOx, 50, 0  
CalibrationHe, 30, 0  
' All done!  
' this last mode persists until we start a new sample.  
' The last entry *must* be "go offline and turn blower on".  
Offline, 1, 0  
' end.
```

7.3 Running a Sample

Quartz filters are stored in a freezer at -15°C or below. An individual batch containing up to 50 filters may be kept in a refrigerator during analysis of that batch.

Allow each petri slide holder containing a quartz filter sample to warm to room temperature just before opening it to take a punch from the filter for analysis. Return the quartz filter to the petri slide holder and the petri slide holder to the refrigerator immediately after starting the analysis.

Punches from filter samples should only be placed in the oven while the computer is in the "Safe to put new sample" mode.

- 7.3.1 Use the precision punch to remove a section from the quartz fiber filter sample for analysis.
- 7.3.2 Open the quartz door to the oven.
- 7.3.3 Partially remove the quartz filter boat from the oven with silicone-coated forceps, and place the sample filter punch on the boat with uncoated forceps.
- 7.3.4 Use the silicone-coated forceps to gently slide the boat into the oven until it is stopped by the tip of the oven thermocouple.
- 7.3.5 Close the quartz oven door making sure that the o-ring seals tightly in the oven ball joint and place a clamp on the ball joint.
- 7.3.6 Check the pressure reading on the monitor screen to make sure no warning flag appears (which would indicate a leak).
- 7.3.7 At the computer, type in (or scan the bar code of) a sample identification name or number in the SAMPLE ID # field. Check the Parameter file, Output Raw Data file, and Instrument Name to make sure they are correct.
- 7.3.8 Enter the sample ID, the initial laser transmittance of the filter punch, and the instrument name or designator in the lab notebook, along with any notes about the appearance of the filter.
- 7.3.9 Press the Start Analysis button.
- 7.3.10 At the end of the analysis, record the final laser transmittance of the filter punch in the lab notebook before opening the oven for the next sample.

7.4 Procedures for Estimating Carbonate Carbon

NOTE: The procedures for estimating carbonate carbon are performed only for clients who specifically request it and who authorize payment for it.

Carbon from calcium carbonate is volatilized near the end of the first (non-oxidizing) heating cycle of the analysis. Instrument FID response for carbonate carbon is included in the response for the organic fraction and must be accounted for either electronically (through integration of the FID response for the carbonate peak) or by performing a second analysis using a filter punch from which carbonate has been chemically removed (by exposure to gaseous hydrogen chloride).

7.4.1 Integration of Calcium Carbonate Peak.

Enter numeric values for the start and end points (which show up as vertical dashed lines on the on-screen thermogram) for manual integration of the calcium carbonate peak. Click the Integrate button to display the recalculated thermogram.

NOTE: Integration of the calcium carbonate peak in this fashion assigns the total peak area between and above the start and end points under the FID trace to carbonate carbon and subtracts this area from the organic carbon total area.

This approach can be used to account for than 60% of the carbonate in a PM10 sample. Fortunately, PM2.5 contains almost no carbonate carbon.

7.4.2 Chemical Removal of Carbonate from Filter Punch.

Expose a second punch from the sample filter to hydrogen chloride vapor in a dessicator, petri dish, or similar chamber containing a small amount of concentrated hydrochloric acid for 1 hr. Remove the filter punch from the chamber and allow acid vapor to volatilize from it for at least 30 minutes before analyzing the punch according to Section 7.3. Disappearance of the calcium carbonate peak confirms the presence of carbonate carbon. Report EC and TC from the first (untreated) analysis; report carbonate carbon (CC) as the difference between the two TC measurements (TC untreated – TC treated); and report OC as (OC untreated – CC).

NOTE: CC actually evolves over several of the OC peaks, and the treatment with HCl vapors can dramatically change the distribution of carbon among the OC Peaks and EC. Some OC peaks become smaller (as expected) and some become larger as a result of the treatment. The HCl apparently reacts with carbon-containing species in the sample and changes the distribution of carbon among the OC Peaks and even EC.

7.5 Shutdown

7.5.1 If intending to return to the analyzer later in the day or at some time over the next several days, click on the STANDBY box. In STANDBY the back oven and methanator oven will be maintained at a lower than normal operating temperature to increase heating coil life. Also the laser will be off and the pressure will be near zero, since there is very little flow.

7.5.2 If not intending to use the instrument for several days choose EXIT from the file menu. This will turn off all power to the ovens, causing them to cool down. Set gas flow rates as follows (or as recommended by the Sunset Laboratory instrument support technician):

H2 set to 4 - 7 cc/min.

Air set to off.

Cal set to off.

He3 set to trickle flow at 6 - 8 cc/min

He2 set to trickle flow at 0 - 4 cc/min

He1 set to trickle flow at 6 - 8 cc/min

He/O2 set to trickle flow at 4 - 6 cc/min

7.5.3 When the program is being shut down for more than a few days all gases should be turned off except for He1 and He3 (about 5-10 cc/min each).

8.0 Calculations

8.1 Blank Correction

In accordance with current EPA guidance, speciated carbon measurements will not be blank-corrected by laboratory personnel.

8.2 Concentrations of Carbon Fractions on the Filter (in $\mu\text{g C}/\text{cm}^2$)

- 8.2.1 The software application used to run the analyzer (OCECInstxxx.exe) automatically stores data acquired during an analysis in comma-delimited ASCII text format for later computation, display, and printing.
- 8.2.2 Results are calculated using a second software application (OCECCalcxxx.exe) provided by Sunset Laboratory. The data for each sample can be printed in graphic form (referred to as a thermogram) with temperature, laser transmittance and absorbance, and FID profiles. Text output on the thermogram includes calculated loadings of OC, EC, and TC, as well as Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C on the filter (each in $\mu\text{g C}/\text{cm}^2$). The uncertainty associated with the OC, EC, and TC measurements are also given on the thermogram. Uncertainty is not estimated by the software for CC, Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC because the limits of integration for these are manually set by the analyst. Uncertainty is also not included with the Pyrol C measurement which has integration boundaries set by the software (time of addition of oxygen to the calculated OC-EC split time). Other text outputs include EC/TC ratio, date, time, calibration constant, punch area, FID1 and FID2 status, calibration area, split time, manual split time, initial absorbance, absorption coefficient of original elemental carbon, instrument name, analyst, laser correction factor, and transit time.
- 8.2.3 The calculation software application (OCECCalcxxx.exe) also creates a tab-delimited output file with additional data columns. In the output file, several header rows are followed by one row of data for each analysis. New rows are added to the bottom of the output file each time the calculation software is run, so the most recent calculations are always at the bottom of the file.

8.3 Masses of Carbon Fractions on the Filter (in $\mu\text{g C}$)

NOTE: Calculations beyond filter concentration are not typically done by the OC/EC Laboratory, which reports filter concentrations of each type of carbon (in $\mu\text{g}/\text{cm}^2$) to RTI's Speciation Program Information Management System (SPIMS). Concentration data for all species are calculated by SPIMS software routines, which divide mass per filter for each analyte (reported by RTI laboratories) by the volume of air sampled (reported by field personnel).

The mass (in μgC) of OC, EC, TC, CC, Pk1 OC, Pk2 OC, Pk3 OC, Pk4 OC, and Pyrol C on the filter are calculated by multiplying the concentration (c) of each type of carbon ($\mu\text{g C}/\text{cm}^2$) by the deposit area (A) of the filter in cm^2 .

$$m = cA$$

NOTE: The filter deposit area is 11.76 cm^2 for a 47-mm quartz fiber filter used for sampling in a filter cassette with a 38.7-mm inside diameter, which defines the deposit area.

$$A = \pi r^2 = (3.14159) \left(\frac{38.7 \text{ mm} \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right)}{2} \right)^2 = 11.76 \text{ cm}^2$$

8.4 Concentrations of Carbon Fractions in Air

Mass (m, in $\mu\text{g C}$) of each type of carbon on a filter can be divided by the volume (V_{air}) of air sampled (in m^3) to calculate concentrations (c_{air}) of each type of carbon in the air sampled.

$$c_{\text{air}} = \frac{m}{V_{\text{air}}}$$

8.5 Measurement Uncertainty

Uncertainties of measurements for OC, EC, and TC are calculated by the data analysis software according to the following equations, each of which contains both an absolute uncertainty and a relative uncertainty.

$$\text{OC unc} = \pm [0.20 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of EC in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{EC unc} = \pm [0.20 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of EC in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{TC unc} = \pm [0.30 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of TC in } \mu\text{gC}/\text{cm}^2)]$$

Uncertainties of measurements for the five OC Peaks have been empirically estimated based on analysis of 127 quartz filter samples from random sites, collected during different seasons, across a two-year period on three different analyzers.

$$\text{Pk1C unc} = \pm [0.20 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of Pk1C in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{Pk2C unc} = \pm [0.20 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of Pk2C in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{Pk3C unc} = \pm [0.30 \mu\text{gC}/\text{cm}^2 + 0.05 * (\text{meas conc of Pk3C in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{Pk4C unc} = \pm [0.30 \mu\text{gC}/\text{cm}^2 + 0.10 * (\text{meas conc of Pk4C in } \mu\text{gC}/\text{cm}^2)]$$

$$\text{PyrolC unc} = \pm [0.20 \mu\text{gC}/\text{cm}^2 + 1.40 * (\text{meas conc of PyrolC in } \mu\text{gC}/\text{cm}^2)]$$

9.0 Quality Assurance and Quality Control

9.1 Instrument Blanks

Run an instrument blank, using a punch from a pre-cleaned quartz fiber filter, at the beginning of each day and after approximately every 30 samples run on the same instrument on the same day. An instrument blank must meet all of the following criteria:

- TC for the blank must be $\leq 0.3 \mu\text{gC}/\text{cm}^2$.
- The FID response to the internal standard injected at the end of the instrument blank analysis is within 90% to 110% of the average FID response to the internal standard for the last (or current) 3-point calibration.

If the instrument blank fails to meet any one of the criteria above, determine if the problem is with the filter or with the instrument, and, if necessary, initiate corrective action to identify and solve any instrument problem before repeating the instrument blank analysis, which must be acceptable before continuing with analysis of other samples.

9.2 Calibrations

Run calibration check samples at the beginning of each day and a full three-point calibration at least once a week. Determine the minimum detection limit (MDL) for total carbon when the analyzer oven or methanator is changed or annually, whichever ever comes first.

9.2.1 Run a complete set of calibration standards (i.e., three different mass loadings) at least once a week. If the least-squares correlation coefficient (r^2) of area counts vs. total mass of carbon, force-fit through the origin (0,0), is not ≥ 0.998 , determine the cause of the non-linearity, 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. In addition, analysis of each of the three standards must meet all of the following criteria:

- The measured mass of total carbon for the calibration standard is within 93% to 107% of the true value.
 - The FID response to the internal standard injected at the end of the calibration standard analysis is within 90% to 110% of the average FID response to the internal standard for all three calibration standards analyses.
 - The response factor (counts/ μgC) for the calibration standard is within 90% to 110% of the average response factor for all three calibration standards analyses.
-

If any one of the sucrose standards analyses fails to meet any of the above criteria, repeat the analysis of that standard or initiate corrective action, if necessary, to solve the problem before analyzing samples.

NOTE: The calibration factor (mass of carbon in the fixed-volume internal standard gas loop) will be updated (1) when the calibration gas standard cylinder is replaced, (2) when measured mass of total carbon for standards differs from the true value by more than 7% on repeat analysis of standards, (3) when the day-to-day measured mass of sucrose standards is consistently higher or consistently lower than the true value by more than 7%, (4) or more frequently at the discretion of the laboratory manager.

9.2.2 Run a sucrose standard calibration check sample after the initial instrument blank each day. The calibration check sample analysis results are valid if all of the following criteria are met:

- The measured mass of total carbon for the calibration check sample within 93% to 107% of the true value.
- The FID response to the internal standard injected at the end of the calibration check sample analysis is within 90% to 110% of the average FID response to the internal standard for the last (or current) 3-point calibration.
- The response factor (counts/ μgC) for the calibration check sample is within 90% to 110% of the average response factor for the last (or current) 3-point calibration.

If the sucrose standard calibration check sample analysis fails to meet any of the above criteria, repeat the analysis of the standard or initiate corrective action, if necessary, to solve the problem before analyzing samples.

9.2.3 Analysis results for a KHP verification standard must meet the same three criteria as results for a daily calibration (Section 9.2.2)

9.2.4 Run at least seven replicates of a low-level standard to determine the MDL for total carbon. The spike-volume of the low-level standard should be 10-20 μL , and the concentration should be such that about 1.5 μg of carbon is delivered to the clean filter punch.

NOTE: A 15.0- μL spike of a 1.05 $\mu\text{g C}/\mu\text{L}$ standard solution onto a nominal 1.50- cm^2 filter punch is a typical example.

The MDL is calculated as three times the standard deviation of at least seven replicate measurements of a quantity of carbon no more than two times the estimated practical quantitation limit (PQL). (The PQL is calculated as ten times the standard deviation of the replicate measurements.) If the MDL is $\geq 0.5 \mu\text{g C}/\text{cm}^2$, investigate the source of the problem and initiate corrective action, if necessary, to correct the problem, then repeat the MDL. An acceptable MDL must be obtained before samples can be analyzed.

9.3 Duplicates

Run a duplicate punch about every tenth filter sample (at least 10% of samples). Agreement between duplicate total carbon measurements depends upon filter loading and the uniformity of the deposit. Acceptance criteria for duplicate measurements at higher filter loadings ($\geq 5 \mu\text{g}/\text{cm}^2$) are based on the relative percent difference (RPD) of the duplicate measurements; and the acceptance criterion for duplicate measurements at low filter loadings ($< 5 \mu\text{g}/\text{cm}^2$) is based on absolute error ($\pm 0.75 \mu\text{g}/\text{cm}^2$), which dominates the uncertainty of the total carbon measurement at low filter loadings. Acceptance criteria for the various concentration ranges are given in the following table.

Total Carbon Concentration Range	Acceptance Criterion
Values greater than $10 \mu\text{g}/\text{cm}^2$	Less than 10% RPD
5 - $10 \mu\text{g}/\text{cm}^2$	Less than 15% RPD
Values less than $5 \mu\text{g}/\text{cm}^2$	Within $0.75 \mu\text{g}/\text{cm}^2$

As stated above, nonuniform filter deposit can cause a difference between duplicate measurements. If the deposit on a filter appears visually to be nonuniform or if a duplicate analysis is run and the duplicate measurements fail the appropriate acceptance criterion in the table above, flag the analysis data for that filter as "Nonuniform Deposit."

9.4 Carbonate Carbon

If carbonate carbon is to be measured and the manual integration method (Section 7.4.1) will be used to estimate its concentration, confirm that the suspected peak appears at the correct location for CaCO_3 in the thermogram. A qualitative CaCO_3 sample must be run (or must have been run since the oven or heating coils in the analyzer were replaced) to determine the exact location at which the calcium carbonate peak shows up in the thermogram whenever carbonate is to be estimated by manual integration. Otherwise, measure carbonate carbon according to Section 7.4.2.

9.5 FID Response to Internal Standard

If the FID response to the internal standard for any sample analysis run on a given day on a given analyzer is outside the range of 95-105% of the average response for all samples run that day on that analyzer, discard the results of that analysis and, if necessary, repeat the analysis with a second punch, if available, from the same filter.

NOTE: An FID response significantly lower than the average occurs when the ball joint at the front of the instrument leaks during the run.

NOTE: See Sections 9.1 and 9.2 for acceptance criteria regarding FID response to the internal standard for instrument blanks and calibration check samples, both of which are run at the beginning of each day.

9.6 Start Integration Times for OC Fractions

Start integration times for Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC are determined from the FID signal in raw data files from analysis of sucrose and KHP standard solutions. Start integration times represent the times at which the FID response reaches a minimum or an inflection point between temperature ramps in the non-oxidizing part of the analysis. The start integration times are checked (1) after repair or replacement of the oven or heating coils in an analyzer or (2) after six months from the previous check or change, whichever comes first.

NOTE: Times at which FID minima occur during analysis of particulate samples can vary between samples by a few seconds because of differences in filter loading and in the composition of material on the filter. Average times at which FID minima occur are very similar for calibration standards and for particulate samples. Start integration times for Pk1 OC, Pk2 OC, Pk3 OC, and Pk4 OC are determined from analysis of sucrose and KHP standards in order to provide comparability between analyzers, which heat at slightly different rates.

NOTE: For small studies, average FID minima times for actual samples can be used for start integration times if all samples to be compared are analyzed on the same analyzer.

9.7 Transit Time

During TOT analysis, the laser signal monitors the transmittance of the filter in real time while FID response to carbon evolved from the filter lags behind because of the time required for gaseous carbon species to travel from the filter to the FID. This lag time is called the transit time. The transit time is used by the calculation software to align FID response properly with laser transmittance for calculation of OC and EC fractions (by integration of FID response) based on the OC/EC split time (which is determined solely from the laser transmittance).

A new transit time must be determined whenever the effective volume of the analysis system between the oven and the FID changes. Such changes include replacement of the oven, replacement of the methanator tube, replacement of the FID, and replacement or modification of any transfer line between the oven and the FID.

9.8 Control Charts

Control charts are used to show instrument performance over time and to compare performance of two or more analyzers.

9.8.1 Plot measured TC for all instrument blanks on all analyzers by date.

9.8.2 Plot linearity (R^2) of 3-point calibrations on all analyzers by date.

- 9.8.3 Plot percent recovery for low, mid-level, and high calibration standards as well as average percent recovery for each 3-point calibration by date. Show $\pm 10\%$ bars for average percent recovery. Prepare separate plots for each analyzer.
- 9.8.4 Plot FID response factors for total carbon for each 3-point calibration by date. Plot response factors measured for each standard (to show range) and the average response factor for all three standards (to show mean). Prepare separate plots for each analyzer.
- 9.8.5 Plot percent recovery for all daily calibration checks on all analyzers by date.
- 9.8.6 Plot relative percent difference of duplicate measurements versus average measured TC for all duplicates. Prepare separate plots for each analyzer.

9.9 Laser Transmittance

Laser reading (displayed in raw data files under the heading "laser") is an important indicator not only of EC loading on the filter punch but also of the condition of the quartz optical flats used for the boat and for the upper and lower windows of the quartz oven.

- 9.9.1 A laser reading $< 1,000$ for a filter punch at the beginning of an analysis indicates a fairly heavy loading of EC in the sample and provides a warning that the OC/EC split point set by the software could be inaccurate because the laser response may "bottom out" during the char-forming, non-oxidizing heating ramp. The absorbance plot on the bottom of the printed thermogram can be used to check the split point.
- 9.9.2 An initial laser reading $\geq 3,000$ for a clean filter punch and a series of final laser readings that drift slightly upward during the last seconds of an analysis (as the oven cools) generally indicate that the quartz optical flats (boat and oven windows) are adequately free of frosting for an accurate assignment of the OC/EC split. If the initial laser reading is $< 3,000$ or if the laser reading drifts slightly downward during the last seconds of an analysis (as the oven cools), the quartz optical flats (boat and oven windows) should be inspected for frosting and the boat or oven or both replaced, if necessary.

NOTE: More recent versions of Sunset Lab's calculation software provides for automatic correction for drifting of the laser during heating and cooling cycles.

9.10 Analyst Training and Validation

Analyst training and validation consists of the following steps:

- The trainee begins by studying and becoming familiar with this SOP.
 - The trainee spends time observing and listening to a trained analyst as he/she demonstrates and describes the procedures required to perform OC/EC analysis.
-

- The trainee learns to perform the procedures under the immediate attention of a trained analyst.
- The trainee spends several days analyzing samples with a trained analyst monitoring the trainee's work, answering any questions the trainee may have, and correcting any mistakes the trainee might make.
- To test the trainee's competence, the trainee, left completely on his/her own, analyzes a minimum of 20 filter samples analyzed earlier by the trained analyst on the same analyzer(s).
- The analysis results for the 20+ filter samples run by both the trained analyst and the trainee are compared using the same criteria used for duplicate analyses (Section 9.3).
- If no more than about 5% of the trainee's analyses fail the duplicate criteria test, the analyst is considered validated to perform the analysis without immediate supervision; otherwise, the trainee must repeat the test after carefully reviewing the procedures he/she used to determine what (if anything other than non-uniform samples) could have caused the high percentage of failures.

NOTE: About 3% to 5% of filters fail the duplicate criteria because of non-uniform deposit. An initial failure by a trainee could be caused by an unusually high percentage of non-uniform filters in the group of test filters, but the test must be repeated and passed successfully to make sure the analyst's technique is not the problem.

NOTE: Analysts who smoke must not be around exposed filter samples or blanks until their clothes and lungs are clear of residual smoke fumes (typically, 15-20 min after they finish a smoking break).

9.11 Instrument Validation

Instruments are validated using the same type of test as that used for analysts (Section 9.10).

- The same experienced analyst operates both the new analyzer and a previously validated analyzer.
 - Instrument blanks and calibration standards are run on the new instrument and the previously validated instrument until all criteria for those QC samples are met on both analyzers.
 - Duplicate punches of at least 10 filter samples are run on the new analyzer at the same time the initial punches from the same filters are run on a validated analyzer.
 - The new analyzer is considered validated if measurement results from no more than 1 or 5%, whichever is more, of the filters used in the test fail the appropriate duplicate criterion (Section 9.3).
-

- If the new analyzer fails the test, it is inspected to identify and correct any problems with the analytical system before the test is repeated.
- The new analyzer must pass the validation test before it can be used to perform analyses that will be reported to clients.

NOTE: About 3% to 5% of filters fail the duplicate criteria because of non-uniform deposit. An initial failure by an analyzer could be caused by an unusually high percentage of non-uniform filters in the test group, but the test is repeated to make sure the analyzer is not the problem.

10.0 References

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DRI STANDARD OPERATING PROCEDURE

**DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT)
of Aerosol Filter Samples – Method IMPROVE_A**

**DRI SOP #2-216r2
Revised July 2008**

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1 INTRODUCTION

1.1 Purpose of Procedure

This standard operating procedure is intended to:

- Provide a basic understanding of the principles of carbon analysis and carbon analyzer operation;
- Describe routine determination of organic, elemental, and carbonate carbon from ambient- and source-filter samples using the DRI Model 2001 Thermal/Optical Carbon Analyzer; and
- Detail the concerns and procedures which will ensure a state-of-the-art carbon analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility (EAF) of the Division of Atmospheric Sciences (DAS) at the Desert Research Institute (DRI), Reno, Nevada, USA.

1.2 Measurement Principle

The operation of the DRI Model 2001 Thermal/Optical Carbon Analyzer is based on the preferential oxidation of organic and elemental carbon (OC and EC) compounds at different temperatures. Its function relies on the fact that organic compounds can be volatilized from the sample deposit in a non-oxidizing helium (He) atmosphere, while EC must be combusted with an oxidizer. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch taken from a quartz-fiber filter; 2) converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂); 3) reducing CO₂ to methane (CH₄) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantifying CH₄ equivalents with a flame ionization detector (FID).

The principal function of the optical (laser reflectance and transmittance) component of the analyzer is to correct for pyrolysis charring of OC compounds into EC. Without this correction, the OC fraction of the sample might be underestimated and the EC fraction might include some pyrolyzed OC. The correction for pyrolysis is made by continuously monitoring the filter reflectance and/or transmittance (via a He-neon laser and a photo-detector) throughout an analysis cycle. The reflectance and transmittance, largely dominated by the presence of light absorbing EC, decrease as pyrolysis takes place and increase as light-absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance and transmittance,

the portion of the EC peak corresponding to pyrolyzed OC can be accurately assigned to the OC fraction. The correction for the charring conversion of OC to EC is essential for a less-biased measurement of carbon fractions (Johnson et al., 1981). The Thermal Optical Reflectance (TOR) and Thermal Optical Transmittance (TOT) charring corrections are not necessarily the same, owing to charring of organic vapors adsorbed within the quartz fiber filter (Chow et al., 2004; Chen et al., 2004). Charring by both reflectance and transmittance is reported in order to determine the differences in OC and EC.

Carbonate carbon can be determined by measuring the CO₂ evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions, as well as the TOR and TOT charring correction, are individually quantified and reported when the IMPROVE_A (Chow et al., 1993, 2001, 2007) temperature protocol is applied. Values routinely reported include total OC, total EC, total carbon (TC, sum of total OC and total EC), and pyrolyzed carbon, monitored by both reflectance (OPR) and transmittance (OPT). Depending on the thermal/optical protocol applied for quantification, thermally-derived subfractions of OC and EC, and of carbonate carbon, are reported.

1.3 Measurement Interferences and Their Minimization

Precision of thermal/optical carbon analysis depends on the sample temperature in the analysis. Therefore, the correlation between sample temperature and thermocouple temperature should be established and calibrated semiannually so that the thermal protocol can truly reflect the sample temperature during the analysis (Chow et al., 2005). The thermocouple's position in relation to the sample, as well as the different heating properties of the thermocouple and the sample, govern the temperature offset. This relationship must be maintained for the temperature calibration to hold. The analyzer must not be used if the sample boat shifts position or becomes loose in its holder.

Carbonate carbon may bias carbon concentrations if it constitutes more than 5% of TC in the ambient or source sample. Carbonate carbon may be measured as either OC or EC depending on the chemical nature of the carbonates and their thermal decomposition temperatures. Acid pretreatment of filter samples can eliminate the carbonate interference (Novakov, 1981, 1982; Rosen et al., 1982). Carbonate carbon has been found at only a few IMPROVE monitoring sites, and the levels at these sites do not appreciably bias OC and EC concentrations (Chow and Watson, 2002).

The presence of certain minerals in some soils can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a darker sample. For samples which contain large fractions of resuspended soils, the split between OC and EC should be examined manually.

Some minerals, again predominantly in soil samples or soil-dominated samples, may affect the laser correction by temporarily changing color or changing the surface texture of the deposit residue. Unlike the effect described above, these changes are reversible and temperature-dependent.

Some colored organic compounds can affect the laser correction, causing increased reflectance or decreased transmittance as these compounds are removed. This effect is ascertained by examining the laser response during the organic portion of the analysis. The split between OC and EC should be examined manually if the effect is large.

The presence of certain elements (Na, K, V, Cr, Mn, Co, Ni, Cu, and Pb), existing either as contaminants on the filters (e.g., glass-fiber filters or borosilicate binders), or as part of the deposit material, has been shown to catalyze the removal of EC at lower temperatures (Lin and Friedlander, 1988). Such catalysis would affect the distribution of carbon peaks during the analysis.

Water vapor (either contained in the deposit or remaining after acidification of the sample punch), if present in sufficient levels, can shift the FID baseline. To eliminate this effect, allow the sample punch to dry in the analyzer by passing carrier gases over it before starting the analysis.

1.4 Ranges and Typical Values of Measurements

Source-dominated or heavily polluted environments, which would normally have carbon concentrations above the working range of the carbon analyzer, may be sampled and analyzed within the range of the carbon analyzer by increasing the filter deposit area or by decreasing the sampling flow in the field equipment. Deposits that are very black, such that the initial reflectance is close to zero, provide a less precise OC/EC split, because additional blackening due to OC charring is not quantified by the reflected light.

The carbon analyzer can effectively measure between 0.05 and 750 $\mu\text{g carbon/cm}^2$ for a typical punch size of 0.5 cm^2 . The upper limit depends on the particular compounds on the filter and the temperatures at which they evolve. This upper limit may be extended by reducing the punch size or extending analysis times at lower temperature plateaus to avoid an over-range FID signal.

Typical carbon values range between 10 and 100 $\mu\text{g C/cm}^2$ for 24-hour ambient samples. The distribution between OC and EC depends on the particulate source types, ranging from negligible levels of EC (e.g., secondary sulfate) to 80% or more EC (e.g., diesel exhaust).

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of thermal carbon methods depend on the variable carbon content of the field blank quartz-fiber filters, as well as the analysis method. For lower LQLs, the unexposed filters should be pre-fired in an oven at high temperatures for several hours to remove any residual carbon contamination (Fung, 1986; Huntzicker, 1986; Rau, 1986; DRI, 2004). All quartz-fiber filters originating from DRI are pre-inspected for defects such as pinholes or tears. They are then pre-fired for a minimum of four hours at 900 °C; 2% are acceptance-tested for blank levels before use in the IMPROVE network. Batches containing filters that fail to pass the preset acceptance levels (1.5 µg OC, 0.5 µg EC, and 2.0 µg TC per cm²) are not used for sample collection. Average pre-fired blank levels are 0.15 ± 0.15 µg OC/cm², 0.00 ± 0.02 µg EC/cm², and 0.15 ± 0.15 µg TC/cm². Because pre-fired filters can adsorb organic vapors during shipping, storage, and exposure in the sampler, the analysis LQL on a particular set of filters depends on the number of field blanks analyzed and the variability in the results from those blanks. LQLs may vary between projects, depending on the sample and sample handling. To reduce the risk of contamination during shipping and storage, samples are vacuum-sealed and stored at < 4 °C. The vacuum sealing results in minimum air space surrounding the filter to ensure the blank levels are kept low.

The minimum detection limits (MDLs) represent the best sensitivity of the method and should always be less than or equal to the LQLs. The IMPROVE_A protocol is based on the analyses of approximately 800 pre-fired laboratory blank quartz-fiber filters analyzed between January 2006 and May 2007. The MDL is defined as three times the standard deviation of their measured results. They are:

total OC	0.39 µg/cm ²
total EC	0.01 µg/cm ²
TC	0.42 µg/cm ²

Acid-evolved carbonate levels in pre-fired quartz-fiber filters have been shown to be quite variable (0.0-1.0 µg/cm²) over time. The reaction of ambient CO₂ with alkaline sites on the quartz fibers may be the cause of such variable blank levels. Acceptance testing for carbonate is only performed for special projects that require carbonate analysis.

The precision of carbon analysis has been reported to range from 2 – 4% (Johnson, 1981). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. This can be demonstrated by the precision of CH₄ standard injection (by the Carle valve), which is always better than sample analysis. For homogeneous deposits containing > 5 µg/cm² (~10 times MDL) TC, precision is generally 10% or better; for inhomogeneous deposits replicates may differ by as much as 30%. The precision of carbonate concentrations is approximately ±10%.

The precision of the laser-dependent split between OC and EC fractions depends upon how rapidly the laser is increasing at the time of the split and whether or not the split falls in the middle of a large carbon peak. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are < 5% of the total measured carbon. If the laser split is greater than 10 seconds and deviations are > 5%, the analysis is investigated for sample anomalies (e.g., inhomogeneous loading, low loading, etc.), instrument laser noise, or O₂ contamination.

The accuracy of TOR for TC, determined by analyzing a known amount of carbon, is between 2-6% (Rau, 1986). Precision of the OC/EC split is between 5% and 10%. This precision is also influenced by the filter loading and source type. Most of the uncertainty for low concentration samples is from the standard deviation of the field blanks or backup filters. Uncertainty is not determined by precision at low levels.

Since the MDL is always less than or equal to the LQL, and the LQL is included in the $\mu\text{g}/\text{m}^3$ uncertainty when the blank (or backup filter, if available) is subtracted, the MDL has no effect on the uncertainty of ambient concentrations. The MDL is most useful to match flow rates and sample duration with expected carbon levels when planning field studies or sampling networks.

1.6 Personnel Responsibilities

Before performing carbon analysis, all analysts in the laboratory should read and understand the entire Standard Operating Procedure (SOP), including routine system calibration, actual analysis, and immediate review of the data as it is produced, and how to correct system problems.

The responsibilities of the laboratory manager or supervisor are: to ensure that the carbon analyses procedures are properly followed; to examine and document all replicate, standard, and blank performance test data; to designate samples for reanalysis; to arrange for maintenance and repair of instruments; to verify an adequate quantity of supplies and gases are in stock to ensure uninterrupted analysis; and to deliver the analysis results in database format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's DAS is responsible for determining the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to periodically review and assess quality assurance and quality control data, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions for IMPROVE_A Thermal Protocol for Carbon Analysis

The following terms are used in this document:

IMPROVE_A Thermal Protocol:	A thermal protocol used in carbon analyzers to quantify carbon fractions evolved at different temperature plateaus and atmospheres. The IMPROVE_A thermal protocol derives from the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal protocol initiated in 1987 (Chow et al., 2005, 2007).
Calibration Injection:	The injection of calibration gases, either CO ₂ or CH ₄ , into the sample stream at the beginning and end of each work day to check instrument performance.
Calibration Peak:	The FID peak resulting from the automatic injection of methane calibration gas (CH ₄ /He) at the end of each analysis run for each sample. All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain µg carbon per sample punch.
FID Split Time:	The time at which the laser split occurs plus the transit time required for thermally evolved carbon to travel from the sample punch to the FID.
Elemental Carbon (EC):	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 580, 740, and 840 °C minus any pyrolyzed OC.
EC1:	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 580 °C.
EC2:	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere from 580 to 740 °C.
EC3:	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere from 740 to 840 °C.
High Temperature OC:	Carbon evolved from the filter punch in a He-only atmosphere at 280, 480, and 580 °C plus pyrolyzed organic carbon. This is OC minus the first OC peak (OC1).
High Temperature EC:	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 740 and 840 °C minus any pyrolyzed organic carbon present in these two peaks. This is EC minus the first EC peak (EC1).

Laser Split:	The separation between OC and EC, which depends on the laser-measured reflectance and/or transmittance of the filter punch returning to its initial value. At this point all pyrolyzed OC has been removed and EC is beginning to evolve.
Lower Split Time:	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).
Organic Carbon (OC):	Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere at 140, 280, 480 and 580 °C plus pyrolyzed organic carbon. This is the same as Volatile Organic Carbon (VOC) plus high-temperature OC.
OC1:	Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from ambient (~25 °C) to 140 °C.
OC2:	Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 140 to 280 °C.
OC3:	Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 280 to 480 °C.
OC4:	Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 480 to 580 °C.
OP:	The carbon evolved from the time that the carrier gas flow is changed from He to 98% He/2% O ₂ at 580 °C to the time that the laser-measured filter reflectance (OPR) or transmittance (OPT) reaches its initial value. A negative sign is assigned if the laser split occurs before the introduction of O ₂ .
Pyrolysis:	The conversion of OC compounds to EC due to thermal decomposition; this may be envisioned as "charring" during the organic portion of the analysis.
Regular Split Time:	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value.
Total Carbon (TC):	All carbon evolved from the filter punch between ambient and 840 °C under He and 98% He /2% O ₂ atmospheres.
Upper Split Time:	The time at which the laser-measured reflectance and/or

transmittance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).

1.8 Related Procedures

Standard Operating Procedures (SOPs), related carbon analysis activities, and other manuals that should be reviewed in conjunction with this document are:

- DRI SOP #6-001 Shipping and Mailing SOPs.
- DRI SOP #6-009 Field and Laboratory Safety SOPs.
- DRI SOP #2-106r6 Pre-Firing of Quartz Filters for Carbon Analysis.

The DRI Model 2001 Thermal/Optical Carbon Analyzer Owner's Manual, revised 3/2004 (Atmoslytic, Calabasas, CA).

The DRI Model 2001 Thermal/Optical Carbon Analyzer Installation, Operation and Troubleshooting Manual, revised 12/2004 (Atmoslytic, Calabasas, CA).

2 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the DRI Model 2001 Thermal/Optical Carbon Analyzer are depicted in Figures 2-1 through 2-3; the complete gas flow schematic is shown in Figure 2-4. Other details of the configuration of the DRI Model 2001 Thermal/Optical Carbon Analyzer are referred to in the owner's manual. The programmable combustion oven is the heart of the carbon analyzer and includes loading, combustion, and oxidation zones in a single quartz "oven" as depicted in Figure 2-5.

In addition to the DRI Model 2001 Thermal/Optical Carbon Analyzer, which is connected to a Pentium compatible computer, the following items are needed for routine carbon analysis:

- Stainless steel punching tool: 5/16-inch diameter, 0.5 cm² nominal area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is resharpened, the punch area must be re-verified. Verification is performed by removing 10 punches from a 47-mm quartz-fiber filter (17.35 cm²); then calculating the punch area [= 17.35 cm² x (initial filter weight minus the final weight after punches have been removed) / 10 times the initial filter weight]. Further verification can be done by taking a precise measurement of the punching tool.
- Syringes: Hamilton Gas-Tight 1000 and 2500 µl syringes for calibration injections; 25 µl syringe for carbonate analysis and for analyzer calibration.
- Quartz filters: Pallflex® Tissuquartz, 2500 QAT-UP (Pall Life Sciences, Ann Arbor, MI) quartz-fiber filter or equivalent.
- Flat-tip tweezers.
- Flat glass plate.
- Logbook/notebook.
- Transparent tape.
- KIMTECH Pure* CL4 Critical Task Wipes and large KimWipes (EX-L).
- Small Styrofoam cooler or refrigerator.

Figure 2-1. DRI Model 2001 Thermal/Optical Carbon Analyzer.

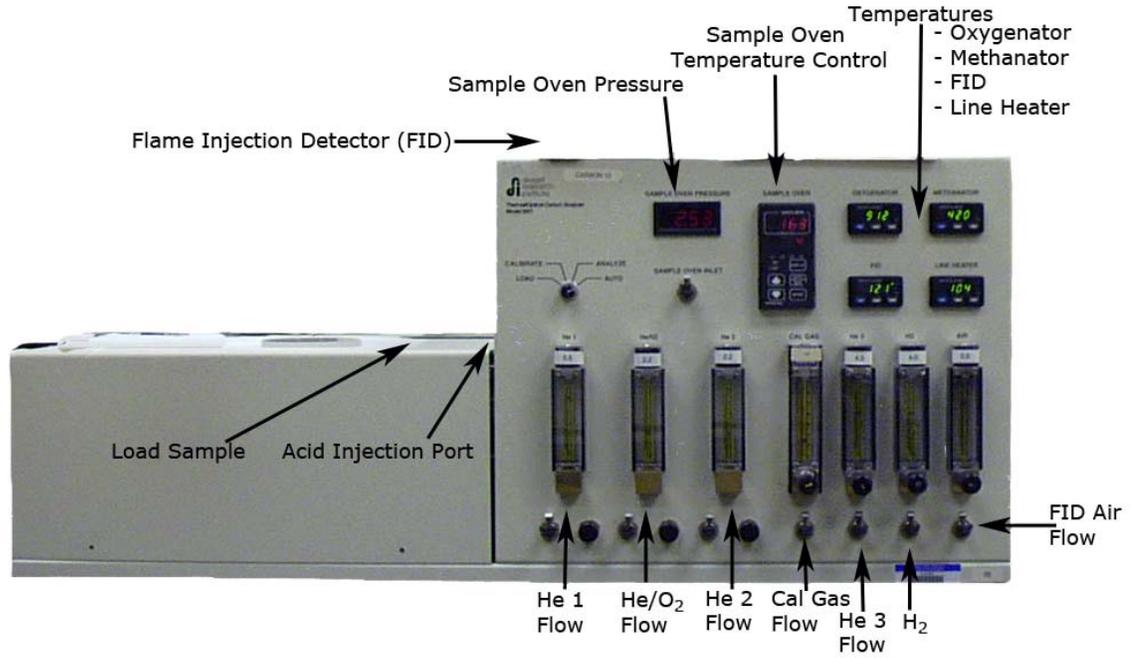


Figure 2-2. DRI Model 2001 Thermal/Optical Carbon Analyzer Schematic Diagram.

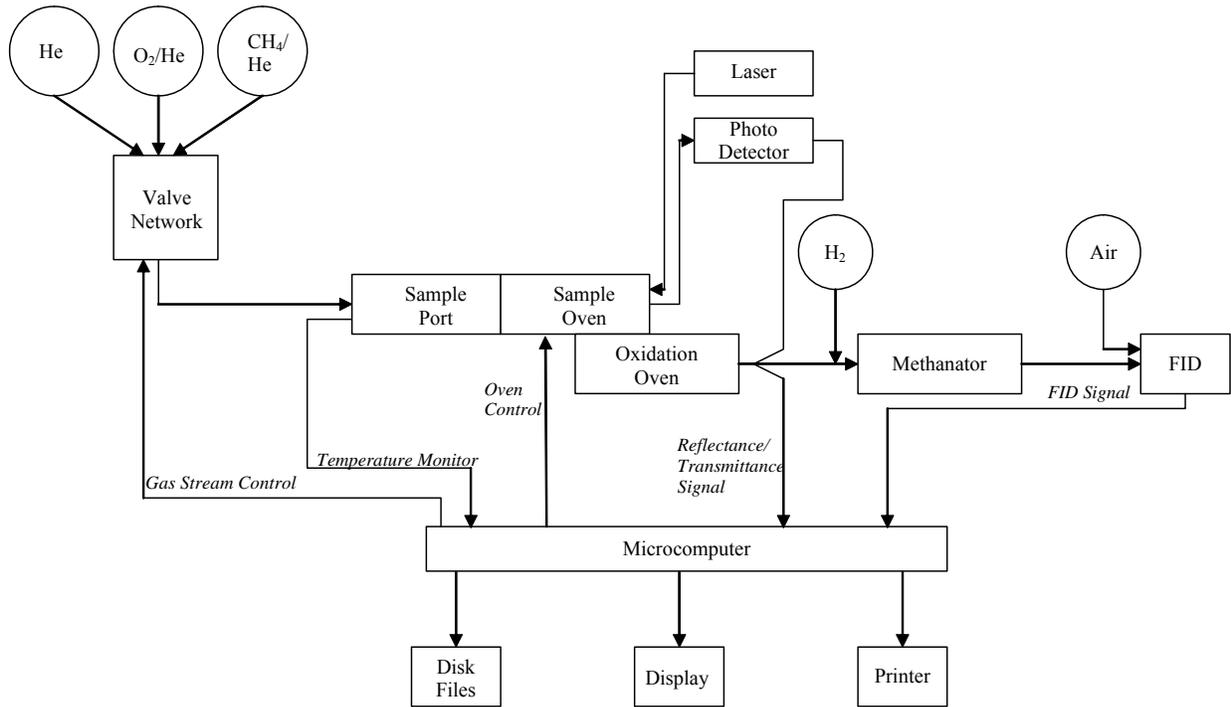
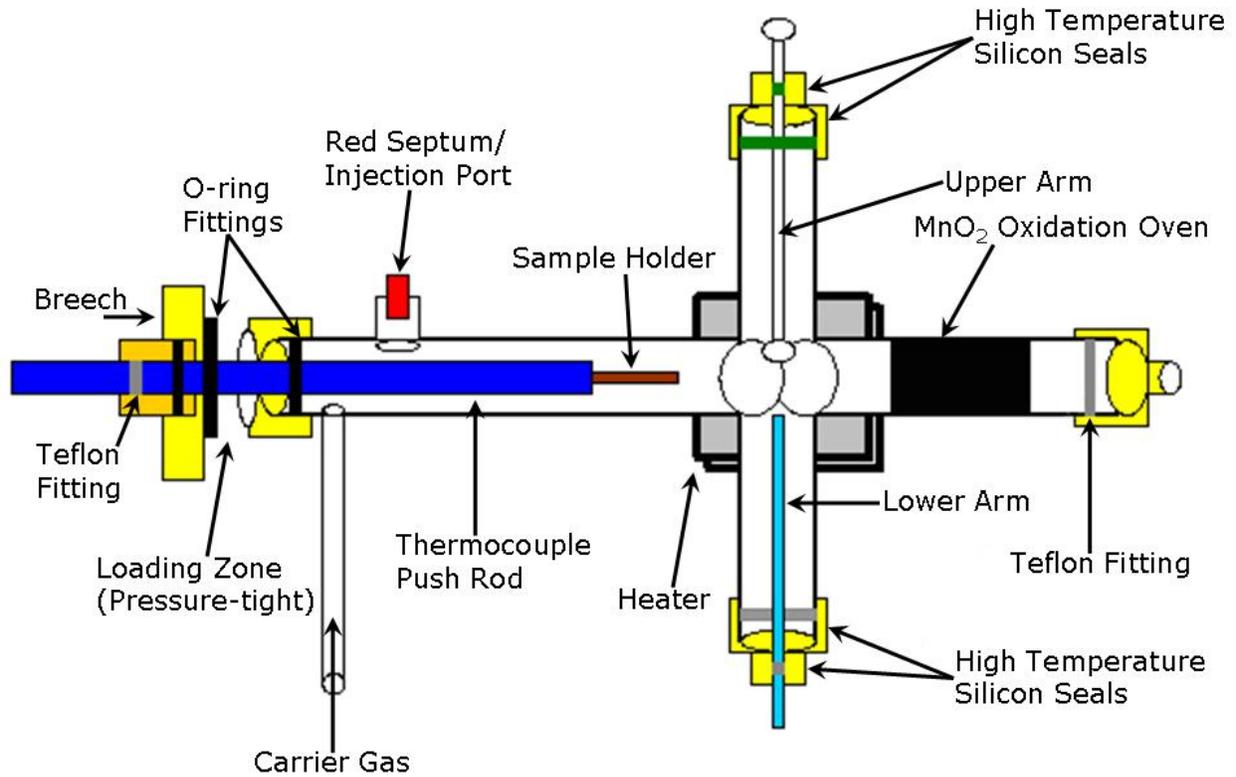


Figure 2-3. DRI Model 2001 Thermal/Optical Carbon Analyzer Sealing Diagram.



Note: In the breech, there is a Teflon-reducing ferrule to seal the pushrod thermocouple, plus two O-rings to seal the breech against the inlet (coupler) connector and one Teflon fitting (See the Model 2001 Owner's Manual for more details).

Figure 2-4. DRI Model 2001 Thermal/Optical Carbon Analyzer Gas Flow Schematic.

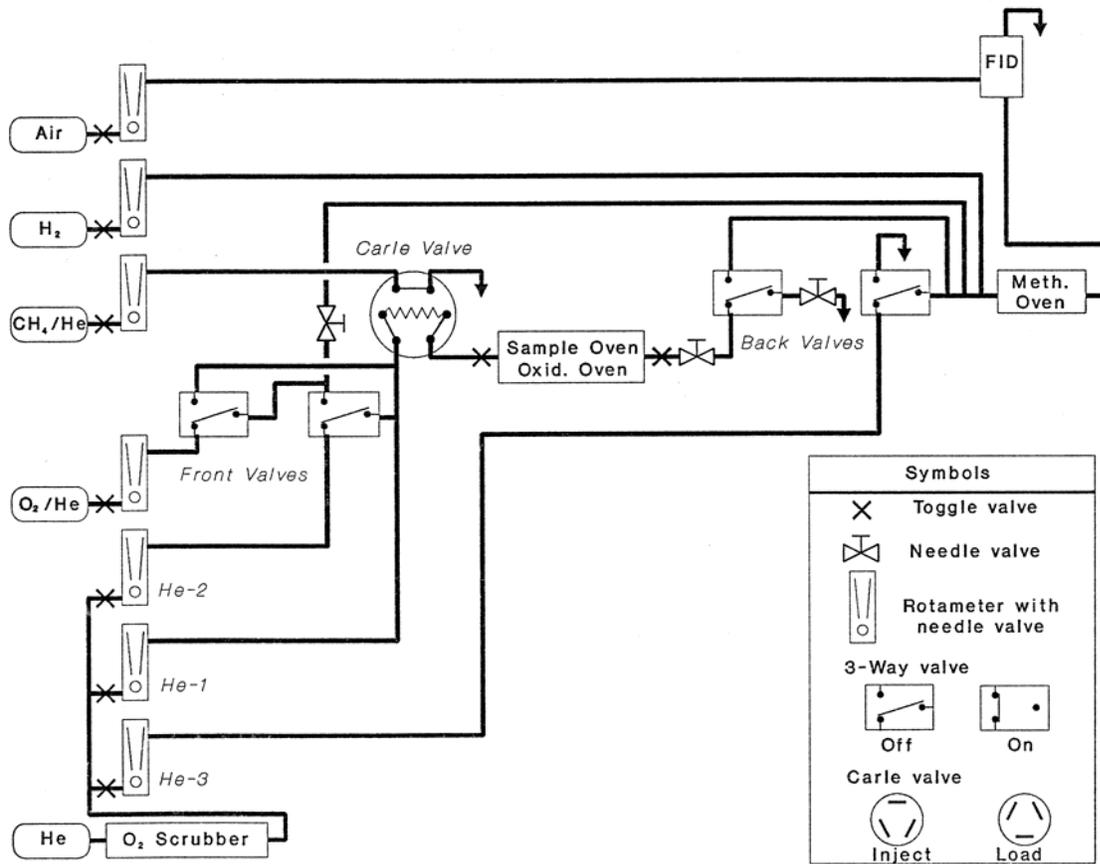
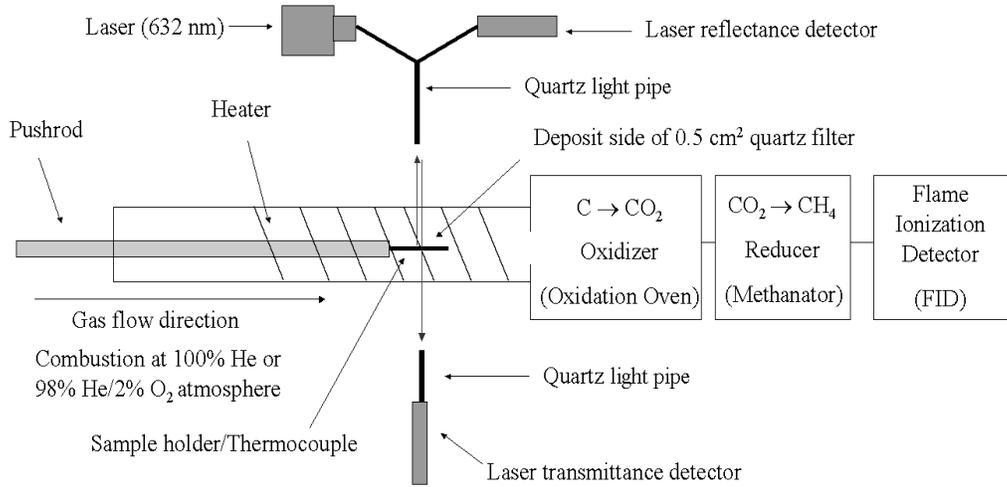


Figure 2-5. DRI Model 2001 Thermal/Optical Carbon Analyzer Combustion Oven.



Title: DRI Model 2001 Thermal/Optical Carbon Analysis
(TOR/TOT) of Aerosol Filter Samples - Method IMPROVE_A

- Blue ice (if using Styrofoam cooler).
- Butane or piezoelectric lighter.
- A copy of *DRICarb.exe* (the analysis program), *Carbon.par* (the analysis parameter file), and Microsoft Access to run *CarbonNetWork.mdb*.

2.1.2 Instrument Characterization

The DRI Model 2001 Thermal/Optical Carbon Analyzer is program-driven. Data is stored automatically to the hard drive via a PC-compatible computer processor board. Response times and signal lag times are built into the parameter file that is loaded when the analysis program begins. The program is driven by the thermal protocol. For example, when using the IMPROVE_A protocol, the program will advance to the next temperature or carrier gas mixture once the FID signal returns to its baseline; i.e., after a minimum of 150 seconds at one analysis condition. A maximum time limit (580 seconds) per analysis condition is also established to prevent a slight baseline drift from holding the analyzer in one condition indefinitely. For the Chemical Speciation Network (CSN, including the Speciation Trends Network [STN]) thermal protocol, the program advances from one specified temperature plateau to the next temperature or carrier gas mixture when the specified analysis time is reached. Both methods require at least one $\sim 0.5 \text{ cm}^2$ punch per filter and do not require sample pre-treatment. The sample punch is destroyed by both methods.

Operator concerns for correct routine operation of the instrument include the following (refer to Section 4 for more details):

- Verify sample oven pressure reading and specified flow range in the front-panel flow meters.
- DO NOT leave the room until the analysis begins.
- Check the graphical printout after each analysis run to ensure that the: 1) FID, 2) temperature, and 3) laser signals are behaving as expected (Section 3.1). Report any anomalies to the lab supervisor immediately.
- The quartz oven is susceptible to breakage. Care should be taken when handling and cleaning.
- Be careful that no fiber from the KIMTECH wipe is left on the sample punch, tweezers, and/or glass plate.

2.1.3 Maintenance

Regular maintenance for the analyzer involves daily checking of compressed gas supplies, cleaning the punching tool and tweezers between each sample with dry KIMTECH wipes, ensuring that the lab is clean, and backing up data files to disc on a daily basis (unless files are automatically backed up to server). Temperature calibrations for the six temperature plateaus (140, 280, 480, 580, 580, 740, and 840°C) need to be performed semiannually (see details in Section 3.2.3). Checks of laser adjustments and leaks are made at least monthly or on an as needed basis. The procedure for leak checks can be found in Section 4.1.2. Additional leak tests are performed with a He leak detector each time a part is replaced, or whenever the analyzer fails the leak check during the daily routine. The system should show no He leaks at the various connections of the quartz cross oven. Since He has high diffusivity, freedom from He leaks will safeguard against O₂ diffusion into the system. These O₂ levels are determined semi-annually using a gas chromatography/mass spectrometry (GC/MS) instrument on the analyzer. Quarterly levels are determined using an O₂ detector that is calibrated against the GC/MS. This is also used when a fresh He cylinder is installed to assure the quality of the gas supply and the condition of the O₂ scrubber. If the *cmdAutoCalibCheck* command is used for calibration, the condition of the catalysts will be indicated and appropriate action can be taken (such as catalyst replacement). All calibrations, repairs, and checks must be recorded in the Carbon Analyzer Logbook (Figure 2-6). Flow rates of all operating gases should be checked and adjusted (if needed) whenever a new quartz oven or methanator is installed or serviced. Additionally, a flow check and balance should be performed as well.

2.2 Spare Parts List

The following spare parts must be kept on hand to ensure minimal interruptions in carbon analysis:

- Quartz furnace tube available from the manufacturer (Atmoslytic, Calabasas, CA).
- Quartz rods: 3 mm nominal diameter, optical quality (Atmoslytic, Calabasas, CA), polished for optical clarity with 104 mm (upper arm) and 119 mm (lower arm) lengths. The version of the carbon analyzer manufactured in 2001 uses a 98 mm rod for the upper arm. Measure the old rods for reference.
- Catalyst ovens: Watlow 15.24 cm length, 2.54 cm tube diameter element from the analyzer supplier.
- Quartz boats (Atmoslytic, Calabasas, CA).
- Quartz wool: For repacking the oxidation oven (Alltech Associates, #4033, Deerfield, IL).

Title: DRI Model 2001 Thermal/Optical Carbon Analysis
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Figure 2-6. DRI Carbon Analysis Logbook Format.

	7/21/08	7/21/08	Cont
			\IMPROVE \D07 \M15 R62133-2 R62145-3
			\IMPROVE \D07 \M15 R62253-3 R62265-3 R62323-2 R62364-2 R62363-2
COW			\IMPROVE \D07 \O15 R62431-2 R62495-3 R62587-3
			C1120080721-1 17794 21400 -2 25051 27755
			\IMPROVE \A08 \Z15 R64746-1 R64745-2 R64753-1 R64756-1 R64759-1
7-22-08 EES			LEAK TEST BAKE OVEN C1120080722-1 28010 28190 27937
			SYSBLK S072208-1
			\IMPROVE \A08 \Z15 R64763-1 R64767-1 R64771-1 R64775-1 R64779-1 R64783-1 R64787-1 R64791-1 R64786-2 R R64796-1 R64794-2

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- Thermocouple rods: 24.13 cm length by 0.32 cm outside diameter (OD), Type-K ground isolated with Inconel sheath (Omega, Part #TJ36-CAIN-18E-9.5, Stamford, CT). Remove 1 cm of the sheath with a file to obtain the longer tip needed in this application.
- FID flame tips: for Gow-Mac #12-800 FIDs (Gow-Mac, #132-117, Bethlehem, PA).
- Septa: Standard 0.32 cm or 0.64 cm cylindrical (Alltech Associates #6524, Deerfield, IL) for injection ports. Silicon septa 0.25 cm and 1.11 cm for oven seals (Alltech #15427 and #15429, Deerfield, IL).
- 1 ml gas tight syringe for gas injections.
- 25 µl syringes for liquid injections.
- Replacement needles for syringes (Alltech #7729-06, Deerfield, IL).
- Replacement oxygen/moisture trap (R&D Separations, Model OT3-2, Rancho Cordova, CA).
- Replacement hydrocarbon trap (R&D Separations, Model HT200-4, Rancho Cordova, CA).
- Replacement indicating oxygen trap (Chromatography Research Supplies, Model 202223, Louisville, KY).
- Viton O-rings: Size 013. Two needed for quartz oven tube inlet.
- Teflon ferrules: Parker or Swagelok style 0.64 cm front and back ferrule for the quartz oven tube outlet connections (Swagelok, T-400-SET, Solon, OH). Refer to instrument user manual for specific ferrule sizes.
- Teflon ferrules: 0.32 cm to 0.64 cm (Alltech Associates, #RF-400/200-T, Deerfield, IL), for the thermocouple rod at the inlet breech. Refer to instrument user manual for specific ferrule sizes (style varies by location on analyzer).
- High temperature silicone seals for quartz light rods and connector, prepared by Alltech Associates, #15427 and #15429, Deerfield, IL.
- Heating element for oven (Watlow, #VC401A06A-0000R [90° bend], Columbia, MO).
- Printer paper and toner cartridge.
- Computer CD for backup if not on server backup.

2.3 Reagents

2.3.1 Chemicals

The following chemicals should be reagent grade or better:

- Potassium hydrogen phthalate (KHP), for calibration (Fisher Scientific, cat #P-243, CAS 877-24-7, Fairlawn, NJ).
- Sucrose, for calibration use (EM Science, #SX1075-1, Gibbstown, NJ).
- Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxidation oven (Nurnberg Scientific, #C5162, Portland, OR; Aldrich Chemicals #24344-2, St. Louis, MO; or equivalent).
- Nickelous nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], crystalline, used to prepare the nickel catalyst in the methanator (Fisher Scientific, cat #N62-5000, CAS 13478-00-70, Fairlawn, NJ).
- Chromosorb A, 20/30 mesh, used as a support for nickel catalyst in the methanator (from any chromatography supplier, such as Alltech cat #2-0165). Both nickelous nitrate and Chromosorb A are for preparing the reduction catalyst in the methanator.
- Hydrochloric acid (HCl), 0.4 molar solution, for use in cleaning punch and quartz ovens, and for use in carbonate analysis (Fisher Scientific, cat #A508-212, CAS 7647-01-0, Fairlawn, NJ).
- Hydrofluoric acid (HF), diluted to 15% may be used for removing the white deposits from devitrification (white deposits of SiO_2) on the quartz oven parts (Fisher Scientific, cat #A147-1LB, CAS 7664-39-3, Fairlawn, NJ). However, proper safety precautions must be followed when using HF and quartz oven parts may become brittle with repeated use.
- Nanopure water (used as described in Section 3.1.3.1).

2.3.2 Gases

The following gases should be ultra-high purity (UHP) grade or better:

- He for a carrier gas, regulated to 15-40 psi with a metal diaphragm regulator. The higher pressure is required due to the pressure drop across the Supelco oxygen scrubber.
- 5% CH_4 by volume in He for calibration injections and calibration peaks; regulated to 10 psi by a metal diaphragm regulator.

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- 5% CO₂ by volume in He for calibration injections; regulated to 10 psi by a metal diaphragm regulator.
- 10% O₂ by volume in He as a carrier gas, regulated to 15 psi by a metal diaphragm regulator.
- Hydrogen for the FID flame, regulated to 15 psi with a metal diaphragm regulator.
- Hydrocarbon-free air to supply O₂ to the FID, regulated to 15 psi by a metal diaphragm regulator from a zero air generator.
- Compressed air for pneumatic activation, regulated to ~25 psi.

At least one backup cylinder per gas type should be kept on hand at all times. Depending on analysis volume, the 90% He/10% O₂ mixture are typically replaced every four to six weeks; H₂ and He are replaced once a week. All gases are replaced when the cylinder pressure drops below 500 psi (unless the cylinders are connected to an automatic change-over module). Check the O₂ scrubber and follow the manufacturer's recommendations for scheduling its replacement.

The flow settings on the flow meters (rotameters) are based on an input of 15 psi for He, 90% He/10% O₂, H₂, and FID air. The pneumatic drivers for the breech should have a pressure of ~25 psi to operate effectively (sealing the opening).

2.4 Forms, Paperwork, and Logbook

All samples are logged in upon receipt at the laboratory. A sample analysis list will be prepared by the laboratory supervisor or designated technician indicating which samples will be analyzed, plus any special instructions. As individual samples are analyzed, entries are made in the Carbon Analyzer Logbook, as shown in Figure 2-6. Figure 2-7 provides an example of the cover sheet of the sample analysis run list. Figure 2-8 provides an example of the Daily Analyzer Checklist that is completed at the start of each day in order to verify analyzer flow and FID response.

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Figure 2-7. DRI Carbon Sample Analysis Run List.

```

IMPROVE A08 Z15 - Mar. 2008: Batch Z1 Quartz

Date      : 05/27/08                      Account: 6300-683-6081

From      : T. Bohannan

To        : Carbon Lab

Analysis: OC/EC                          by TOR : 200 samples, data in IMOETZ1I.DBF

Sample Overview:

This analysis list covers samples from the NPS IMPROVE project.  These are 200
PM2.5 samples on 25 mm Quartz filters, including no lab blanks and no field
blanks.  These samples were collected with an Improve sampler.

Analysis Overview:

Sample deposit area: 3.53 cm2
Analysis start date: When Ready
Analysis deadline  :
Sample location   : Carbon Lab

Analysis Details:

Replicate 10% on Model 2001.  Flag all abnormalities.

Carbon analysis data will be stored in the D:\IMPROVE\A08\Z15 directory.
```

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Figure 2-8. DRI Carbon Daily Analyzer Checklist.

Daily Analyzer Check List CA#: 7 Month: August 2005

Date	Leak Check/ Op's Init.	System Pressure (T<100°C)	Reflectance*	Transmittance*	System Blk (TC) in µg	Calibratn OC3 Area	Calibratn EC1 Area	Calibratn LT/RPy Area	Calibratn Peak Area	Comments
8/10 AM	TUB	2.34	1626	1032	0.06	26499	26019	26231	26180	
8/10 PM	GHH					26235	26102	25999	26172	
8/20 AM	SMS	2.34	1621	1041	0.05	26209	25523	25733	25820	
8/2 PM	GHH					26185	25693	26112	26154	
8/3 AM	TUB	2.31	1594	1015	0.10	26138	25514	25729	26115	
8/3 PM	SMS					23776	23030	21816	23262	Calib. low
8/4 AM	TUB	2.33	1590	1011	0.07	26332	26230	26287	26301	
8/4 PM	GHH					26455	26501	26499	26487	
8/5 AM	SMS	2.32	1601	1017	0.11	25998	25878	25799	25907	
8/5 PM	GHH					26101	26058	26011	26100	
8/8 AM	SMS	2.30	1586	1020	0.08	26282	26324	26338	26455	FID out
8/8 PM	GHH					25900	25876	25888	25901	
8/9 AM	TUB	2.31	1581	1021	0.00	26199	26155	26174	26282	
8/9 PM	GHH					25843	25779	25850	25888	
8/10 AM	TUB	2.35	1587	1015	0.03	26111	26114	26156	26200	
8/10 PM	SMS					26099	26178	26210	25975	
8/11 AM	TUB	2.34	1577	1009	0.12	26101	26207	26228	26305	
8/11 PM	GHH					26158	26178	26242	26278	
8/12 AM	SMS	2.33	1572	1005	0.07	25449	25472	25442	25501	
8/12 PM	GHH					25555	25501	25772	25552	
8/15 AM	TUB	2.34	1570	999	0.15	26163	26174	26112	26117	Low
8/15 PM	SMS					26540	26555	26580	26590	
8/16 AM	TUB	2.31	1575	1001	0.02	25846	25872	25888	25779	
8/16 PM	GHH					25999	25842	25912	25978	Leaking
8/17 AM	TUB	2.32	1572	998	0.01	26152	26178	26165	26118	
8/17 PM	GHH					26185	26112	26202	26282	
8/17 AM	SMS	2.33	1577	1002	0.00	25437	25482	25405	25407	
8/18 PM	GHH					26178	26187	26192	26182	
8/18 AM	TUB	2.31	1567	1011	0.10	25899	25990	25888	25872	System bl. high
8/19 PM	SMS					26001	25998	25925	25965	
8/20 AM	TUB	2.30	1571	1009	0.06	26058	26075	26117	26014	
8/20 PM	TUB					25972	25942	25968	25786	

* Test on a blank filter is placed on "Analyze" position.

3 CALIBRATION PROCEDURES AND STANDARDS

3.1 Instrument Calibration

The calibration procedures for the carbon analyzers are of four types: 1) the end-of-run calibration peak; 2) the routine beginning and end-of-day calibration injections of He/CH₄ and He/CO₂ (or the auto calibration check using the *cmdAutoCalibCheck* command); 3) full instrument calibration, performed every six months, using KHP, sucrose, and the two calibration gases; and 4) temperature calibrations performed every six months using temperature-sensitive indicating liquids with different melting points.

3.1.1 End-of-Run Calibrations (Description)

The end-of-run calibration consists of a set quantity of He/CH₄ calibration gas which is automatically injected by the carbon program. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis run and requires no operator intervention. The integrated calibration peak counts should be checked by the operator immediately after each run to confirm that the analyzer is operating satisfactorily. Calibration peak area counts should be greater than 20,000 and within an acceptable range for the specific analyzer. Check daily records to compare and determine analyzer performance and stability.

3.1.2 Routine Calibrations (Description)

Routine calibrations must be performed at the beginning and end of each day, either manually or by using the automated routine calibration command (*cmdAutoCalibCheck*) in the *CarbonNetWork* database Command table.

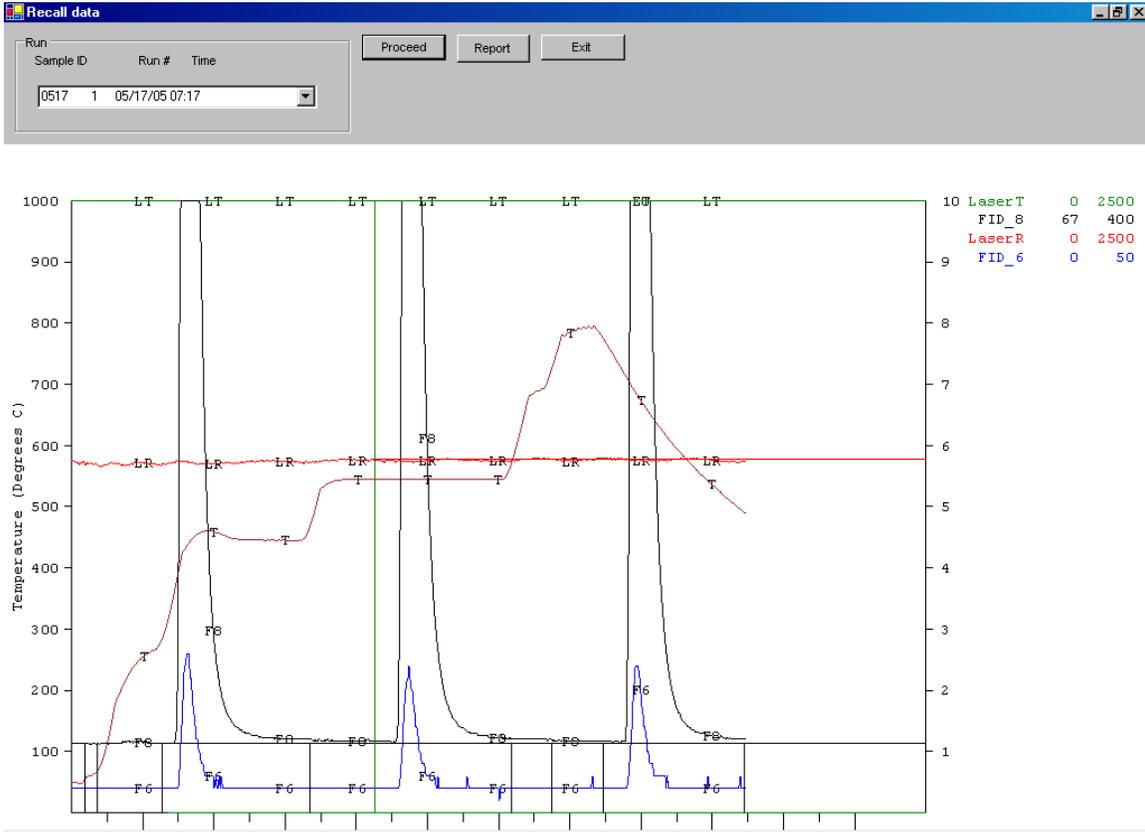
3.1.2.1 Automated Routine Calibration (Description & Instructions)

The automated calibration uses the Carle valve to inject the CH₄ standard once in a He-only atmosphere, once in a He/O₂ atmosphere, and finally, the normal calibration peak at the end of analysis. The three peaks should have similar areas if the catalysts are in good condition and the calibration factor holds (See Figure 3-1). Use the following steps to perform this automated calibration:

- From the *DRICarb.exe* Welcome screen, select “Analysis” from the “Main” submenu.
- Set Type to “Sample” and select *cmdAutoCalibCheck* from the drop-down menu in the “Command table” field.

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Figure 3-1. Calibration thermogram from the *cmdAutoCalibCheck* command of the DRI Model 2001 Thermal/Optical Carbon Analyzer.



- The project name should be “CALIB”, Batch # should be “MM” for the month, Sub-batch # should be “DD” for the day, and the Sample ID should be in the format “CxxYYYYMMDD” where “xx” is the analyzer number (e.g. C0720050710 for analyzer number 7, run on July 10, 2005).
- Set the Run # (“1” for first calibration of the day and “2” for second calibration of the day, etc.). Enter “1” in the Punch area, and Deposit area fields. Click on “OK” and then click “Run”.
- Review the thermogram and record these values in the logbook and on the Daily Analyzer Checklist as shown in Figure 2-8. The three calibration peak counts (OC3, EC1, LtPyMid) should be above 20,000 and within the acceptable range for the specific analyzer, and should be almost identical in area (and within 10% of the “Calibration Peak Area” value show on the tabular printouts). Check the average C value for the calibration gas against those posted on each carbon analyzer.
- Whenever the MnO₂ or Ni catalyst is replaced, an automated routine calibration should be run to confirm that the previous calibration curve holds.

3.1.2.2 Manual Routine Calibration (Instructions)

- From the *DRICarb.exe* Welcome screen, select “Analysis” from the “Main” submenu.
- Set Type to “Calib” and select *cmdCalib-HeO₂* (for example) from the drop-down menu in the “Command table” field. The setup screen is shown in Figure 3-2.
- Project name, Batch #, and, Sub-batch # are not required or available fields for entry. The sample ID should be in the format “MIxxYYYYMMDD” for CH₄ injection or “CIxxYYYYMMDD” for CO₂ injection where xx is the analyzer number (e.g. MI0720050710 for a CH₄ injection on analyzer number 7, run on July 10, 2005).
- Set the Run # (“1” for first calibration of the day and “2” for second calibration of the day, etc.). Click on “OK” and then click “Run”.
- Select the atmosphere for calibration under the “Cal Gas” (either CH₄ or CO₂) menu and select the proper “Carrier Gas” (either HeO₂ or He; HeO₂ for beginning of day and HE only for end of day). These should be alternated with the calibration gas. Verify the command table matches the options selected.

Figure 3-2. Setup Screen for Manual Gas Calibration for the DRI Model 2001 Thermal/Optical Carbon Analysis Program.

- Choose “OK” to proceed with the analysis, or “Exit” to leave the program. The analysis will start with the following screen as shown in Figure 3-3. You will note that the top portion contains all the information in the analysis Setup screen. The bottom half will display the thermogram when the run is initiated.
- Start a run by clicking on “Run”. After the computer states, “Please load gas syringe”, flush the gas syringe with the calibration gas at least three times and then load it with the calibration gas. The computer will then state, the “Time remaining until load - XX seconds” and then “Inject calibration gas”. Follow the verbal instructions to inject the calibration gas through the septum. Inject the gas through the septum. Hold the plunger down with needle still inside septum for 10 seconds, or until peak appears.
- Calibration gas injections should be in the following ranges for 1000 μl gas:

Manual Injection	Lower Allowable Limit	Upper Allowable Limit
CH ₄	20.36 μg carbon ^{1*}	22.50 μg carbon ^{1*}
CO ₂	20.28 μg carbon ^{2*}	22.41 μg carbon ^{2*}
Final Calibration Peak	20,000	--

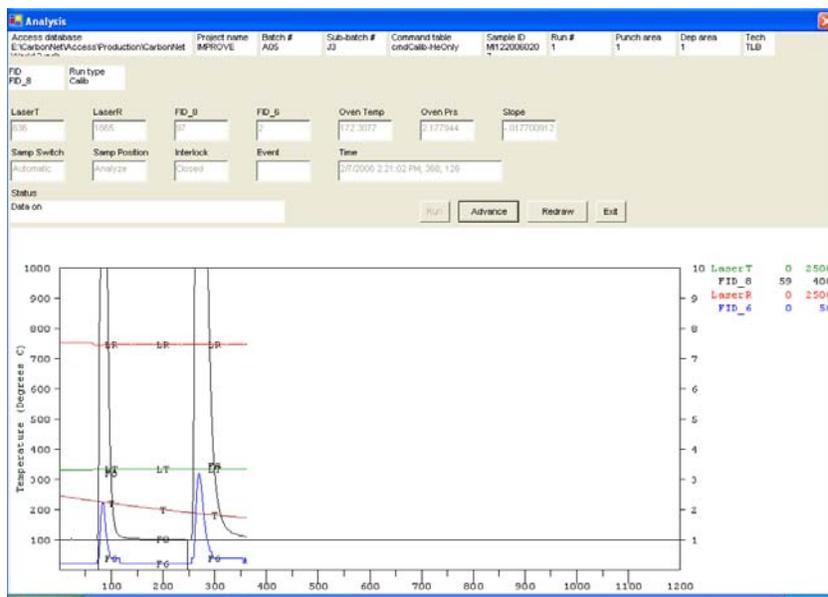
¹ Calculated in a real laboratory environment. For a 5.12% CH₄ standard at 646 mm Hg at 24 °C, actual mass of methane is 21.43 μg carbon.

² Calculated in a real laboratory environment. For a 5.10% CO₂ standard at 646 mm Hg at 24 °C, actual mass of carbon dioxide is 21.34 μg carbon.

* Lower Allowable Limit equals to 5% lower than the actual mass; Upper Allowable Limit equals to 5% higher than the actual mass. Limits should be adjusted according to the real laboratory environment.

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Figure 3-3. The Analysis Screen during Manual Gas Calibration for DRI Model 2001 Thermal/Optical Carbon Analysis Program.



- Note: Each time the MnO₂ or Ni catalyst is replaced, the instrument calibration should be checked to confirm that the previous calibration curve holds. A flow check and balance should always be performed after catalyst changes. Additional checks can be done by running a comparison sample (if available) or running two points from the six CH₄/He calibration volumes and two points from the six CO₂/He volumes used in the full calibration. The calibration peak area may also need to be checked for significant changes that would require a full calibration to calculate a new slope.

3.1.3 Full Calibration (Description)

Full instrument calibration, performed semiannually or as needed, establishes the calibration slope used in converting counts to μg of carbon, as explained in the next section. Instrument calibration involves spiking pre-fired quartz punches with 5.0 to 20.0 μl of the 1800 ppm KHP and sucrose solutions and injecting 200 to 1000 μl of the CH₄ and CO₂ gases.

Four types of standards are used to calibrate the carbon analyzers: 5% nominal CH₄ in He, 5% nominal CO₂ in He, KHP, and sucrose. Only the calibration gases are used on a daily basis as analyzer performance monitors. KHP and sucrose are used in conjunction with CH₄ and CO₂ semiannually to establish the calibration curve of each analyzer.

3.1.3.1 Preparation, Ranges and Traceability of Standards

The calibration is done by injection of a known volume of the standard to yield a calibration curve of peak area ratio of injected carbon: CH₄ (internal standard) versus µg C injected (Internal Standard Calibration Method). For the best accuracy, the temperature and pressure at the time of analysis need to be taken into account. For a 100% CH₄ or CO₂ standard at 760 mm Hg at 20 °C, each microliter = 0.499 µg carbon. For a 5% standard, it will be 0.02495 µg C/µl at standard temperature and pressure (STP; 20 °C, 760 mm Hg). The Ideal Gas Law should be used to correct for the temperature and pressure of the laboratory.

$$\text{Actual } \mu\text{g C per } \mu\text{L} = \left(\frac{\text{Pa}}{760} \right) \left(\frac{1}{T + 273.15} \right) \left(\frac{1}{0.08206} \right) \times \% \text{ of cal gas} \times 12$$

where Pa is pressure in mmHg, T is ambient temperature.

The calibration gases are traceable to NIST standards. The calibration gases are assayed for exact concentrations by the gas supplier; the assay value is obtained from the tag on the cylinders and is typically determined by GC.

To prepare an 1800 ppm standard, the KHP is dried at 110 °C for two hours before dispensing. Transfer 0.3826 g of KHP into a glass 100 ml volumetric flask after the KHP has come to room temperature inside a desiccator. The weight of KHP used must be recorded. Dilute to volume with 0.4 ml concentrated hydrochloric acid (HCl) and 99.6 ml Nanopure water. Mix the KHP thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration, nominally 1800 ppm carbon, is calculated by:

$$\text{Actual } \mu\text{g C per mL} = \left(\frac{\text{weight of KHP used in g}}{\text{vol of solution prep in ml}} \right) \left(\frac{\text{no of carbon in KHP} \times 12}{\text{MW of KHP}} \right)$$

$$\text{e.g.} = \left(\frac{\text{weight of KHP used in g}}{100 \text{ ml}} \right) \left(\frac{8 \times 12}{204.23} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right)$$

The nominal 1800 ppm standard, the sucrose solution, is prepared by transferring 0.428 g of sucrose into a glass 100 ml volumetric flask. Dilute to volume with acidified Nanopure water (see blank solution preparation instructions below). Mix the sucrose thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40

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days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration is calculated by:

$$\text{Actual } \mu\text{g C per mL} = \left(\frac{\text{weight of sucrose used in g}}{\text{vol of solution prep in ml}} \right) \left(\frac{\text{no of carbon in sucrose} \times 12}{\text{MW of sucrose}} \right)$$

$$\text{e.g.} = \left(\frac{\text{weight of sucrose used in g}}{100 \text{ ml}} \right) \left(\frac{12 \times 12}{342.31} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right)$$

To prepare a blank solution, add 0.4 ml of concentrated HCl to a glass 100 ml volumetric flask and dilute to volume with Nanopure water. This acidified Nanopure water is made fresh each time a 1800 ppm KHP stock solution is prepared.

Only a limited set of primary standards (NIST-traceable) currently exist for carbon analysis. Ideally, such standards should include a range of organic compounds from low- to high-molecular weights and with varying degrees of susceptibility to pyrolysis, as well as EC and carbonate compounds. Currently, KHP, sucrose, and the two calibration gases are used at DRI for calibration and system audit purposes.

3.1.3.2 Calculating Calibration Slope

The calibration slopes derived from the two gases and the KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and the sensitivity of the FID. Note that the current calibration procedure is based only on TC, as no routine procedure exists to check the accuracy of the OC/EC split. An example of the spreadsheet is shown in Figure 3-4.

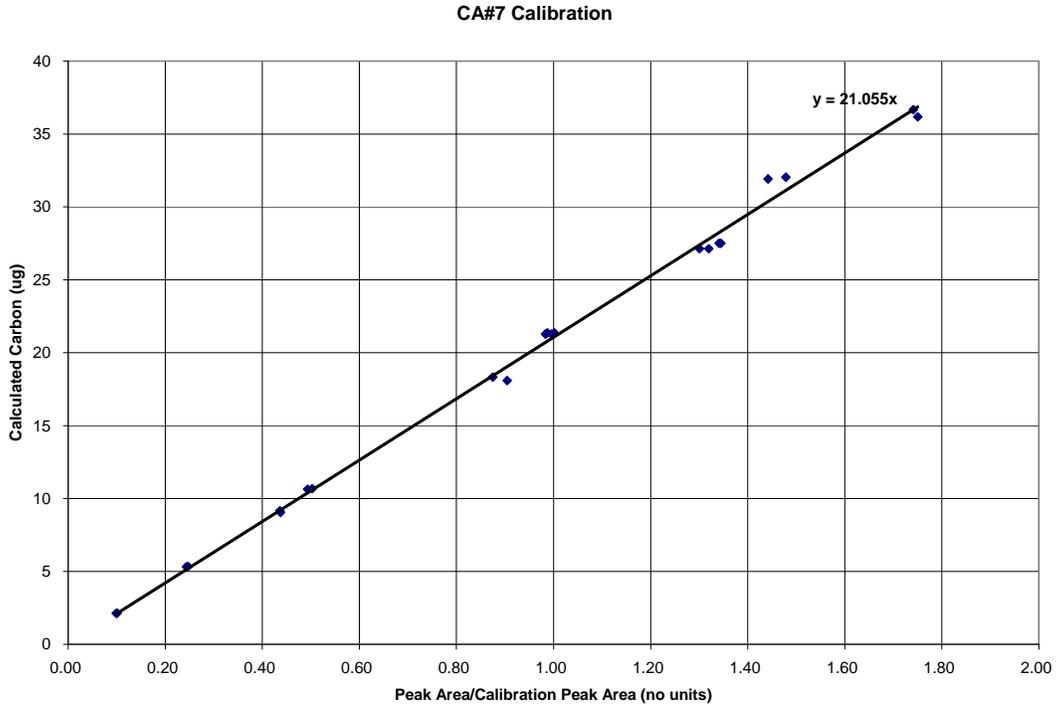
3.1.3.3 Typical Accuracy of Calibration Standards

The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays, the accuracy of the preparation of the KHP and sucrose solutions, and the technician's injection technique. The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure (Section 3.1). Figure 3-5 shows an example of plotted calibration curves.

Figure 3-4. Example of calibration summary worksheet used to determine calibration slope.

Calibration Standard	Run #	volume (µL)	C in CH ₄ /He (µg)	Injection Peak Counts	Calibration Peak Counts	Injection/Calibration	Slope
CH ₄	MI040106-1	200	4.18	4913	25194	0.1950	21.45
CH ₄	MI040106-2	500	10.46	12240	25095	0.4877	21.44
CH ₄	MI040106-3	700	14.64	17081	25502	0.6698	21.86
CH ₄	MI040106-4	1000	20.92	24094	25769	0.9350	22.37
CH ₄	MI040106-5	1000	20.92	24011	25846	0.9290	22.51
CO ₂	CI040106-1	200	4.13	4807	25738	0.1868	22.10
CO ₂	CI040106-2	500	10.32	12196	25901	0.4709	21.92
CO ₂	CI040106-3	700	14.45	17214	26114	0.6592	21.92
CO ₂	CI040106-4	1000	20.64	24425	26204	0.9321	22.14
CO ₂	CI040106-5	1000	20.64	24433	25969	0.9409	21.94
SUC	SU20060401-5UL	5	9.01	12490	25952	0.4813	18.72
SUC	SU20060401-10UL	10	18.02	22626	25987	0.8707	20.70
SUC	SU20060401-15UL	15	27.03	32686	26140	1.2504	21.62
SUC	SU20060401-15UL	15	27.03	35584	26336	1.3512	20.01
SUC	SU20060401-20UL	20	36.04	44753	26087	1.7155	21.01
KHP	KHP20060401-5UL	5	9.00	11546	26386	0.4376	20.56
KHP	KHP20060401-10UL	10	17.99	23878	26608	0.8974	20.05
KHP	KHP20060401-15UL	15	26.99	33340	26702	1.2486	21.62
KHP	KHP20060401-15UL	15	26.99	33156	26530	1.2498	21.60
KHP	KHP20060401-20UL	20	35.99	44472	26504	1.6779	21.45

Figure 3-5. Example DRI Carbon Analyzer Calibration Curves.



3.1.3.4 Data Treatment for Calibration Data

- Calibration values are plotted as ratio of the integrated sample peak counts to the calibration peak counts vs. the actual calculated μg carbon (Figure 3-5). Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH_4/He , and CO_2/He). The slope (m) is calculated from:

$$\left(m = \frac{\sum (y_i x_i)}{\sum (x_i^2)} \right)$$

The standard deviation (s) is calculated by:

$$\sigma = \sqrt{\frac{1}{n-1} \frac{\sum (y_i - mx_i)^2}{\sum x_i^2}}$$

where:

$$x_i = \frac{(\text{injected carbon peak area})}{(\text{calibration peak area})}$$

and:

$$y_i = \text{calculated carbon in spiked filter or manual injection } (\mu\text{g})$$

- Note that this is a special form of the regression formula which ensures that the curve passes through the origin.
- The resulting slope is compared to previous calibration results. New values should be no more than 10% different than previous calibrations if no major analyzer changes have been made. If variation is $> 10\%$, calibration must be redone to verify values.
- The new slope for each analyzer (derived from combined CH_4 , KHP, and sucrose data) is placed into the *Carbon.par* file for each analyzer; this file contains analyzer parameters which are read into the Carbon program when it is first started. Therefore the *Carbon.par* file must be edited while the program is closed and the parameters

will take affect when the program is restarted. The date and version number in the *Carbon.par* file is also updated.

- Calibration data and plots are retained electronically and in file folders stored with the raw analysis data.

3.1.3.5 Calculations

The conversion of integrated peak counts to μg of carbon for each peak in the thermogram is performed by the computer at the end of the analysis program. For reference purposes, the calculation is:

$$\text{peak } \mu\text{g C/punch} = \frac{(\text{integrated peak counts above baseline}) \times (\text{calibration slope})}{(\text{internal calibration n counts})}$$

For IMPROVE_A thermal protocol, the peaks reported are: four organic peaks (OC1, OC2, OC3, and OC4) corresponding to 140, 280, 480, and 580 °C in He atmosphere, respectively; three elemental carbon peaks (EC1, EC2, and EC3) corresponding to 580 °C after the introduction of O₂, 740, and 840 °C, respectively; and three pyrolyzed organic carbon peaks (Lower, Regular, and Upper Splits) by reflectance and transmittance, corresponding to the peaks after the introduction of O₂ and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively, for the reflectance and transmittance optical charring correction (see Section 1.7 and Figure 4-4). The EC reported includes pyrolyzed carbon.

Carbon values per punch are converted to $\mu\text{g C/cm}^2$ by:

$$\mu\text{g C/cm}^2 = \frac{(\mu\text{g C/punch})}{(\text{puncharea})}$$

Finally, carbon values are converted to $\mu\text{g C/filter}$ by:

$$\mu\text{g C/filter} = (\mu\text{g C/cm}^2) (\text{filterdepositarea})$$

3.2 Instrument Calibration Instructions

3.2.1 Full Gas Calibration

- To perform the full calibration, select “Analysis” from the Main menu of the *DRICarb.exe* program Welcome screen.

- Choose “Calib” under the “Type” drop down menu. Project name, Batch #, and, Sub-batch # are not required. In the “Command table drop-down”, select *cmdCalib-He* (for example). Fill out the Sample ID, Run #, and Tech Initials fields. The sample ID should be in the format, “MIxxYYYYMMDD_ zzzz” (where “MI” is for CH₄ injection; use “CI” for CO₂ injection; xx is for the analyzer number and zzzz is the volume of gas injected). You can also select FID ID (typically FID_8) to determine the FID peak area and make comments and flag the analysis from this screen before the analysis starts.
- Select the atmosphere for calibration under the “Cal Gas” menu and select the proper “Carrier Gas”. (He-only gas is recommended when doing full gas calibrations.) Verify the command table matches the options selected.
- Enter the technician initials in the “Tech initials” field.
- Choose “OK” to run the analysis, or “Exit” to leave the program. The analysis will start with the screen as shown in Figure 3-2. You will note that the top portion contains all the information in the Setup screen. The bottom half will display the thermogram when the run is initiated.
- Start a run by clicking on the Run command button. After the computer states “Please load gas syringe” flush the gas syringe with the calibration gas at least three times and then load it with the calibration gas. Time remaining until load will be stated, and then “Inject calibration gas”. Inject the gas through the septum. Hold the plunger down with needle still inside septum for 10 seconds, or until peak appears.
- The CO₂ and CH₄ calibrations are run using the “Calibration” options from the main menu. The following volumes are injected:
 - 200 µl CO₂ gas (use 1000 µl syringe)
 - 500 µl CO₂ gas (use 1000 µl syringe)
 - 700 µl CO₂ gas (use 1000 µl syringe)
 - 1000 µl CO₂ gas (do once with 1000 µl syringe and once with 2500 µl syringe)
 - Repeat for CH₄
- Record these calibration values in the logbook as in Figure 2-6.
- The integrated peak counts are extracted manually from the tabular printouts and entered into the spreadsheet which is used to determine the final calibration.

3.2.2 Full Sucrose and KHP Calibrations

- To perform the full calibration, select “Analysis” from the Main menu of the *DRICarb.exe* program Welcome screen.
- Choose “Sample” under the “Type” drop down menu. Complete the information about the sample, including: Project Name, Batch #, and Sub-batch #. The Project name should be “SUKHPCAL”, the Batch # should be “MM” for the month; and the Sub-batch # should be “DD” for the date.
- A clean blank quartz punch is baked in the analyzer oven at 900 °C for 10 minutes using *cmdBakeOven* from the Command table.
- After baking the quartz punch, change to *cmdImproveA* under Command table.
- Perform system blank before running KHP or sucrose.
- Enter the Sample ID number or place your mouse cursor in the field. The sample ID should be in the format, “SUxxYYYYmmdd_zz” (where “SU” is for sucrose spiking; use “KHP” for KHP spiking; xx is the analyzer number and zz is the volume [05, 10, 15, or 20 µl]). You can also select FID ID (typically FID_8) to determine the FID peak area and make comments and flag the analysis from this screen before the analysis starts.
- Enter the Run #; the Punch area and Deposit area should be “1” for the filter being analyzed.
- Enter technician initials in the “Tech initials” field.
- After the punch has cooled to less than 50 °C, the KHP or sucrose solution (prepared as described in Section 3.1.3.1 and kept at room temperature) is injected onto the punch using a 25 µl syringe. The following volumes are used:
 - 5 µl KHP and sucrose solution
 - 10 µl KHP and sucrose solution
 - 15 µl KHP and sucrose solution (do twice)
 - 20 µl KHP and sucrose solution
 - no injection (as a system blank; see Section 4.1.5.1)

- 20 μ l acidified Nanopure water only (check of background level of Nanopure water)
- Flush the syringe at least three times with the calibration solution before taking up the volume for injection. Pump the syringe plunger to remove any trapped bubbles.
- Slowly spike the solution in the center of quartz punch and wash the syringe with Nanopure after use. If the solution is spiked too quickly it will bead up and run off the punch.
- Click “OK” on the analysis “Setup” screen. The boat will load to the calibration position.
- The computer will ask, “Would you like to proceed or would you like to delay analysis?” Enter the length of time in seconds you wish to delay the beginning of the analysis in the Delay box. This is used to purge dry a filter disc that has been deposited with an aliquot of KHP or sucrose standard solution, or when the sample is acidified for carbonate removal. In general, allow ~1 minute of purge time for every μ l of solution deposited (e.g., 5 μ l=300s, 10 μ l=600s, 15 μ l=900s and 20 μ l=1200s). Click “OK” and analysis will begin.
- Allow the punch to dry thoroughly; the punch will turn from translucent to opaque as it dries. The punch must be dry to avoid water vapor effects on the FID and the laser reflectance and transmittance signals. Select the *cmdImproveA* option from the analysis menu to start.
- The integrated peak counts for all seven temperature fractions for the sample and calibration peaks are recorded. The total peak is calculated by adding the peak area from OC1, OC2, OC3, and OC4, as well as EC1, EC2, and EC3. Pyrolysis counts are not included in the total.

3.2.3 Temperature Calibrations

Temperature calibrations are performed semiannually on all instruments to verify that the sample temperature is as accurate as possible.

3.2.3.1 Temperature Indicators

Since it is not possible to sense the temperature of the sample directly, materials were sought that: 1) could be placed where the sample would normally be located, and 2) would cause sharp reactions when known temperatures were achieved. Quick-drying temperature-indicating liquids of different melting points, Tempilaq^o G (Tempil, Inc., South Plainfield, NJ, USA), were used as temperature indicators in muffle furnaces. A Tempilaq^o G set contains long-chain hydrocarbons suspended in an organic solvent, which change their appearance at 44 specific temperatures

spanning 80-1000 °C. The accuracy of Tempilaq° G is certified within ±1% of its designated temperature and is traceable to the National Institute of Standards and Technology (NIST). Tempilaq° G is bottled in liquid form and dries quickly to a dull, opaque film when applied to a surface. As the surface is heated to the designated temperature, the film liquefies and is accompanied by a change of appearance that can be optically monitored to determine sample temperature.

3.2.3.2 Analyzer Preparation

Preparation of the Model 2001 analyzer for temperature calibration includes the following:

- Change par file to 1 and 0 for slope intercept (par file must be edited with the program closed).
- Disconnect the back valve to prevent contaminating the system
- Replace existing MnO₂ oven with a clean backup oven (without a catalyst) to prevent contamination of the main oven. Install without connecting to the back valve.
- Connect an Erlenmeyer flask with ice in it where the oven connects to the back valve. This will help condense the organics when the Tempilaq is heated up.

3.2.3.3 Standard Preparation

Temperature calibration requires two pre-fired quartz-fiber filter (#2500 QAT-UP, Pall Life Sciences, Ann Arbor, MI) punches (0.5 cm² for DRI analyzer) and a clean matching-sized quartz disk (Continental Glass Engineering, Burbank, CA). Quartz-fiber filter punches are sliced in half (horizontally) with a filter-slicing device (Fung et al., 2004). A thin layer of Tempilaq° G (~25 µL) is uniformly applied to the glass and/or quartz disk surface with a 0.1 ml Eppendorf graduated Combitip (Brinkman Instruments Inc., Westbury, NY), and, before drying, is immediately covered with a sliced filter punch. For cost savings, a glass, instead of quartz, disk can be prepared by a technician in the lab from a glass slide cover and used for Tempilaq° G at temperatures > 520 °C. Higher temperatures require the quartz disc to prevent melting. The disc sandwich (i.e., temperature standard) is then loaded on a sample holder for analysis. The mass of applied Tempilaq° G is determined gravimetrically to ensure its mass is ~10%.

3.2.3.4 Temperature Program

After insertion of the temperature standard into the analyzer, the temperature is slowly (2 °C/min) ramped across a 50 °C range containing the specified Tempilaq° G melting point. This slow ramping creates a quasi-equilibrium condition that allows the phase transition point to be

resolved. Temperature indicators 121 through 510 are replicated three times and 704 and 816 are replicated twice. When the specified temperature is reached, the Tempilaq[®] G liquefies, causing a detectable change in reflectance and transmittance.

Figure 3-6 demonstrates the thermocouple temperature, reflectance, and transmittance as a function of thermal analysis time. In the example provided, the reflectance and transmittance remained relatively flat until the temperature approaches its specified value of 184 °C. Figure 3-7 compares the time series of reflectance, transmittance, and their respective first- and second-order derivatives. The second-order derivative (change in the slope) recorded the inflection point of reflectance or transmittance that provided the best indication of the attainment of the designated temperature. Thermocouple temperature at this critical point was recorded as “measured” temperature. The temperature deviation (ΔT) between the sample and the thermocouple temperatures is determined by comparing the rated Tempilaq[®] G temperature with this measured value (Chow et al., 2005).

In the Model 2001, the reflectance-based method generally gave a lower liquefying temperature than the transmittance-based method, within ± 2 °C. Given the uncertainty in the Tempilaq[®] G temperature rating of $\pm 1\%$, calibrations based on the two optical methods were considered to be equivalent; therefore, their means were used. Among temperature indicators that achieve an adequate signal/noise ratio, temperature indicators of 121, 184, 253, 510, 704, and 816°C were chosen for IMPROVE_A protocol temperature calibration (Chow et al., 2005, 2007). Note, the 510 °C temperature experiences charring and therefore, transmittance results are variable.

Figure 3-6. Temperature ramping with a Tempilaq^o G temperature indicator rated at 184 °C. Also shown are reflectance and transmittance of the temperature indicator (if available). The vertical dashed line indicates the achievement of the rated temperature.

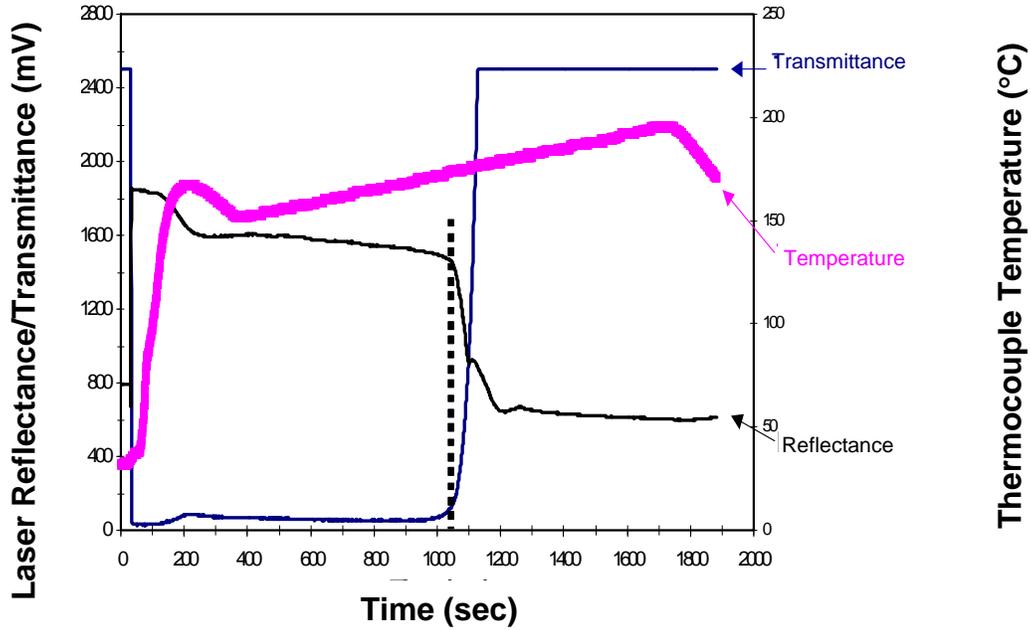
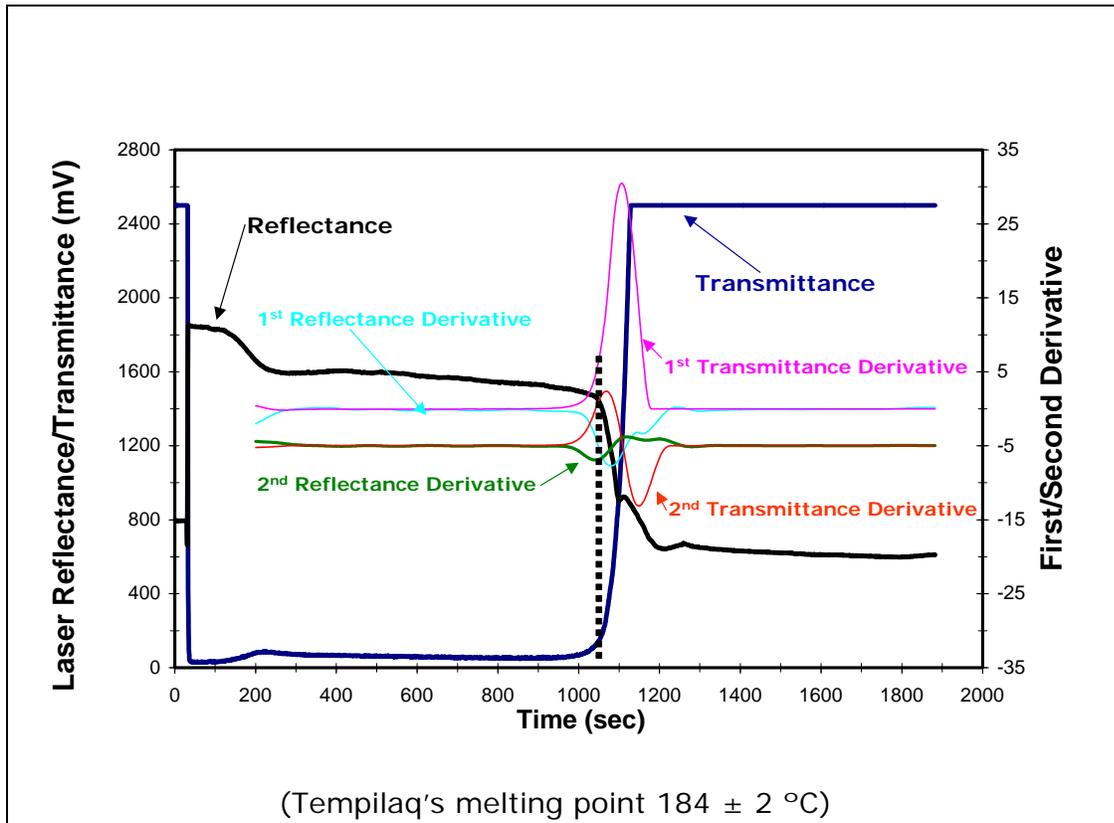


Figure 3-7. Reflectance and transmittance measurements and their first and second derivatives over time with a Tempilaq^o G temperature indicator rated at 184 °C (Figure 3-6). The vertical dashed line indicates the achievement of the rated target temperature.



4 PROCEDURES

4.1 Detailed Procedures

4.1.1 Analyzer Start-Up

When the analyzer is started up for the first time, or after an extended period of non-operation, it will take a period of conditioning to reach a stable system background. At start-up, allow all the gases to purge through the system for ~30 minutes before heating the various zones in a stepwise manner. Allow the FID and Line Heaters to reach operating temperatures of 120 °C and 105 °C, respectively, before heating up the oxygenator and methanator. Heat both catalysts at 120 °C for about half an hour, then in ~100 °C increments with ~30 min. hold time until the final temperatures of 912 °C and 420 °C are reached for the oxygenator and methanator, respectively.

The following steps outline analyzer start-up:

- Check all gas cylinder pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis.
- Check that all gas delivery pressures are correct:

Hydrogen (H ₂)	15 psi
Helium(He)	15-40 psi (check label on regulator for current setting)
Compressed air	15 psi for FID, 25 psi for breech actuation
O ₂ /He mix	15 psi
CH ₄ /He mix	10 psi
CO ₂ /He mix	10 psi

- Check that the FID is lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. If the FID is not lit (as immediately after the H₂ or compressed air cylinders are changed), relight the flame by turning the H₂ rotameter to the upper limit (as posted on the flow meter) and holding a butane lighter or match over the FID stack. A soft pop indicates that the flame has been lighted. Verify that the flame remains lit by the tweezers test. Often the flame will not stay lit the first try, especially

after the H₂ cylinder is changed and air gets into the gas lines. Return the rotameter to the operation setting after the flame is lit.

- Check and readjust, if necessary, all gas flows at the analyzer. The correct readings are posted on each rotameter. Read through the center of the ball. If drastic adjustments are required on one analyzer, recheck that flows on the other analyzers have not been affected.
- Turn on the computer monitor. Note: the computers are generally left on at all times; only the monitors are turned off when the analyzers are not in use.
- Confirm that the date and time on the computer are correct.
- Wipe the sample tweezers, flat glass plate, and punching tool with clean KIMTECH wipe, taking care not to contact the cleaned surfaces with fingers or other dirty items. Check to make sure that no fibers from the KIMTECH wipe are left on the surfaces.
- Begin the daily entry in the Carbon Analyzer Logbook. Entries should follow the format in Figure 2-6.
- Make sure that the printer has enough paper for the day and that the toner cartridge is producing legible text and graphics.
- Go to C:\CarbonNet, then double click the *DRICarb.exe* program icon to begin the carbon program (or double click the *DRICarb.exe* shortcut on the computer desktop). The DRI welcome screen appears as depicted in Figure 4-1. Verify that the correct version of the software and database are being used. For normal analysis, the database should be “*CarbonNetWorkXX.mdb*”, where *XX* is the analyzer number.

If for some reason the program freezes, allow the sample oven to cool to below 200 °C and then close the program and restart *DRICarb.exe*.

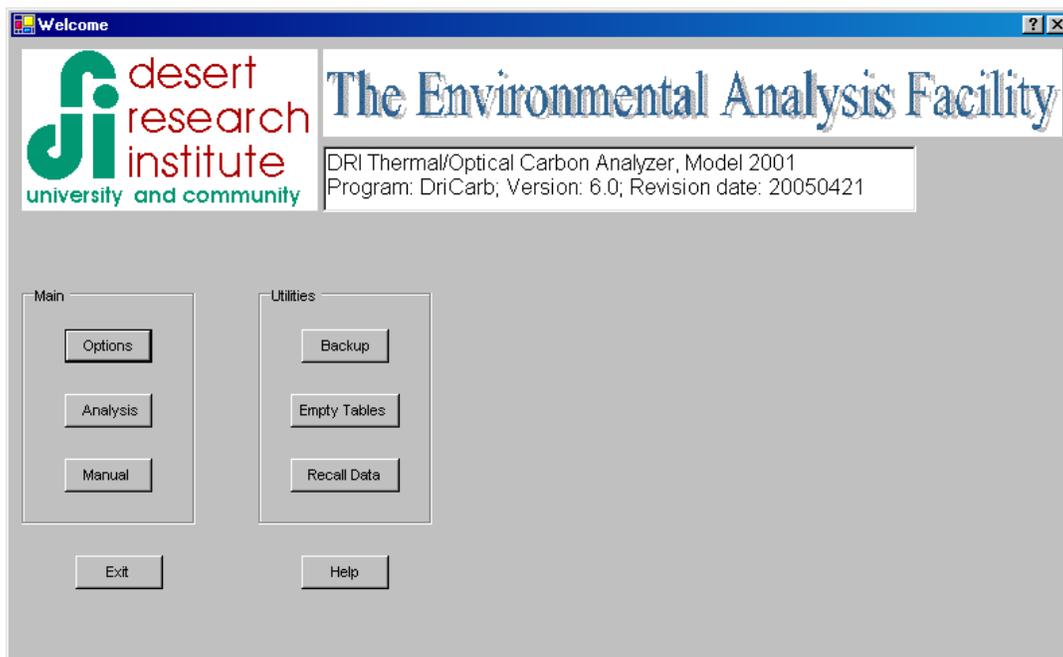
4.1.2 Leak Checks

Perform leak checks daily to detect leakage in the sample oven.

4.1.2.1 Manual Leak Check

- With the breech closed, flip the oven outlet toggle on the side of the analyzer down (off) and let the sample oven pressure reach ~3 psi. Most systems are working in the ~2-2.5 psi range, but a leak is easier to detect when the pressure is at ~3 psi. Close the oven inlet toggle, on the front of the analyzer, and watch for a decline in the sample oven pressure.

Figure 4-1. DRI Welcome Screen.



NOTE: When using the carbon analysis software, clicking on the Exit button closes the program. Exiting in the midst of an analysis is not advisable, as the analyzer will revert to the default settings (see settings under Options\Manual); in such a case, a hot thermocouple will retract, possibly damaging the Teflon seal.

A "leak free" condition is indicated by a steady pressure reading, or a decline of 0.01 psi or less per second (~ 0.01 ml/sec).

- If the pressure is stable, flip the outlet oven toggle and then the inlet oven toggle back to the on position (up). This is to avoid pressurizing the oven if the inlet toggle is flipped first.
- If the pressure is not stable, use a He leak detector (Alltech, Deerfield, IL) to locate the leak. Check the following items and correct accordingly:
 - All ferrules (especially the reducing ferrule), fittings and seals.
 - Quartz oven.
 - All tubing.
 - Thermocouple.

– Breech O-ring.

- If the system still leaks, wipe all threads and ferrules with a dry KIMTECH wipe, reassemble, and retry.
- Also, check the breech O-ring to ensure that it sits squarely in the groove and that there is sufficient pressure to close the breech.
- Refer to the carbon analyzer's *Troubleshooting Manual* for additional tips and procedures.

Once the system passes the leak test, make sure that the analyzer's multi-function switch (at the left of the front panel) is set at Auto in order to continue with routine analysis. Allow the system pressure to return to its original value and record this value on the Daily Analyzer Checklist shown in Figure 2-8. The pressure should be consistent with previous day's values.

4.1.3 Oven Bake

A daily oven bake is performed to ensure the system is clean before beginning analysis. The oven bake can be performed manually or by using an automated command from the command table.

4.1.3.1 Manual Oven Bake

Use the following procedure to perform a manual oven bake:

- Select "Manual" from the "Main" submenu. From the "Manual" screen, select "Control" on the drop-down menu list. (Note: analyzer must be in "Auto" mode for the manual control to work.) This will bring up the "Control" screen. Change the "Oven Temperature" field to "1000". Change the "Sample Position" field to "Analyze". Click "Go". This will heat the oven to approximately 950 °C, depending on the instrument's calibration. Exercise caution when working around hot surfaces of the analyzer.
- Repeat until the system is clean. Sample runs or calibrations may then begin.
- System blanks (section 4.1.5.1) are run after the oven bake.
- Stop bake after 15 minutes; set temperature to 5 °C

4.1.3.2 Automatic Oven Bake

Use the following procedures to perform an automatic oven bake:

Title: DRI Model 2001 Thermal/Optical Carbon Analysis
(TOR/TOT) of Aerosol Filter Samples - Method IMPROVE_A

- From the main welcome screen, select “Analysis”.
- Set Type to “Sample” and select *cmdBakeOven* from the drop-down menu in the “Command table” field.
- Use Project Name “SYSBLK”, Batch # “MM” for the month and Sub-batch # “DD” for the day.
- The Sample ID should be in the format “BxxYYYYMMDD” where “xx” is the analyzer number and YYYY is the year (e.g. B0720050715 for analyzer number 7 on July 15, 2005,).
- Set the Run #, Punch area, and Deposit area fields to “1”. Click “OK”, then “Run”.
- Repeat until the system is clean. Sample runs or calibrations may then begin.
- System blanks (Section 4.1.5.1) are run after the autocalibration (Section 3.1.2.1) has been completed and shows an acceptable range.
- The following items should be checked and recorded on the Daily Analyzer Checklist shown in Figure 2-8. These values can be obtained by choosing the manual option from the main welcome screen.
 - Reflectance and transmittance (must be measured with a clean blank filter in the “analyze” position).
 - Reflectance range should be between 1400 and 2000 and consistent with previous days’ values.
 - Transmittance range should be between 800 and 1300 and consistent with previous days’ values.
 - System blank values
 - Total carbon must be less than 0.2 ug/cm²
 - Calibration values
 - Specific to analyzer and must be consistent with previous days’ values.

4.1.4 OC/EC Analysis

Based on the analysis list for the day, retrieve the samples to be analyzed from the sample freezer and place in a Styrofoam cooler with blue ice, or in the analysis room refrigerator.

Routine analysis procedure assumes carbonate will not be measured. For carbonate analysis, refer to Section 4.1.5.2, "Carbonate Analysis".

Always execute the *cmdBakeOven* command to bake the oven before beginning analysis each day (refer to section 4.1.3). This will ensure the system is clean ($< 0.2 \mu\text{g TC/cm}^2$). Run a system blank with the IMPROVE_A protocol.

4.1.4.1 Analysis Preparation

- Verify the computer date and time is correct.
- Verify sample oven pressure reading and specified flow ranges in the front-panel flow meters.
- Wipe the flat glass plate, tweezers, and punching tool thoroughly with a dry KIMTECH wipe.
- Based on the analysis list, remove the sample to be analyzed from the Styrofoam cooler or refrigerator.
- Record the filter ID in the analyzer log book (Figure 2-6).
- Open *DRICarb.exe* from the c:\CarbonNet folder or use the desktop "shortcut" to *DRICarb.exe*. Verify correct software version number on the Welcome screen.
- Select "Analysis" from the "Main" submenu of the Welcome form. This will initiate the analysis protocol, as shown in Figure 4-2a and 4-2b. You can also select FID ID (typically FID_8) to determine the FID peak sensitivity.
- In the analysis "Setup" form, enter "Sample" for the Type.
- Polarity should default to "Unipolar".
- Fill out the information about the sample, including: Project Name, Batch #, and Sub-batch #.
- Under "Command table" select *cmdImproveA*.

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- Enter the Sample ID number, or place your mouse cursor in the field and use a barcode scanner to read the barcode on the Petri dish.
- Enter the Run #, Punch area and Deposit area for the filter being analyzed.
- Enter technician initials in the “Tech initials” field.
- Select any pre-analysis flags from the drop-down menu in the “Flags” field. A list of valid choices is presented on the screen.
- Visually examine the filter and note any non-uniformity or unusual deposit. Remove it from the Petri slide or Petri dish with tweezers, handling the filter only by the edge. Place the filter on the flat glass plate and remove a sample punch by pushing down gently on the punching tool. Rocking the punching tool slightly will ensure that the punch is completely severed. Try to remove the punch from the edge of the deposit to avoid wasting the filter, while trying to avoid areas of non-uniform deposits.
- Leaving the sample punch in the punching tool, place the punching tool on a clean KIMTECH wipe. Return the filter to the Petri slide or dish, being careful to handle only the filter with the tweezers.
- If this is the first run of the day, or if the analyzer has been cooled down, the analyzer will verbally prompt you to load the punch (“Please load filter analysis”). If the analyzer was previously used, it will cool to 100 °C, then pull the boat back to the calibration position, continue cooling to 50 °C, and pull the boat back to the load position for the next analysis.

4.1.4.2 Loading the Filter Punch

- Use tweezers to remove punch from punch tool and place in analyzer boat.
- Click “OK” on the analysis “Setup” screen. The boat will load to the calibration position and the computer will ask, “Would you like to proceed or would you like to delay analysis?” Enter any appropriate flags and click “Commit”. Check to make sure a 90-second delay is in the “delay” box. Click “OK” and analysis will begin.
- Wipe the tweezers, flat glass plate, and punching tool with a clean KIMTECH wipe.

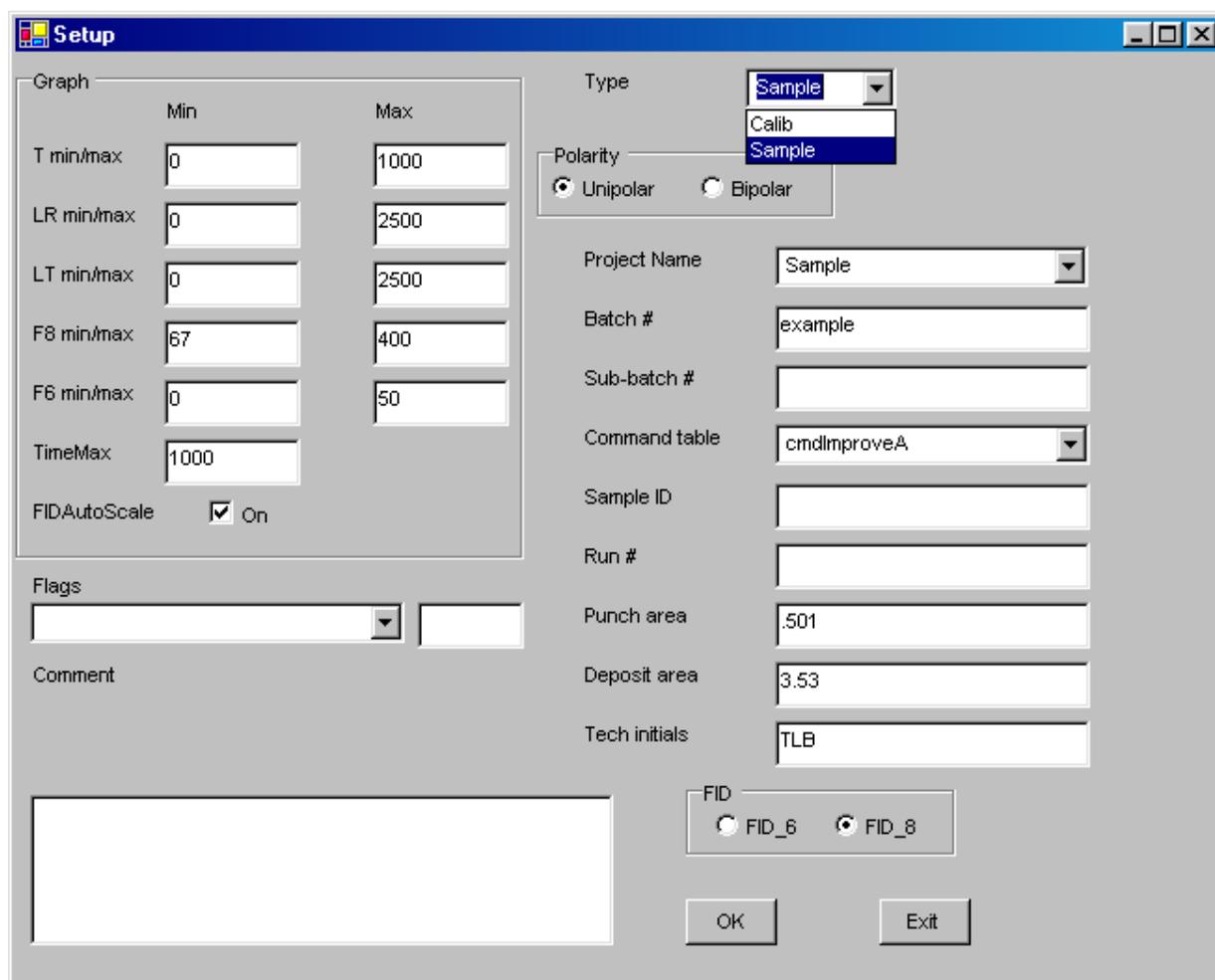
4.1.4.3 Post-Analysis

At the end of each analysis, data is saved to the database, split times are calculated, carbon peaks are integrated, and tabular and graphical printouts are produced. The sample boat will retract to

the calibration position when it is sufficiently cooled by the fan (to < 100 °C) and will continue to cool until it reaches less than 50 °C.

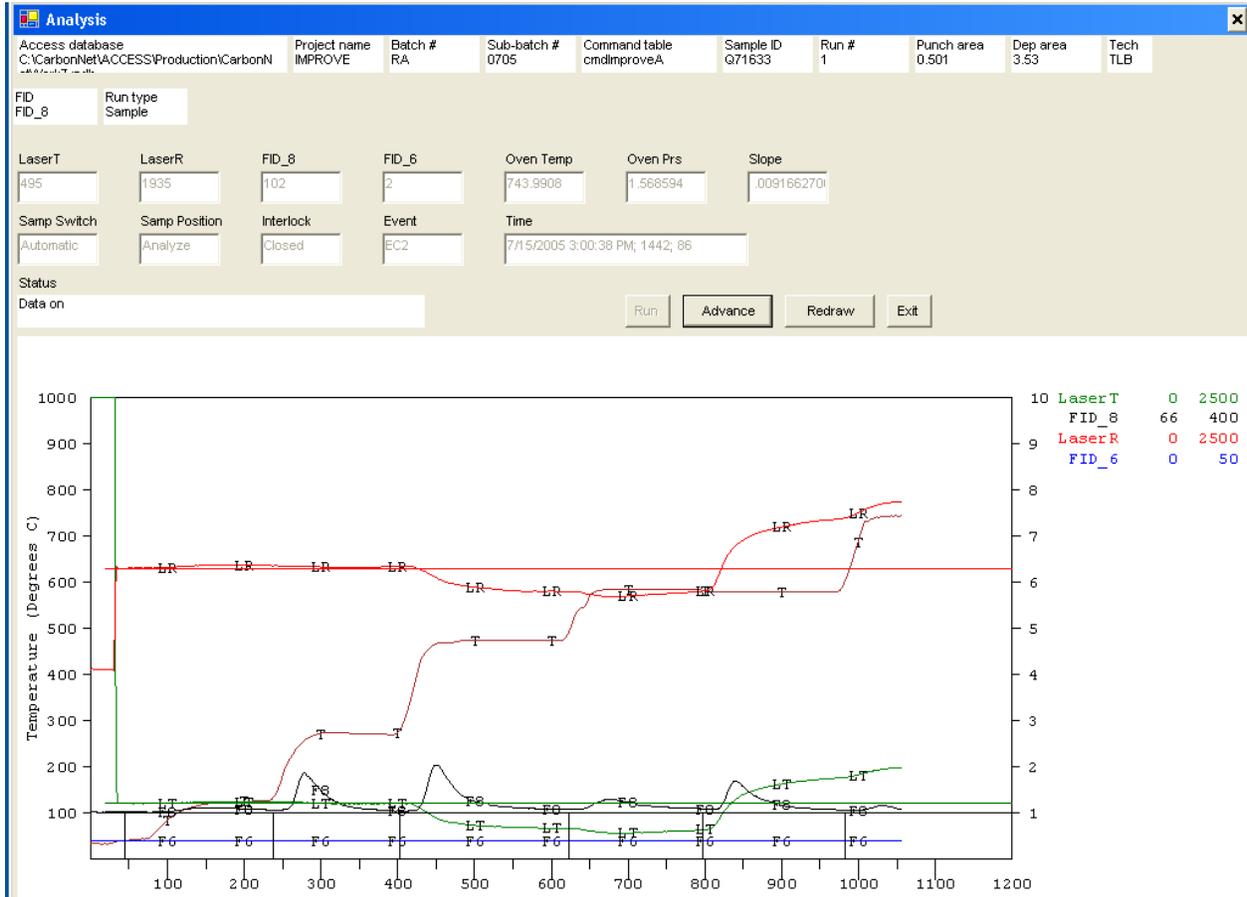
- Examine the tabular printout (Figure 4-3) to confirm that the calibration peak counts are within specifications (typically >20,000 counts and within acceptable range for specific analyzer, see Section 3.1).

Figure 4-2a. Setup Screen for the DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Title: DRI Model 2001 Thermal/Optical Carbon Analysis
 (TOR/TOT) of Aerosol Filter Samples - Method IMPROVE_A

Figure 4-2b. The Analysis Screen during Sample Analysis for DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Title: DRI Model 2001 Thermal/Optical Carbon Analysis
 (TOR/TOT) of Aerosol Filter Samples - Method IMPROVE_A

Figure 4-3. Tabular Printout from DRI Model 2001 Thermal/Optical Carbon Analysis Program.

```

CARBON ANALYSIS RESULTS
Analyzer #9 Technician: TLB
-----
Analysis ID      : FSH00023-9.OEC
Sample ID       : FSH00023
Punch area      : 0.560 cm2
Deposit area    : 1.000 cm2

Analysis Start   : 07/22/08 09:20      Calculation    : 07/22/08 10:10
Analysis Stop    : 07/22/08 10:10

-----
Anal program ver: P6.0 (12/19/06)      Parm file ver  : V0430
Calib. slope     : 21.18 ug C/peak ratio Baseline time  : 11 sec
Calib. intercept: 00.00 ug C
Reflectance unc.: 010 counts           Transmission unc: 010 counts
Sample transit   : 18 sec

-----
Calibration peak area: 25238 millivolt-seconds
Initial FID baseline : 104 millivolts
Final FID baseline   : 104 millivolts

-----
Laser reflectance initial baseline : 1157 millivolts
Laser reflectance minimum          : 1032 millivolts at 1015 sec
Laser reflectance final baseline   : 1842 millivolts
Laser transmittance initial baseline : 155 millivolts
Laser transmittance minimum        : 0 millivolts at 676 sec
Laser transmittance final baseline  : 860 millivolts

-----
Reflect Split Time Laser FID Split Time
Lower split : 1277 sec 903 millivolts 1295 sec
Regular split: 1280 sec 905 millivolts 1298 sec
Upper split : 1282 sec 902 millivolts 1300 sec

-----
Transmit Split Time Laser FID Split Time
Lower split : 1328 sec 2500 millivolts 1346 sec
Regular split: 1329 sec 2500 millivolts 1347 sec
Upper split : 1332 sec 2500 millivolts 1350 sec

-----
Peak Area Carbon
OC1 OC 1710 mv-secs 2.56 ug C/cm2 2.56 ug C/filter
OC2 OC 3337 mv-secs 5.00 ug C/cm2 5.00 ug C/filter
OC3 OC 5008 mv-secs 7.51 ug C/cm2 7.51 ug C/filter
OC4 OC 3482 mv-secs 5.22 ug C/cm2 5.22 ug C/filter
EC1 EC 8128 mv-secs 12.18 ug C/cm2 12.18 ug C/filter
EC2 EC 245 mv-secs 0.37 ug C/cm2 .37 ug C/filter
EC3 EC 0 mv-secs 0.00 ug C/cm2 .00 ug C/filter
LRPyMin Py 2829 mv-secs 4.24 ug C/cm2 4.24 ug C/filter
LRPyMid Py 3101 mv-secs 4.65 ug C/cm2 4.65 ug C/filter
LRPyMax Py 3274 mv-secs 4.91 ug C/cm2 4.91 ug C/filter
LTPyMin Py 5899 mv-secs 8.84 ug C/cm2 8.84 ug C/filter
LTPyMid Py 5935 mv-secs 8.89 ug C/cm2 8.89 ug C/filter
LTPyMax Py 6041 mv-secs 9.05 ug C/cm2 9.05 ug C/filter
    
```

Figure 4-3, continued.

Computed carbon - ImproveA Protocol - Negative Pyrolysis Areas Allowed
 Analyzer #9 Technician: TLB

Analysis ID : FSH00023-9.OEC
 Sample ID : FSH00023
 Punch area : 0.560 cm2
 Deposit area : 1.000 cm2

Analysis Start : 07/22/08 09:20 Calculation : 07/22/08 10:10
 Analysis Stop : 07/22/08 10:10

Reflectance	VOC	Regular OC	HighTemp OC	Regular EC	HighTemp EC	TC
Lower Split	2.56	24.53	21.96	8.31	.37	32.83 ug C/cm2
	2.56	24.53	21.96	8.31	.37	32.83 ug C/filter
Regular split	2.56	24.93	22.37	7.90	.37	32.83 ug C/cm2
	2.56	24.93	22.37	7.90	.37	32.83 ug C/filter
Upper Split	2.56	25.19	22.63	7.64	.37	32.83 ug C/cm2
	2.56	25.19	22.63	7.64	.37	32.83 ug C/filter

Transmittance	VOC	Regular OC	HighTemp OC	Regular EC	HighTemp EC	TC
Lower Split	2.56	29.13	26.56	3.71	.37	32.83 ug C/cm2
	2.56	29.13	26.56	3.71	.37	32.83 ug C/filter
Regular split	2.56	29.18	26.62	3.65	.37	32.83 ug C/cm2
	2.56	29.18	26.62	3.65	.37	32.83 ug C/filter
Upper Split	2.56	29.34	26.78	3.49	.37	32.83 ug C/cm2
	2.56	29.34	26.78	3.49	.37	32.83 ug C/filter

 Regular Reflectance Transmittance
 OC/TC: .76 .89
 EC/TC: .24 .11
 OC/EC: 3.16 7.99

$$\begin{aligned}
 OC &= OC1 + OC2 + OC3 + OC4 + OCPyro \\
 TC &= OC1 + OC2 + OC3 + OC4 + EC1 + EC2 + EC3 \\
 EC &= TC - OC \\
 VOC &= OC1 \\
 OCHighTemp &= OC - OC1 \\
 ECHighTemp &= EC2 + EC3 - \max(OCPyro - EC1, 0)
 \end{aligned}$$

- Examine the thermogram (Figure 4-4) for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis.
- Examine the laser signal at the end of the run.
- If a problem is found, register it in the analyzer log book and run list, and notify the lab supervisor immediately.
- Add any appropriate analysis flags to the post-analysis form that appears at the end of the run.
- Mark the analysis date on the sample analysis run list.
- Using clean tweezers, remove the punch from the boat and tape it to the thermogram with transparent tape, ensuring that the punch is deposit-side up.

Repeat the above steps for additional analysis runs.

4.1.5 Special Analyses

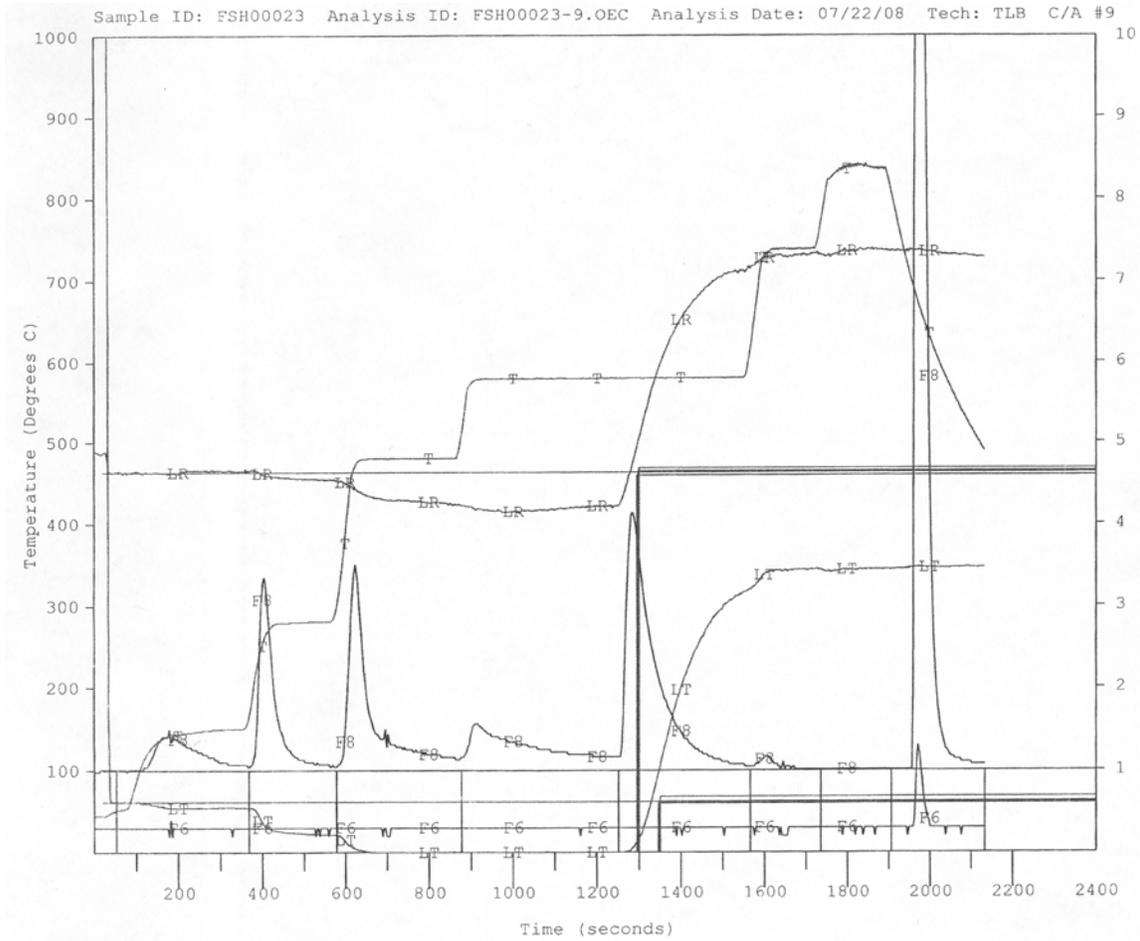
4.1.5.1 System Blanks

System blanks are run at the beginning of each day. Follow the steps outlined in Section 4.1.3 on oven baking with the following exceptions:

- Follow the routine analysis procedure (Section 4.1.4), but when prompted to load filter punch, remove the filter from the previous day and leave the boat empty for the analysis.
- Use Project Name “SYSBLK”, Batch # “MM” for the month, and Sub-batch # “DD” for the day. Punch area and Deposit area should be “1”.
- Use a Sample ID number “SBYYYYMMDD” derived from the current date, where YYYY is the year (e.g. SB20050718 for July 18, 2005.).
- Calculated carbon concentrations should not be more than 0.2 µg carbon. Values greater than this warrant additional system blanks. Samples may not be analyzed until the system blank is <0.2 µg carbon.

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Figure 4-4. Graphical output (thermogram) from the DRI Model 2001 Thermal/Optical Analysis Program.



4.1.5.2 Carbonate Analysis

- Enter the Sample ID, Run #, Punch area, and Deposit area. Select *cmdImproveA_Carbonate* from the “Command table” drop-down field and start the analysis program.
- Follow the steps under Section 4.1.3 until the sample punch is loaded into the boat. Load sample and click “OK”. When asked if you want to delay or continue analysis, click “OK”. After 90 seconds the punch automatically centers under the acid injection port. The computer will prompt you to inject the hydrochloric acid (HCl), and then will state “Load syringe” and “XX seconds to acid injection”.
- Prior to acidification (approximately 90 seconds elapsed analysis time), flush the 25 µl syringe with 0.4 M HCl into a waste beaker.
- Inject 20 µl of 0.4 M HCl through the septum port to the sample, ensuring that the needle bevel is turned toward the punch and that the needle tip is touching the top of the punch.
- When the analysis is underway, flush the syringe with Nanopure water to prevent corrosion of the syringe plunger.
- After analysis, the program will delay any further analysis for 900 seconds to allow the punch to dry.
- After the carbonate analysis is completed, a tabular summary and a copy of the graph will be printed (similar in format to Figures 4-3 and 4-4). Select *cmdImproveA* from the “Command table” drop-down field and click “OK”. Click “Run” on the analysis Setup screen. The program will automatically cycle into the normal OC/EC analysis, using the same Sample ID. Heat from the oxidation oven will dry the sample in this position (for approximately 15 minutes) without prematurely baking carbon from the sample; the sample temperature should not exceed 42 °C. When the punch is dry proceed with normal OC/EC analysis.

4.1.6 Analyzer Shut-Down

After the final sample for the day is analyzed, shut down the analyzers using the following procedures:

- Leave the last analyzed punch in the boat with the boat positioned in the Calibrate position. This punch will be used as the system blank the following morning and then taped to the corresponding thermogram.

- Perform end-of-the-day calibration gas injection routine, or use *cmdAutoCalibCheck* command, and record the calibration peak counts. Any values outside the expected ranges should be investigated and rerun. Because low values from the end-of-day calibration could potentially invalidate the entire day's runs, any deviation from the accepted ranges must be noted and the cause identified. Notify the lab supervisor.
- Leave the *DRICarb.exe* software open.
- If desired, He-1, Cal Gas, He-2, and Air may be turned off with the toggle valves to conserve gases. However, all other gases should be left on as long as the oxygenator and methanator are heated.
- Place all of the day's printouts, including calibration data in a file folder labeled with the date and analyzer number. Place on the lab supervisor's desk for Level I validation (Section 6.4).
- Leave the computers and analyzers on overnight unless the potential for power outages or surges exists. Turn off the monitors overnight.
- Make a final check of the gas cylinder pressures to ensure that gas flow, especially the compressed air, will continue until someone will be available to check them again.
- Move the samples and blue ice in the Styrofoam cooler or refrigerator back into the sample storage freezer and verify that the freezer is completely closed.
- If the 25 or 50 μ l syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water and tightly cap all solutions. Store solutions in the refrigerator. Freezer storage may cause crystallization.
- Lock the carbon analysis room.

4.2 Abbreviated Procedures

4.2.1 Analyzer Start-Up

- Check pressures and delivery pressures in all gas cylinders.
- Check that all FIDs are lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. Relight if necessary.
- Check all gas flows at the analyzer; readjust if necessary.

- Turn on the computer monitor.
- Confirm that the date and time on the computer are correct.
- Execute the *DRICarb.exe* either from the shortcut on the computer desktop or from C:\CarbonNet\.
- Confirm that the printers have enough paper for the day and that the toner cartridge is producing legible text and graphics.
- Wipe the sample tweezers, flat glass plate, and punching tool with a clean KIMTECH wipe.
- Begin the daily entry in the Carbon Analyzer Logbook.
- Bake the oven for 10 minutes, or bake during leak test.
- Perform a leak test, involving isolating the oven and operating the Carle valve.
- Execute the *cmdAutoCalibCheck* command to verify the analyzer's performance.
- Retrieve the samples to be analyzed from the sample freezer and place in the styrafoam cooler or refrigerator.
- Complete Daily Analyzer Check Sheet posted on each analyzer.

4.2.2 Leak Checks and Oven Baking

- Use manual option to set temperature to 900 °C and let analyzer reach this temperature.
- With breech closed, flip oven outlet toggle to the off position and let sample oven pressure reach ~3 psi.
- Flip the oven inlet toggle to the off position and watch for a decline in the sample oven pressure. If system is leak free, the pressure will remain stable.
- If the system is not stable, use a He leak detector to locate the leak; disassemble and reassemble the port fitting if necessary and check the O-ring for correct placement and pressure.
- When system is stable, flip both the inlet and outlet oven toggles back to the on position.

- An oven bake can also be executed without a leak check by selecting *cmdBakeOven* from the drop-down menu in the “Command table”.
- Update the Daily Analyzer Checklist and verify values are within expected range.

4.2.3 OC/EC Analysis

4.2.3.1 Analysis Preparation

- Clean the tweezers, flat glass plate, and punching tool with dry KIMTECH wipe.
- Based on the analysis list, remove the sample to be analyzed from the Styrofoam cooler or refrigerator. Verify the sample ID against the analysis list.
- Remove a sample punch from the filter.
- Record the Sample ID in the analyzer logbook, along with any comments on the condition of the deposit or any other conditions which might affect analysis results.

4.2.3.2 Loading the Filter Punch

- Begin the analysis by clicking on “Analysis” in the Welcome window and inputting the Project Name, Batch #, and Sub-batch #, verify the Command table is correct and enter the Sample ID, Run #, Punch area, Deposit area and Tech Initials.
- Enter Flags if appropriate (e.g., b1, i4, etc.)
- After the boat has cooled to 50 C or less, remove the previously analyzed sample punch and load the current sample punch.
- Clean the tweezers, flat glass plate, and punching tool with a dry KIMTECH wipe.
- Replace the Petri slide or Petri dish containing the filter into the Styrofoam cooler or refrigerator.
- Upon analysis completion, use a small piece of transparent tape to attach the sample punch to its thermogram, ensuring that the deposit side is facing up.
- At the end of the analysis, the push rod will automatically be pulled back to the Calibrate position to begin cooling.

4.2.3.3 Post Analysis

- Examine the thermogram for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis. Examine the tabular printout to confirm that the calibration peak counts are within specifications (see Section 3.1). Finally, examine the laser signal at the end of the run. Indicate successful analyses on the sample analysis list by recording the date. Notify the lab supervisor of any problems and record them in the log book and on the run list.
- Repeat the above steps for additional samples.

4.2.4 Special Analyses

4.2.4.1 System Blanks

- Go through all the steps for a normal analysis, but do not remove the punch from the previous analysis. Proceed with the routine analysis.
- Use project name "SYSBLK", Batch # "MM" for the month and Sub-batch # "DD" for the day. Punch area and Deposit area should be "1".
- Calculated carbon concentrations from the system blank should not be more 0.2 μg carbon. Values greater than this warrant an additional system blank or oven bake.

4.2.4.2 Carbonate Analysis

- Follow the steps under Routine OC/EC Analysis until the sample punch is loaded into the boat.
- Enter the Sample ID, Run #, Punch area, and Filter area.
- When prompted for injection, spike 20 μl 0.4 M HCl onto the filter punch.
- Flush the syringe with Nanopure water between samples.
- Continue the normal OC/EC analysis when the carbonate cycle is complete, following the 20 minute delay allowed for drying.

4.2.5 Analyzer Shut-Down:

- Leave the last analyzed punch in the boat with the boat positioned in the Calibrate position. This punch will be used as the system blank the following morning and then taped to the corresponding thermogram.
- Execute the cmdAutoCalibCheck command to verify the analyzer's performance.
- When the analysis is complete, record the calibration peak counts and calculated injection calibration in the logbook. Any values outside the ranges defined in Section 3.1 should be investigated and rerun.
- Backup the day's data files to disk, if not automatically backed up on a server.
- Remove the printouts and attach them to a file folder labeled with the date and analyzer number. Place on the lab supervisor's desk.
- Turn off the computer monitors.
- Make a final check of the gas cylinder pressures.
- Move the samples and blue ice in the Styrofoam cooler or refrigerator back into the sample storage freezer and verify that the freezer is completely closed.
- If the 25 or 50 μ l syringe was used for carbonate analysis, thoroughly rinse the syringe with Nanopure water and tightly cap all solutions. Store at 4 °C.
- Lock the carbon analysis room.

5 QUANTIFICATION

5.1 Measurement Calculations

Section 3.1.3 contains the equations used to determine measurement values.

5.2 Precision (Uncertainty) Calculations

Precision is determined from replicate measurements as the average fractional difference between original and replicate analysis concentrations. Concentration uncertainty is the fractional precision times sample concentration. If sample concentration times fractional precision is zero, then the detection limit is used as concentration uncertainty.

The precision calculation program for chemical analysis methods also allows for rejection of outliers and selection of concentration ranges for precision calculations. The uncertainty is calculated using the following formulas:

$$CV = \frac{\sum_{i=1}^N \frac{2 \times |c_i - c_{i,r}|}{c_i + c_{i,r}}}{N}$$

$$Unc_i = \sqrt{(CV \times c_i)^2 + MDL^2}$$

Where CV = coefficient of variance

N = number of samples

c_i = concentration of initial analysis

$c_{i,r}$ = concentration of sample “ i ” replicate analysis

Unc = uncertainty

6 QUALITY CONTROL

6.1 Performance Testing

System blanks are performed at the beginning of each day to confirm the system is not introducing bias in the carbon results and to confirm that the laser signal is not temperature-dependent. Contamination is potentially due to:

- Operator practices, such as improper cleaning of tweezers and punch.
- Teflon particles on the push rod getting into the heated zone of the quartz oven.
- Sample boat contamination.
- Contamination of the carrier gas.
- Fibers left on the punch tool or on the flat glass plate during cleaning.
- Contamination from field operator.
- Contamination from normal use of analyzer.
- Maintenance/part replacement.

A temperature-dependent laser signal is potentially due to:

- Physical coupling of the push rod to the boat during the run.
- Boat movement due to loose boat holder.
- A quartz rod (laser light pipe) ready for replacement. As quartz is heated to high temperatures, devitrification (white deposits of SiO_2) occurs that leads to a decrease in the laser intensity. The end surface becomes frosty. The bottom light pipe also receives droppings of quartz particles from filter discs during analysis. Thus, the bottom light pipe will deteriorate faster than the upper light pipe. Microscopic cracks in the quartz rod will increase internal reflectance of the laser light; as the number of these cracks multiply, the effect of temperature on these cracks, and thus on the reflectance, becomes an interference in the laser signal.

As described in Section 3.1, the calibration peak at the end of each analysis run serves as a regular standard; the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration gases further serve as standards.

Only a limited set of primary standards (NIST-traceable) currently exist for carbon analysis. These do not include a range of organic compounds from low- to high-molecular weights, with varying degrees of susceptibility to pyrolysis, or EC and carbonate compounds. The *cmdAutoCalibCheck* command check allows the condition of the catalysts to be monitored and verified.

6.2 Reproducibility Testing

Replicates of analyzed samples are performed at the rate of one per group of ten samples. The replicate is selected randomly and run immediately after each group of ten is completed. The random analyzer for the replicate is identified using a chart created in Microsoft Excel (shown in Figure 6-1) using the random number generator, which results in replicate analysis on the same and different analyzers.

This practice provides a better indication of potential differences if samples are analyzed by different laboratories. The $\mu\text{g}/\text{cm}^2$ values for OC, EC and TC are compared with the original run. The values should meet the following criteria:

Range	Criteria
OC, EC & TC $< 10 \mu\text{g}/\text{cm}^2$	$< \pm 1.0 \mu\text{g}/\text{cm}^2$
OC and TC $\geq 10 \mu\text{g}/\text{cm}^2$	$< 10\%$ of average of the 2 values
EC $\geq 10 \mu\text{g}/\text{cm}^2$	$< 20\%$ of average of the 2 values

Notice that the criteria converge at $10 \mu\text{g}/\text{cm}^2$. Replicates which do not meet the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include poor response (as reflected in the calibration peak areas) or poor laser signals affecting the splits between OC and EC. Typical sample anomalies include inhomogeneous deposits or contamination during analysis or from the field sampling location. Inconsistent replicates for which a reason cannot be found must be rerun again unless the filter condition will not allow an additional representative punch to be taken.

When samples are analyzed with an automated sample loader, the sample chamber tray will be set up such that the loader number six location will be a replicate of the first sample, the 12th location a standard spike of sucrose or KHP, and the 18th location a replicate of the sample in loader position.

6.3 Control Charts and Procedures

Control charts are updated at the beginning of each month. These charts include a month of calibration data and are posted in the carbon room until the end of the month, after which they are filed with the raw analysis results.

Figure 6-1. Example of carbon analyzer replicate checklist.

CARBON ANALYZER REPLICATE CHECKLIST																											
In order to keep track of the replicates between machines on large projects, please use the checklist below by placing an "X" in the appropriate box. For example in the first group below, once you have completed 10 runs on the run list, randomly select one QID from those 10 analyses, find that analyzer # in the "Orig Run" column and replicate it on the analyzer number listed in the next available box in the "Replicate On" section. Place an "X" on that number to indicate the replicate has been done. If an analyzer is not operating, draw a straight line through it and go to the next number in the column.																											
ORIG RUN	Replicate On																										
CA6	6	6	12	7	8	14	11	8	11	13	13	14	6	9	7	7	6	10	8	11	14	9	8	13	10	9	7
CA7	14	9	7	7	14	12	12	12	6	9	13	8	11	10	7	12	11	6	7	11	7	13	14	10	12	9	6
CA8	11	9	9	8	14	13	10	13	6	14	14	7	10	6	12	11	8	6	6	6	12	13	8	10	12	11	10
CA9	7	8	9	13	8	9	10	13	6	6	8	6	7	9	7	13	11	10	11	7	14	8	12	14	14	13	11
CA10	9	11	6	8	7	13	11	13	9	14	8	12	9	12	9	7	11	7	11	6	12	9	9	8	11	14	10
CA11	10	12	9	14	9	12	13	11	9	10	7	6	10	8	9	6	11	13	11	11	8	13	12	9	10	7	6
CA12	13	7	14	13	12	14	9	12	14	12	13	13	12	6	7	7	9	9	13	12	11	10	8	6	12	14	11
CA13	14	10	11	9	8	9	8	6	13	12	6	11	10	11	8	11	11	12	7	6	7	7	8	12	10	12	6
CA14	9	9	14	14	12	8	14	6	7	14	6	12	8	9	7	13	7	14	12	7	12	12	12	9	9	8	6

The control chart gives a plot of calibration peak counts as percent deviation from a historical mean versus date. Instances where the calibration peak area deviates by more than 10% from the historical mean must be investigated and the cause must be corrected. The historical mean covers results from the previous three months and is updated either quarterly, when the CH₄ calibration gas is changed, when the catalysts are renewed, or when extensive repairs are performed.

6.4 Data Validation

6.4.1 Analysis Flags

During Level 0 validation (see Section 6.4.2), unusual conditions of the deposit or analysis problems are noted on the analysis printouts. Errors in pre-analysis data entry (e.g., in filter ID, punch size, deposit area) are corrected.

Flags are applied to the Access file created from the analysis results (see Section 6.4.2). The analysis flags commonly used are presented in Table 6-1. Note that all results flagged with "v" must include a description of the reason for invalidating the sample in the remarks field unless a subcode is included which provides additional information (such as v3-“potential contamination”).

6.4.2 Daily Validation

Level 0 validation is performed by manually checking the tabular and thermogram printouts the day after the analysis is performed. The laboratory supervisor or a designated technician is responsible for checking the data. The following items are checked on the tabular data (Figure 4-3):

- The filter ID is correct and Punch #.
- For calibration runs, the tabular and thermogram printouts are checked to make sure the catalysts are operating at required level.
- The analysis date and time is correct.
- The punch area is correct; errors in entry require that the calculated carbon concentrations be recalculated.
- The deposit area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.
- The calibration peak area is in the correct range (Section 3.1).
- The initial and the final FID baseline readings are within three counts of each other; excessive FID baseline drift is a cause for re-analysis. NOTE: Some very heavily loaded filters will have an FID baseline drift greater than three counts no matter which carbon analyzer the sample is run on; typically a FID baseline drift greater than three counts signals either a problem with the sample (e.g., very light or very heavy loading) or with the carbon analyzer.
- The lower laser split time and the upper laser split time are within 10 seconds of each other. If the times differ by more than 10 seconds, check that the lower split OC and upper split OC differ by no more than 5%. OC values which differ by more than 5%, unless due to a small change in laser signal resulting from an extremely clean or very dark sample, requires re-analysis. Comments should be added to the data file print out as follows:
 - If Regular OC Reflectance split is greater than 5% note “RO” in comments field; If Transmittance split is greater than 5% note “TO” in comments field.

Table 6-1. Common DRI Analysis Flags.

DRI STANDARD OPERATING PROCEDURE

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Validation Flag	Sub Flag	Description
b		Blank.
	b1	Field/dynamic blank.
	b2	Laboratory blank.
	b3	Distilled-deionized water blank.
	b4	Method blank.
	b5	Extract/solution blank.
	b6	Transport blank.
c		Analysis result reprocessed or recalculated.
	c1	XRF spectrum reprocessed using manually adjusted background.
	c2	XRF spectrum reprocessed using interactive deconvolution
d		Sample dropped.
f		Filter damaged or ripped.
	f1	Filter damaged, outside of analysis area.
	f2	Filter damaged, within analysis area.
	f3	Filter wrinkled.
	f4	Filter stuck to PetriSlide.
	f5	Teflon membrane separated from support ring.
	f6	Pinholes in filter.
g		Filter deposit damaged.
	g1	Deposit scratched or scraped, causing a thin line in the deposit.
	g2	Deposit smudged, causing a large area of deposit to be displaced.
	g3	Filter deposit side down in PetriSlide.
	g4	Part of deposit appears to have fallen off; particles on inside of PetriSlide.
	g5	Ungloved finger touched filter.
	g6	Gloved finger touched filter.
h		Filter holder assembly problem.
	h1	Deposit not centered.
	h2	Sampled on wrong side of filter.
	h4	Filter support grid upside down- deposit has widely spaced stripes or grid pattern.
	h5	Two filters in PetriSlide
i		Inhomogeneous sample deposit.
	i1	Evidence of impaction - deposit heavier in center of filter.
	i2	Random areas of darker or lighter deposit on filter.
	i3	Light colored deposit with dark specks.
	i4	Non-uniform deposit near edge - possible air leak.

Table 6-1, continued.

Validation Flag	Sub Flag	Description
m	m1	Analysis results affected by matrix effect. Organic/elemental carbon split undetermined due to an apparent color change of non-carbon particles during analysis; all measured carbon reported as organic.
	m2	Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
	m3	A non-typical, but valid, laser response was observed during TOR analysis. This phenomena may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely unaffected.
	m4	FID drift quality control failure
n	n1	Foreign substance on sample.
	n2	Insects on deposit, removed before analysis.
	n3	Insects on deposit, not all removed.
	n4	Metallic particles observed on deposit.
	n5	Many particles on deposit much larger than cut point of inlet.
	n6	Fibers or fuzz on filter.
	n7	Oily-looking droplets on filter.
	n8	Shiny substance on filter.
	n9	Particles on back of filter.
q	q1	Standard.
	q2	Quality control standard.
	q3	Externally prepared quality control standard.
	q4	Second type of externally prepared quality control standard. Calibration standard.
r	r1	Replicate analysis.
	r2	First replicate analysis on the same analyzer.
	r3	Second replicate analysis on the same analyzer.
	r4	Third replicate analysis on the same analyzer.
	r5	Sample re-analysis.
	r6	Replicate on different analyzer.
	r7	Sample re-extraction and re-analysis. Sample re-analyzed with same result, original value used.
s		Suspect analysis result.

Table 6-1, continued.

Validation Flag	Sub Flag	Description
v		Invalid (void) analysis result.
	v1	Quality control standard check exceeded $\pm 10\%$ of specified concentration range.
	v2	Replicate analysis failed acceptable limit specified in SOP.
	v3	Potential contamination.
	v4	Concentration out of expected range.
	v5	Instrument error
	v6	Operator error
w		Wet Sample.
	w1	Deposit spotted from water drops.
y		Data normalized
	y1	XRF data normalized to a sulfate/sulfur ratio of three
	y2	Each species reported as a percentage of the measured species sum

- If Regular EC Reflectance split is greater than 20% note "RE" in comments field; If Transmittance split is greater than 5% note "TE" in comments field.
- Calculated carbon values for calibration injection runs are within 10% of the current mean value for the injected gas type on that analyzer.

Acceptance runs for pre-fired quartz filters result in $< 1.5 \mu\text{g}/\text{cm}^2$ OC, $< 0.5 \mu\text{g}/\text{cm}^2$ EC, and $< 2.0 \mu\text{g}/\text{cm}^2$ TC for IMPROVE_A thermal protocol. Filters which exceed these levels must be re-fired or rejected.

Items which are found to be okay are underlined in red. Items which have problems are circled in red.

The thermograms are checked for the following (Figure 4-4):

- The initial FID baseline is flat, indicating that the analyzer has been thoroughly purged before analysis began.
- The final FID baseline prior to the calibration peak is within three millivolts of the initial FID baseline; excessive drift is cause for reanalysis.

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- The laser reflectance signal during the first two minutes, prior to sample introduction to the “Analysis” position, appears near the bottom of the graph and shifts position once the sample is in the “Analysis” position. The transmittance signal will be out-of-scale until the sample is in the “Analysis” position.
- The laser signal should dip below the initial laser line until O₂ is introduced, at which point the signal should rise steeply. (For most samples, charring does occur). High temperature soot samples may not show this characteristic.
- The temperature readings reflect stable and smooth temperatures at each level and quick transitions between levels.
- Problems or deviations from normal should be circled in red. If the sample punch taped to the thermogram is not white, it is also circled.

If examination of the tabular and thermogram printouts results in a decision that a sample should be reanalyzed, write "Rerun" in red on the printouts and prepare a re-analysis list. This list should be posted immediately after the validation is complete, and those samples should be rerun as soon as they can be conveniently fit into the current day's analyses.

Evidence of persistent analyzer problems must be resolved, either by physically examining the analyzer or reviewing the problems with the analyzer operator.

6.4.2.1 Validation of Final Data File

The following steps are followed to create an Excel or dbf file containing carbon data and to perform Level "I" validation on it:

- Each analyzer will have an Access database containing all of the raw carbon data.
- A query (manual or automated by connected server) is used to generate the project data in $\mu\text{g}/\text{cm}^2$ or $\mu\text{g}/\text{filter}$ and a validation report is then generated from this query.
- The output of the Access query is saved or exported as an Excel file or database report for data validation and processing. The MS Excel file naming convention calls for a name in the following format:

xxOETmnt.xls

where:

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xx is the two-character project identifier

OET is organic/elemental carbon

nn is the two- or three-digit batch number (generally used to distinguish between different projects for the same client or between sampling quarters for an extended project)

t is the sample type based on sampler technology:

A is agricultural burn emissions dilution sampler

C is combination particle/gaseous sampler

D is dichotomous sampler for PM_{2.5}, PM_{coarse}, and PM₁₀

G is gaseous

H is high-volume sampler

I is IMPROVE/NPS sampler

P is MiniVol Sampler

Q is audit samples

R is resuspension chamber

S is sequential filter sampler (SFS)

W is wet Deposition

X is unknown

Y is y-sampler (DRI source sampler)

- The final MS Excel or dbf file name is specified on the analysis list posted in the carbon room.
- Begin validation by matching the filters listed on the analysis list with the filters listed on the MS Excel or database printout. There must be at least one entry on the printout for every filter listed on the analysis list.
- Flag field and lab blanks while the list is being reviewed by placing "b1", "b2", "b3", or "b6" in the second column of the printout. Because the MS Excel or database printout is sorted by ID number, replicates and reruns will be grouped together.
- Indicate missing data by writing the missing filter ID in the margin with an arrow drawn to the appropriate place of insertion. Scan the printout for unusual IDs which may have been mistyped or misread by the scanner during analysis. Generally, these will appear at the beginning or end of the printout, due to the sorting process. Make sure that all samples listed on a rerun list appear on the printout.
- Resolve all missing data. Scan the deposit area column for incorrect entries. Circle the incorrect entries to ensure that corrected values replace those currently in the database.

- Scan the filter IDs for multiple entries of ID numbers. Under normal conditions, the only times multiple entries should occur are reruns and replicates. All multiple entries must be flagged to indicate the reason for their existence.
- Scan for missing runs. The most common example is the first run being aborted or lost for some reason, and the only entry in the MS Excel file is the second run. An entry for the first run must be inserted, flagged as invalid, and labeled as to the reason it was invalid. All punches taken from the filters MUST be accounted for and documented in the file.
- Pull the analysis folders and go through the analysis summaries and thermograms one by one. Check for the conditions listed in Section 6.4.2
 - Reflectance and Transmittance Regular OC Lower Split and Upper Split are within 5% and Regular EC Lower Split and Upper Split are within 20%. OC values which differ by more than 5%, unless due to a small change in laser signal resulting from an extremely clean or very dark sample, requires reanalysis. Comments should be added to the print out as follows:
 - If Regular OC Reflectance split is greater than 5% note “RO” in comments field; If Transmittance split is greater than 5% note “TO” in comments field.
 - If Regular EC Reflectance split is greater than 20% note “RE” in comments field; If Transmittance split is greater than 5% note “TE” in comments field.
 - Punch discoloration after analysis is complete (See Table 6.1 for m2 flag)
- Verify and resolve all circled items and missing flags.
 - Determine if analyses flagged by the operator are legitimate. These flags are determined by the operator at the end of the analysis run (Section 6.4) and are defined in Table 6-2.
 - If the temporary flag is not warranted, draw a line through the flag to indicate that it should be removed.
 - If the sample should be rerun, add it to a rerun list.
 - If the analysis has some anomaly, but still appears to be legitimate, either flag or add notes to the comments field as appropriate.

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- Analysis flags are defined in Table 6-1.
- Invalid samples without a definitive void flag must have an entry in the comments field to describe the reason that the sample is invalid. Typical notes and comments are presented in Table 6-3.
- Scan the OC and EC columns looking for unusually high or low values. At this time make sure that the field blanks and/or lab blanks are all close to one another. Circle any possible outliers for further investigation.
- Compare replicates against original run. The values should meet the following criteria:

Range	Criteria
OC, EC & TC < 10 $\mu\text{g}/\text{cm}^2$	< $\pm 1.0 \mu\text{g}/\text{cm}^2$
OC and TC $\geq 10 \mu\text{g}/\text{cm}^2$	< 10 % of average of the 2 values
EC $\geq 10 \mu\text{g}/\text{cm}^2$	< 20 % of average of the 2 values

- Check the OC/TC ratio. Typical rural samples should not be less than 0.65. Circle any possible outliers for further investigation.
- Scan for records where EC is greater than OC. These may require additional investigation, depending on loading and sample source. Circle records for further investigation.
- Scan blanks for OC being greater than $3.95 \times$ deposit area and for EC greater than the deposit area. Rerun any unusually high blanks.
- Compare primary and secondary filters for validity. Secondary filters should have OC and EC measurements less than the corresponding primary filter. Typical rural secondary filters should have $\text{EC} \leq 3.8$. OC should be less than or equal to 18. Circle any records that require further investigation.
- All operator-generated flags must be either converted to standard analysis flags (Table 6-1) or removed. The flags in Table 6-2 are temporary flags only and are not recognized as legitimate analysis flags at DRI.
- After all thermograms have been reviewed and all possible reruns have been identified, post the rerun list in the carbon room and have the reruns done as soon as possible.

Table 6-2. DRI Carbon Analysis Operator Temporary Data Validation Flags.

Flag	Description
EI	Error in sample ID
EA	Error in sample deposit area
ST	Suspect temperature profile
SF	Suspect FID signal
SL	Suspect laser signal
Mi	Miscellaneous problem
m2	Non-white sample punch after analysis
v	Invalid run
r	Replicate
b	Blank
i	Inhomogeneous
f	Filter media damaged
g	Sample deposit damaged
d	Sample dropped
n	Foreign substance on filter
w	Sample wet

Table 6-3. DRI Carbon Analysis Validation Comments

Comments	Description
"Anomalous laser"	Despite good initial laser, laser signal drifted above initial laser signal before dropping (typical of auto emissions).
"Operator error"	Used with "v" flag; operator exited program unexpectedly.
"Analyzer malfunction"	Used with "v" flag; analyzer malfunction or problem beyond the control of the operator such as plugged FID, broken oven heater, etc.
"Poor replicate"	Replicate is outside the normal criteria, but no reason can be found for the discrepancy.
"Poor initial laser"	Used with "v" flag; severe coupling or boat not pushed in time for calculation of initial laser signal.
"Potential contamination"	Used with "v" flag; rerun of sample yields lower values or different peaks. Typically used with blanks or reruns of replicates.
"Power failure"	Used with "v" flag; power surge or power failure.

- Review the data from the reruns, looking for inconsistencies. Confirm that the reasons for the rerun have been addressed. Mark the printout with the new values for manual insertion into the MS Excel or database file. Previous runs must be flagged as invalid or the reruns flagged as replicates.
- Finally, all comments, flags, insertions, and other changes made to the printout are entered into the MS Excel or database file. After all changes are made, generate a new printout. Label the new printout with the file name and printout date. Assemble a copy of the printout and the MS Excel or database file for the person putting the final report together.

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8 CHANGE DOCUMENTATION

7/24/2008 – Made following changes to document:

- Revised cover page to include signature lines
- Updated Section 2 (Apparatus, Instrumentation, Reagents and Forms) with current information and forms
- Updated Figures 2-1 and 2-3 with more current and detailed information
- Renamed Quantification to Calibration and moved to Section 3
- Moved Temperature Calibration to Section 3
- Updated text and formulas in Section 3.1.3.1 under preparation of standards for clarification and accuracy.
- Updated Figure 3-4 with new worksheet and new volumes.
- Moved Procedures to Section 4 and updated to include additional details where needed
- Moved Quantification to Section 5; added precision calculations.
- Updated Quality Control (Section 6)
- Updated References as needed (Section 7)
- Added Section 8 (Change Documentation)
- Added Section 9 (Appendix A)

APPENDIX A: Abbreviations and Acronyms

°C	Degrees Celsius
µg/m ³	Micrograms per cubic meter
µl	Microliters
Cal Gas	Calibration Gas
Calibration Injection	The injection of calibration gases, either CO ₂ or CH ₄ , into the sample stream at the beginning and end of each work day to check instrument performance.
Calibration Peak	The FID peak resulting from the automatic injection of methane calibration gas (CH ₄ /He) at the end of each analysis run for each sample. All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain µg carbon per sample punch.

Chemicals Used:

H ₂	Hydrogen
HF	Hydrofluoric Acid
HCl	Hydrochloric Acid
He	Helium
CO ₂	Carbon Dioxide
CH ₄	Methane
O ₂	Oxygen
Na	Sodium
SiO ₂	Silicon Dioxide
K	Potassium
KHP	Potassium hydrogen phthalate
V	Vanadium
Cr	Chromium
Mn	Manganese
MnO ₂	Manganese Dioxide
Co	Cobalt
Ni	Nickel
Cu	Copper
Pb	Lead

DRI	Desert Research Institute
EC	Elemental Carbon
EC1	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 580 °C.
EC2	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere from 580 to 740 °C.
EC3	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere from 740 to 840 °C.
Elemental Carbon (EC)	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 580, 740, and 840 °C minus any pyrolyzed OC.

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FID	Flame Ionization Detector
FID Split Time	The time at which the laser split occurs plus the transit time required for thermally evolved carbon to travel from the sample punch to the FID.
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
High Temperature EC	Carbon evolved from the filter punch in a 98% He/2% O ₂ atmosphere at 740 and 840 °C minus any pyrolyzed organic carbon present in these two peaks. This is EC minus the first EC peak (EC1).
High Temperature OC	Carbon evolved from the filter punch in a He-only atmosphere at 280, 480, and 580 °C plus pyrolyzed organic carbon. This is OC minus the first OC peak (OC1).
IMPROVE IMPROVE_A Thermal Protocol	Interagency Monitoring of PROtected Visual Environments A thermal protocol is used in carbon analyzers to quantify carbon fractions evolved at different temperature plateaus. The IMPROVE_A thermal protocol derives from the IMPROVE thermal protocol initiated in 1987 (Chow et al., 2005).
Laser Split	The separation between OC and EC, which depends on the laser-measured reflectance and/or transmittance of the filter punch returning to its initial value. At this point all pyrolyzed OC has been removed and EC is beginning to evolve.
Lower Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).
LQL	Lower quantifiable limit
M	Mole
MDL	Minimum detection limit
NIST	National Institute of Science and Technology
OC	Organic Carbon
OC1	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from ambient (~25 °C) to 140 °C.
OC2	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 140 to 280 °C.
OC3	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 280 to 480 °C.
OC4	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 480 to 580 °C.
OP	The carbon evolved from the time that the carrier gas flow is changed from He to 98% He/2% O ₂ at 580 °C to the time that the laser- measured filter reflectance (OPR) or transmittance (OPT) reaches its initial value. A negative sign is assigned if the laser split occurs before the introduction of O ₂ .
OPR	Pyrolyzed carbon measured by reflectance

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OPT	Pyrolyzed carbon measured by transmittance
Organic Carbon (OC)	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere at 140, 280, 480 and 580 °C plus pyrolyzed organic carbon. This is the same as Volatile Organic Carbon (VOC) plus high- temperature OC.
psi	Pounds per square inch
Pyrolysis	The conversion of OC compounds to EC due to thermal decomposition; this may be envisioned as "charring" during the organic portion of the analysis.
QA	Quality Assurance
QC	Quality Control
Regular Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value.
SiO ₂	Silicon Dioxide
STN	Speciation Trends Network
TC	Total Carbon
TOR	Thermal/Optical Reflectance
TOT	Thermal/Optical Transmittance
Total Carbon (TC)	All carbon evolved from the filter punch between ambient and 840 °C under He and 98% He /2% O ₂ atmospheres.
VOC	Volatile Organic Carbon
UHP	Ultra-High Purity
Upper Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).
ΔT	Temperature Deviation

Title: Analysis of Semi-Volatile Organic Compound by GC/MS

DRI STANDARD OPERATING PROCEDURE

**Analysis of Semi-volatile Organic Compounds by GC/MS
DRI SOP #2-750.5
Revised**

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1.0 PURPOSE/APPLICABILITY

This method describes the analysis of semi-volatile organic compounds (SVOC) in air. The SVOCs include non-polar analysis of Polycyclic Aromatic Hydrocarbons (PAH), Aliphatic Hydrocarbon Analysis (Alkanes), Hopanes and Steranes, and Polar analysis. The method uses a sampling train consisting of a Teflon-impregnated glass fiber (TIGF) filter backed up by a PUF/XAD/PUF sandwich solid adsorbent. The separate portions of the sampling train are extracted and combined dependent on analyses. The analysis method is gas chromatography/mass spectrometry (GC/MS). Mass spectrometry provides definitive identification of SVOCs.

This method follows the procedure described in EPA Method TO-13 (June 1988, EPA/600-4-89/017). The exceptions are that 1) the DRI procedure uses a XAD-4 sandwich adsorbent trap where TO-13 recommends either PUF or XAD-2, and 2) the DRI procedure calls for more rigorous cleaning than the EPA method.

2.0 MATERIALS/APPARATUS

2.1 Sampling Substrates

100 mm TIGF filters (Pall Gellman, ultrapure quality), PUF, and XAD-4 (Fisher Scientific) are obtained. Cleaning is as per Section 4 below. All solvents are Fisher Scientific Optima or HPLC grade.

2.2 GC/MS

The chromatographic system consists of a Varian CP-3800 gas chromatograph equipped with an 8200 CX Autosampler and interfaced to a Varian Saturn 2000 Ion Trap Mass Spectrometer. The alternative system consists of a Varian CP-3800 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer. Column is a CP-Sil8 30mx0.25 mmX025XX (Chrompack).

3.0 PERSONNEL QUALIFICATION

This SOP assumes that personnel performing the procedures are familiar with basic laboratory practice and operation of Dionex Accelerated Solvent Extractor (ASE), rotary evaporators, and the Varian GC/MS system and Saturn Workstation 5.2 computer software. Specific requirements for these instruments are found in the appropriate manuals.

4.0 SUBSTRATE CLEANING PROCEDURE

4.1. Filters

Teflon-impregnated glass fiber (TIGF) filters (Pall Life Sciences, Type T60A20) are cleaned by sonication for 10 minutes in dichloromethane (CH_2Cl_2) twice, with the solvent replaced and drained, and sonicated for 10 minutes in methanol twice with the solvent replaced. Filters are then dried in a vacuum oven at -15 to -20 in Hg, 50°C for minimum of 24 hours, weighed (if necessary), placed in foil packages that have been fired at 500°C for 4 hours, placed in Uline metallic ZipTop static shielding bags, and stored at room temperature.

If quartz filters (Pall Gellman, ultrapure quality), are used, they are baked at 900°C for 4 hr before use.

4.2 PUF Plugs

PUF plugs are cleaned by first washing with distilled water, followed by Dionex ASE extraction for 15min/cell with ~ 170 mL acetone at 1500 psi and 80°C , followed by Dionex ASE extraction for 15min/cell with ~ 170 mL of 10% diethyl ether in hexane under the same conditions. The extracted PUF plugs are dried in a vacuum oven at -15 to -20 in Hg, 50°C for approximately 3 days or until no solvent odor is detected. If storage is necessary, PUF plugs are stored in clean 1L glass jars with Teflon lined lids wrapped in aluminum foil. Powder-free nitrile gloves are worn at all times when handling PUF plugs.

4.3 XAD-4

New XAD-4 is washed with LiquinoxTM soap and hot water, followed by DI water. It is then placed in a Buchner funnel under vacuum, then transferred to the Dionex ASE and extracted for 15min/cell with ~ 170 mL of methanol at 1500 psi and 80°C , followed by dichloromethane (CH_2Cl_2), then acetone under the same instrument conditions. The XAD-4 is then dried in a vacuum oven at -15 to -20 in Hg and 50°C . The cleaned XAD-4 is then transferred to a clean 1L glass jars with an air tight teflon-lined lid. The jar is wrapped with aluminum foil to protect the XAD-4 from light, and stored in a clean room at room temperature.

4.4 Certification of Substrate

An aliquot of each batch of cleaned XAD-4 (20g) and TIGF filters are extracted same as samples. Deuterated standards are added to the sample prior to extraction in the Dionex

ASE with ~170 mL dichloromethane (CH₂Cl₂) for 15 min/cell at 1500 psi and 80°C, followed by ~170 mL acetone extraction under the same conditions. The extract is then concentrated to 1ml and analyzed by GC/MS. Any batch determined to have excessive impurities (more than 10 ng/ul of naphthalene and other compounds in method) will be re-cleaned and checked again for purity.

4.5 Assembly of XAD and PUF/XAD/PUF Cartridge

The glass cartridges and screen assemblies are washed with Liquinox™ soap and hot water followed by DI water and oven dried. Powder-free nitrile gloves are worn at all times during the cartridge assembly. For XAD-4 cartridges, one assembly of spring, o-ring and screen is placed at the bottom of a clean glass cartridge followed by 20g of XAD-4 and another assembly of screen, o-ring and spring. The XAD cartridge is then placed in Uline ZipTop metallic static shielding bags and stored in a clean room at room temperature.

For PUF/XAD-4/PUF cartridges, one PUF plug is put at the bottom of a clean glass cartridge followed by 10 g of XAD-4 and a second PUF plug. The PUF/XAD/PUF cartridge is then placed in Uline ZipTop metallic static shielding bags and stored at room temperature.

5.0 SAMPLE SHIPPING, RECEIPT, AND STORAGE

XAD-4 cartridge and filter sets are assigned a unique Project Media Identification (PMI) number and logged (date stamped) into the Laboratory Information Management System (LIMS) when assembled and shipped. Cartridges are packed in a tin can with field data sheets with the same unique PMI number and shipped in coolers on blue ice prior overnight.

In the field, exposed samples are stored at 0-4°C in a refrigerator or freezer and shipped to DRI priority overnight in ice chest (DRI's original shipping containers) with blue ice. Upon receipt by the laboratory, the samples are logged into the LIMS by PMI number, and field data is recorded (sampling location, date, and start and stop time, elapse timer, and flow rate). If the time span between sample login and extraction is greater than 24 hours, the samples must be kept cold at 0-4°C in a freezer or refrigerator. The exposure of the sample media to ultraviolet light emitted by fluorescent lights must be minimized.

6.0 EXTRACTION OF SUBSTRATE

6.1 Addition of Internal Standards

6.1.1 Polycyclic Aromatic Hydrocarbon (PAH), non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

naphthalene-d ₈	9.486	ng/μl
biphenyl-d ₁₀	7.008	ng/μl
acenaphthene-d ₁₀	5.997	ng/μl
phenanthrene-d ₁₀	5.991	ng/μl
anthracene-d ₁₀	5.000	ng/μl
pyrene-d ₁₂	4.993	ng/μl
benz(a)anthracene-d ₁₂	2.004	ng/μl
chrysene-d ₁₂	1.997	ng/μl
benzo[k]fluoranthene-d ₁₂	1.000	ng/μl
benzo[e]pyrene-d ₁₂	0.700	ng/μl
benzo[a]pyrene-d ₁₂	0.703	ng/μl
benzo[g,h,i]perylene-d ₁₂	0.600	ng/μl
coronene-d ₁₂	0.500	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples and the final volume of extracts during analysis.

6.1.2 Hopane and Sterane, non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

cholestane- d ₆	0.375	ng/μl
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The amount of internal standards added should correspond to the expected range of concentrations found in real samples.

6.1.3 Aliphatic Hydrocarbon Analysis (Alkanes), non-polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter, PUF/XAD/PUF):

dodecane-d ₂₆	10.9	ng/μl
hexadecane-d ₃₄	2.36	ng/μl
eicosane-d ₄₂	1.88	ng/μl

octacosane-d ₅₈	4.9	ng/μl
tetracosane-d ₅₀	1.89	ng/μl
hexatriacontane-d ₇₄	10.2	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples.

6.1.4 Polar Organic Compounds, polar

Prior to extraction, the following deuterated internal standards are added to each sample (filter-sorbent pair):

cholesterol-2,2,3,4,4,6-d ₆	9.85	ng/μl
levoglucosan-u-13C ₆	31.25	ng/μl
hexanoic-d ₁₁ acid	4.5	ng/μl
benzoic-d ₃ acid	4.5	ng/μl
decanoic-d ₁₉ acid-	4.5	ng/μl
palmitic-d ₃₁ acid	4.5	ng/μl
heptadecanoic-d ₃₃ acid	4.4	ng/μl
myristic-d ₂₇ acid	3.3	ng/μl
succinic-d ₄ acid	2.55	ng/μl
phthalic 3,4,5,6-d ₄ acid	4.6	ng/μl

The amount of internal standards added should correspond to the expected range of concentrations found in real samples and the final volume of extracts during analysis.

6.2 Extraction of PUF, XAD-4, and Filter

Depending on analyses, PUF, XAD-4 and Filter will be extracted in the following combinations. Solvents are selected to optimize the polarity range desired for analyses.

6.2.1 Non-Polar Analysis Only

Filters and XAD-4 are extracted twice with approximately ~170 mL of dichloromethane (CH₂Cl₂) using the Dionex ASE for 15 min/cell at 1500 psi and 80°C.

Since PUF media degrades when extracted with dichloromethane, the PUFs are extracted twice with ~170 mL of acetone using the Dionex ASE for 15 min/cell at 1500 psi and 80°C. This method gives good recovery for PAH, aliphatic hydrocarbons (alkanes), and hopanes and steranes.

6.2.2 Polar and Non-Polar Analyses

Filters and XAD-4 are extracted with ~170 mL dichloromethane (CH₂Cl₂) using the Dionex ASE for 15 min/cell at 1500 psi and 80°C followed by ~170 mL acetone extraction under the same conditions.

Since PUF media degrades when extracted with dichloromethane, the PUFs are extracted twice with ~170 mL of acetone using the Dionex ASE for 15 min/cell at 1500 psi and 80°C. This method gives good recovery for PAH, aliphatic hydrocarbons (alkanes), hopanes and steranes, and polar organic compounds.

6.3 Treatment of Extracts

6.3.1 Non-Polar Analysis Only

Extracts are concentrated to ~1ml by rotary evaporation at 35 °C under gentle vacuum, and filtered through a 0.2 µm Anotop™ 10 Whatman leuc-lock filter on 4 mL glass syringe), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate is collected in a 4 mL amber glass vial for a total volume of ~4 mL.

Approximately 200 µl of acetonitrile is added at this time and the extract is split into two fractions. Each fraction is then concentrated using a Pierce Reacti-Therm under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971) to 100-200 µL. The final extract volume is adjusted to 100 µL with acetonitrile.

6.3.2 Polar and Non-Polar Analyses

Extracts are concentrated to ~1ml by rotary evaporation at 35 °C under gentle vacuum, and filtered through a 0.2 µm PTFE disposable filter device (Whatman Pura disc™ 25TF), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate is collected in a 4 mL amber glass vial for a total volume of ~4 mL.

Approximately 200 µl of acetonitrile is added at this time and the extract is split into two fractions. Each fraction is then concentrated under a gentle stream of ultra-high purity (UHP) nitrogen with hydrocarbon and water traps to 100-200 µL. The final extract volume is adjusted to 100 µL with acetonitrile.

6.4 Cleanup of Samples (non-polar analysis)

For complex samples that contain analytical interference, the following method is used to clean up the sample using silica gel semi-prep Solid Phase Extraction (SPE 6-mL 0.5-g LC-SI, Supelco Silica).

1. Assuming SVOC in 100 μ L acetonitrile, concentrate to 25 μ L and add 25 μ L dichloromethane and 150 μ L hexane.
2. Condition SPE-Silica cartridge with 1.5 mL hexane/benzene (1:1), followed by 1.5 mL hexane.
3. Transfer sample into the SPE-Silica cartridge.
4. Elute sample with 1.5 mL hexane, followed by 3 mL hexane/benzene (1:1) in separate 4 mL vials.
5. Concentrate to 100 μ L (only hexane should remain) and transfer to GC vial insert and concentrate to 20 μ L.
6. Rinse original vial with 100 μ L dichloromethane and concentrate to 40 μ L (hexane/DCM (1:1)) and dilute to total volume of 100 μ L with acetonitrile.

The hexane fraction contains the non-polar aliphatic hydrocarbons (alkanes), and hopanes and steranes, and the hexane/benzene fraction contains the PAH and N-PAH.

6.5 Silylation of Polar Organic Compounds (polar analysis)

If extracts have been split for polar and non-polar analysis, the fraction for the polar analysis is derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, cholesterol, sitosterol, and levoglucosan. Depending upon the expected range of analytes, it is recommended to split the second fraction into two equal fractions, thus providing a second opportunity for a clean silylation reaction.

1. The extract is reduced to a volume of 50 μ L using a Pierce Reacti-Therm under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971).
2. 50 μ L of silylation grade pyridine is added to vial.
3. 150 μ L of bis(trimethylsilyl)trifluoroacetamide is added slowly to each vial and immediately capped.
4. The sample is then placed into thermal plates (custom) containing individual vial wells with the temperature maintained at 70°C for 3 hours.
5. The samples are then analyzed by GC/MS within 18 hours.

7.0 ANALYSIS

7.1 Instrument Method

The samples are analyzed by the electron impact (EI) GC/MS technique, using a Varian CP-3800 gas chromatograph equipped with a 8200 CX Autosampler and interfaced to a Vairan Saturn 2000 Ion Trap Mass Spectrometer or Varian CP-3400 gas chromatograph with a model CP-8400 Autosampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer

Injections are 1 μ l in size in the splitless mode onto a 30m long 5% phenylmethylsilicone fused silica capillary column (J&W Scientific type DB-5ms): CP-Sil8 Chrompack (30m x 0.25mm x 0.25 mm) for PAH, hopanes and steranes, alkanes and polars; and CP-Sil24 Chrompack (30m x 0.25mm x 0.25 mm) for N-PAH.

Identification and quantification of the analytes are made by Selected Ion Storage (SIS), by monitoring the molecular ions of each analyte and each deuterated analyte.

7.2 Preparation Stage

A. The instrument (GC/MS) preparation steps are as follows:

- 1) Check for air and water in the system (Ion Time = 100, a total ion current (TIC) below 700 is preferred).
- 2) Adjust calibration gas pressure for Ion Trap instrument (75% preferred).
- 3) Check calibration gas pressure ~ 75%.
- 4) Perform autotune for electron multiplier setting, mass calibration, and RF ramp.

Identification and quantification of the analytes are made by Selected Ion Storage (SIS), by monitoring the molecular ions of each analyte and each deuterated analyte.

7.3 Calibration

Calibration curves are made by the molecular ion peaks of the analytes using the corresponding deuterated species as internal standards. If there is no corresponding deuterated species, the one most closely matching in volatility and retention characteristics is used.

National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH), with the addition of the internal standards listed in Section 6.1.1-6.1.4 and the targeted PAH not present in this mixture, is used to make calibration

solutions. Six concentration levels for each analyte of interest are employed. Table 1 lists the concentration levels of standard compounds in calibration solutions. The calibration curve for each calibrated compound is constructed; Figures 1 through 6 show examples of acceptable calibration curves. After the calibration is completed, a standard solution is injected to perform calibration checks. If deviations from the true values exceed $\pm 20\%$, the calibration procedure is repeated or new calibration levels must be prepared. One replicate analysis and one calibration check is performed for every 10 injections of samples. If difference between true and measured concentrations exceeds $\pm 20\%$, the system is recalibrated. During batch processing, calibration is performed before each batch.

8.0 REPORTING

Each sample is reported initially in terms of mass per sample ($\mu\text{g}/\text{sample}$). Ambient concentrations in terms of mass per volume (i.e., ng/m^3 or other units if requested) are reported based upon the sample volume adjusted for ambient temperature and pressure, or reported as "standard" volume.

All information for the sample is recorded and combined into both a printed report and an Excel file for inclusion in the database (see Appendix).

8.1 Method Detection Limits (MDLs)

Method detection limits are 0.01-0.03 $\text{ng}/\mu\text{l}$ for PAH, hopane and sterane, and alkane compounds, and 0.03-0.04 $\text{ng}/\mu\text{l}$ for polar compounds.

8.2 Measurement Uncertainty

Measurement uncertainty is reported as one-sigma standard deviation between replicate tests (when 3 tests conducted under same conditions) or the combined root mean square of the analytical measurement uncertainty, which is defined by the following equation:

$$\sqrt{(\text{replicate precision} * \text{analyte concentration})^2 + (\text{analyte detection limit})^2}$$

This equation incorporates the analyte detection limit for each compound so when concentrations approach zero the error is reported as the analyte detection limit. When multiple samples are pooled the difference between samples is typically greater than the precision of any of the analytical techniques employed. Most data has relatively small reported measurement uncertainty's which shows the reproducibility of the samples.

When larger errors (>30% of reported concentration) are observed, it is typically because the concentrations of the analyte were close to the detection limit of the measurements.

Table 1. Calibration Levels for PAH analysis (bold compounds co-elute and are quantified together)

Compound	Level 1 (ng/uL)	Level 2 (ng/uL)	Level 3 (ng/uL)	Level 4 (ng/uL)	Level 5 (ng/uL)	Level 6 (ng/uL)
1-ethylnaphthalene	0.359	0.718	1.436	2.873	11.491	45.965
1,2-dimethylnaphthalene	0.361	0.722	1.444	2.887	11.548	46.193
1,4-chrysenequinone	0.240	0.479	0.958	1.917	7.667	30.667
1,6 + 1,3 dimethylnaphthalene	0.719	1.438	2.876	5.753	23.012	92.047
1,8-dimethylnaphthalene	0.240	0.481	0.962	1.924	7.695	30.781
1-methylfluorene	0.298	0.596	1.192	2.383	9.533	38.133
1-methylphenanthrene	0.200	0.400	0.799	1.598	6.392	25.568
1-methylpyrene	0.240	0.481	0.961	1.922	7.688	30.752
1-phenylnaphthalene	0.199	0.398	0.796	1.591	6.365	25.461
2-ethylnaphthalene	0.357	0.714	1.428	2.856	11.424	45.696
1,4+1,5+2,3-dimenafluene	1.078	2.156	4.313	8.625	34.501	138.005
2,6-dimethylnaphthalene	0.352	0.704	1.408	2.817	11.267	45.067
2-methylbiphenyl	0.360	0.720	1.441	2.881	11.525	46.102
2-methylphenanthrene	0.246	0.492	0.983	1.967	7.867	31.467
2-phenylnaphthalene	0.358	0.716	1.433	2.866	11.463	45.853
3,6-dimethylphenanthrene	0.203	0.406	0.813	1.625	6.500	26.000
3-methylbiphenyl	0.361	0.721	1.442	2.884	11.537	46.149
4H-cyclopenta(def)phenanthrene	0.000	0.000	0.000	0.000	0.000	0.000
4-methylbiphenyl	0.369	0.738	1.475	2.950	11.800	47.200
4-methylpyrene	0.240	0.479	0.958	1.917	7.667	30.667
5+6 methylchrysene	0.559	1.119	2.237	4.475	17.899	71.595
7-methylbenz(a)anthracene	0.279	0.558	1.117	2.233	8.933	35.733
7-methylbenzo(a)pyrene	0.290	0.579	1.158	2.317	9.267	37.067
9,10-dihydrobenzo(a)pyren-7(8H)-one	0.281	0.561	1.122	2.244	8.976	35.904
9-anthraldehyde	0.371	0.742	1.483	2.967	11.867	47.467
9-fluorenone	0.280	0.560	1.120	2.240	8.961	35.845
9-methylanthracene	0.239	0.479	0.958	1.916	7.663	30.653
acenaphthene*	0.201	0.402	0.804	1.609	6.435	25.739
acenaphthenequinone	0.202	0.404	0.808	1.617	6.467	25.867
acenaphthylene	0.200	0.400	0.800	1.600	6.400	25.600
anthrone	0.277	0.554	1.108	2.217	8.867	35.467

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BaP*	0.160	0.321	0.642	1.283	5.133	20.533
benz(a)anthracene*	0.200	0.400	0.799	1.599	6.395	25.579
benz(a)anthracene-7,12-dione	0.279	0.558	1.117	2.233	8.933	35.733
benzanthrone	0.360	0.720	1.440	2.880	11.518	46.073
anthracene*	0.159	0.319	0.638	1.276	5.103	20.411
anthraquinone	0.280	0.559	1.119	2.237	8.949	35.795
benzo(k*+b+j)fluoranthene	0.397	0.794	1.587	3.174	12.697	50.789
benzo(g,h,i)perylene*	0.200	0.400	0.800	1.600	6.401	25.602
benzo(c)phenanthrene	0.200	0.400	0.800	1.601	6.403	25.613
benzonaphthothiophene	0.240	0.479	0.958	1.917	7.667	30.667
BeP*	0.202	0.403	0.807	1.613	6.453	25.813
chrysene*	0.190	0.379	0.758	1.517	6.067	24.267
coronene*	0.160	0.320	0.640	1.280	5.118	20.474
dibenz(ah+ac)anthracene	0.323	0.645	1.291	2.582	10.327	41.307
dibenzofuran	0.278	0.556	1.111	2.223	8.890	35.560
fluorene	0.241	0.481	0.963	1.925	7.700	30.800
fluoranthene	0.252	0.503	1.006	2.013	8.050	32.200
indeno(1,2,3-cd)pyrene	0.161	0.321	0.642	1.284	5.136	20.544
perinaphthenone	0.279	0.558	1.116	2.232	8.928	35.712
perylene	0.200	0.400	0.800	1.600	6.400	25.600
phenanthrene*	0.201	0.401	0.802	1.604	6.417	25.667
pyrene*	0.196	0.392	0.783	1.567	6.267	25.067
retene	0.277	0.555	1.109	2.219	8.875	35.499
2,3,5-trimethylnaphthalene	0.199	0.399	0.797	1.594	6.378	25.511
2,4,5-trimethylnaphthalene	0.277	0.554	1.108	2.217	8.867	35.467
1,4,5-trimethylnaphthalene	0.239	0.478	0.957	1.914	7.654	30.616
xanthone	0.240	0.481	0.961	1.923	7.691	30.763
1-methylnaphthalene	0.361	0.723	1.446	4.338	17.351	69.403
2,7-dimethylnaphthalene	0.300	0.599	1.198	3.594	14.377	57.507
bphenyl*	0.360	0.720	1.440	4.319	21.597	107.983
bibenzyl	0.362	0.724	1.448	4.345	21.723	108.617
2-methylnaphthalene	0.430	0.860	1.720	5.160	25.800	129.000
naphthalene*	0.359	0.717	1.435	5.739	34.432	206.592

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 2. Calibration Levels for Hopanes and Steranes Analysis

Compound	Level 1 ng/uL	Level 2 ng/uL	Level 3 ng/uL	Level 4 ng/uL	ng/uL
cholestane-d6*	0.750	0.750	0.750	0.750	0.750
cholestane	0.250	0.500	1.000	2.000	4.000
17 α -21 β (H) Hopane (19)	0.250	0.500	1.000	2.000	4.000
17 β (H)-30-Norhopane (17a)	0.250	0.500	1.000	2.000	4.000
17 β (H)-21 β (H) Hopane (23)	0.250	0.500	1.000	2.000	4.000

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 3. Calibration Levels for Aliphatic Hydrocarbon Analysis (Alkanes), bold compounds co-elute and are quantified together

Compound	Level 1 ug/uL	Level 2 ug/uL	Level 3 ug/uL	Level 4 ug/uL	Level 5 ug/uL	Level 6 ug/uL	Level 7 ug/uL	Level 8 ug/uL
2,6,10-trimethylundecane_(norfarnesane)	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
2,6,10-trimethyldodecane_(farnesane)	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetradecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptadecane + 2,6,10,14-tetramethylpentadecane_pristane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-hexadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
2,6,10-trimethylpentadecane_norpristane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-decylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-undecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octadecane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000

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Compound	Level 1 ug/uL	Level 2 ug/uL	Level 3 ug/uL	Level 4 ug/uL	Level 5 ug/uL	Level 6 ug/uL	Level 7 ug/uL	Level 8 ug/uL
2,6,10,14-tetramethylhexadecane_ phytane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-dodecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tridecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetradecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heneicosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-eicosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-docosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tricosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetracosane-d50*	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-tetracosane* + n-hexadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-pentacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-nonadecylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-heptacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-eicosylcyclohexane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-hexacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000
n-octacosane	0.050	0.500	1.000	100.000	200.000	2.500	5.000	10.000

*deuterated forms of these compounds are added to samples prior to extraction as surrogate for quantitation

Table 4. Calibration Levels for Polar Organic Compounds Analysis

Compound	Level 1 ng/uL	Level 2 ng/uL	Level 3 ng/uL	Level 4 ng/uL	Level 5 ng/uL	Level 6 ng/uL
4-pentenoic	0.323	2.155	6.464	10.773	15.083	18.315
hexanoic acid	0.300	2.400	7.199	12.960	18.144	21.384
heptanoic	0.334	2.228	6.685	11.142	15.598	18.941
me-malonic	0.321	2.570	7.710	12.850	17.990	21.203
guaiacol	0.268	2.680	7.370	15.075	20.100	25.125
benzoic acid	0.300	2.400	7.199	12.960	18.144	21.384

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octanoic	0.314	2.091	6.272	10.453	14.635	17.771
glycerol	0.348	2.320	6.960	11.600	16.240	19.720

Compound	Level 1 ng/uL	Level 2 ng/uL	Level 3 ng/uL	Level 4 ng/uL	Level 5 ng/uL	Level 6 ng/uL
maleic	0.328	2.620	7.860	13.100	18.340	21.615
succinic acid	0.300	2.400	7.199	12.960	17.820	21.060
4-methylguaiacol	0.385	3.851	10.591	21.664	28.885	36.106
methylsuccinic acid	0.300	2.400	7.199	12.960	17.820	21.060
o-toluic	0.313	2.500	7.500	12.500	17.500	20.625
picolinic acid	0.300	2.400	7.199	12.960	18.144	21.384
m-tolic	0.327	2.613	7.840	13.067	18.293	21.560
1,2,4-butanetriol	0.300	2.400	7.199	12.960	18.144	21.384
nonanoic	0.318	2.120	6.360	10.600	14.840	18.020
p-toluic	0.169	1.128	3.384	5.640	7.896	9.588
3-methylpicolinic	0.321	2.568	7.704	12.840	17.976	21.186
6-methylpicolinic	0.319	2.550	7.650	12.750	17.850	21.038
2,6-dimethylbenzoic	0.269	2.150	6.450	10.750	15.050	17.738
4-ethylguaiacol	0.260	2.598	7.146	14.616	19.488	24.360
syringol	0.266	2.655	7.301	14.934	19.913	24.891
glutaric acid	0.300	2.400	7.199	12.960	17.820	21.060
2-methylglutaric	0.319	2.550	7.650	12.750	17.850	21.038
2,5-dimethylbenzoic	0.260	2.080	6.240	10.400	14.560	17.160
3-methylglutaric	0.261	2.085	6.256	10.427	14.597	17.204
2,4-dimethylbenzoic	0.263	2.100	6.300	10.500	14.700	17.325
3,5-dimethylbenzoic	0.256	2.050	6.150	10.250	14.350	16.913
2,3-dimethylbenzoic	0.272	2.172	6.516	10.860	15.204	17.919
n-decanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
4-allylguaiacol	0.284	2.843	7.817	15.990	21.320	26.650
4-methylsyringol	0.283	2.832	7.788	15.930	21.240	26.550
3,4-dimethylbenzoic	0.269	2.153	6.460	10.767	15.073	17.765
adipic acid	0.300	2.400	7.199	12.960	17.820	21.060
t-2-decenoic	0.318	2.123	6.368	10.613	14.859	18.043
cis-pinoic acid	0.300	2.400	7.199	12.960	17.820	21.060
3-methyladipic	0.328	2.623	7.868	13.113	18.359	21.637
4-formylguaiacol	0.283	2.832	7.788	15.930	21.240	26.550
undecanoic	0.315	2.523	7.570	12.617	17.663	20.818
isoeugenol	0.300	3.000	8.250	16.875	22.500	28.125
pimelic acid	0.300	2.400	7.199	12.960	17.820	21.060

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acetovanillone	0.266	2.655	7.301	14.934	19.913	24.891
lauric acid	0.300	2.400	7.199	12.960	17.820	21.060

Compound	Level 1 ng/uL	Level 2 ng/uL	Level 3 ng/uL	Level 4 ng/uL	Level 5 ng/uL	Level 6 ng/uL
phthalic acid	0.300	2.400	7.199	12.960	17.820	21.060
levoglucosan	0.300	2.400	7.199	12.960	18.144	21.384
syringaldehyde	0.266	2.655	7.301	14.934	19.913	24.891
tridecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
suberic acid	0.300	2.400	7.199	12.960	17.820	21.060
isophthalic acid	0.300	2.400	7.199	12.960	17.820	21.060
azelaic acid	0.300	2.400	7.199	12.960	17.820	21.060
myristoleic	0.307	2.046	6.138	10.230	14.322	17.391
myristic acid	0.300	2.400	7.199	12.960	17.820	21.060
sebacic	0.165	1.098	3.294	5.489	7.685	9.332
pentadecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
undecanedioic	0.165	1.099	3.296	5.493	7.691	9.339
palmitoleic	0.318	2.120	6.360	10.600	14.840	18.020
palmitic acid	0.300	2.400	7.199	12.960	18.144	21.384
isostearic	0.312	2.080	6.240	10.400	14.560	17.680
dodecanedioic acid	0.165	1.099	3.296	5.493	7.691	9.339
heptadecanoic	0.323	2.585	7.756	12.927	18.097	21.329
1,11-undecanedicarboxylic	0.171	1.141	3.424	5.707	7.989	9.701
oleic acid	0.300	2.400	7.199	12.960	18.144	21.384
elaidic acid	0.300	2.400	7.199	12.960	17.820	21.060
stearic acid	0.300	2.400	7.199	12.960	18.144	21.384
1,12-dodecanedioic	0.166	1.105	3.315	5.525	7.735	9.393
nonadecanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
dehydroabietic acid	0.300	2.400	7.199	12.960	17.820	21.060
eicosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
pentadecanedioic acid	0.166	1.105	3.315	5.525	7.735	9.393
abietic acid	0.300	2.400	7.199	12.960	18.144	21.384
heneicosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
docosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
tricosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
tetracosanoic acid	0.300	2.400	7.199	12.960	17.820	21.060
cholesterol	0.750	5.999	17.998	32.400	44.550	52.650
b-sitosterol	0.750	5.999	17.998	32.400	44.550	52.650

APPENDIX

SVOC Program Information

I. Before Running

A. Each project must be listed in the database "H:\db_prg\oalproj.dbf.". Fill in the following columns:

Column	Value
NUM	Use the next number in sequence
PROJ_NAME	A short description you will recognize
PROJ_CODE	The two-digit project code MUST be unique
ROOT_DIR	The directory where the project data are stored
STATUS	"c" for current, or "o" for old
SVOC	enter 1 to run the SVOC programs, 0 otherwise.

B. For each project, there is a list of target compounds for analysis. This list is in the directory "H:\db_calib\svoc\" and it is called AAcmpd.dbf, where AA is the project code in the oalproj.dbf database. In this same directory is a database called "Template.dbf" which is a template you can copy to make the new ones. The fields you must fill in are:

Column	Description
Field_Name	The mnemonic for the PAH or PAH uncert.
Field_Type	ignore this
Field_Len	ignore this
Field_Dec	ignore this
Compound	The long name for the compounds only, enter nothing for uncert. This MUST exactly match the way it is in the mass spec calibration file.
Type	Enter "c" for a compound, nothing for uncert.

C. If you intend to import GCMS data, you must use Lantastic to attach the GC/MS computer's c: (hard) drive to a drive on the local machine.

II. Running

A. Run the genbatch program and follow inputs.

B. IF this is the first time you have worked on this project, you must first run the option "N" which creates a new set of files. This will make the files you will need.

C. You now can quit the programs and enter samples into the 'lab' database. This is the database the import program uses to determine what to import.

D. If the sample is run diluted, that file name and process status are also noted. When there is no diluted sample, just leave the name blank and set the dil_f_proc bit to zero. After the samples are imported, the program automatically enters a 2 for the proc bit.

Column	Description
PID	Standard ID
XMSFLAG	Mass Spec flag
F_NAME	Mass Spec file name for main analysis
F_PROC	Process bit for main (0=do nothing, 1= import normally, 2=import done).
DIL_F_NAME	Mass Spec file name for diluted analysis (if done)
DIL_F_PROC	Process bit for diluted (0=do nothing, 1= import normally, 2=import done).
SAMPLNO	Sample number
LOT	Lot numbers
ANALDATE	Date of analysis
COMMENTS	Notes

E. Once the import is done, AND the field data have been entered, you may continue with the rest of the processing, simply by following the sequence.

F. For the first batch of any project, the menu looks like:

```
** FILE CREATING FOR BATH 1 ONLY **  
N FOR Creating New Project Files  
6 FOR Importing XMS data.  
** Copying files from current Batch \data to \report  
3 FOR Copying Field data.  
4 FOR Copying analysis (xms) data.  
** Continue Processing Field  
5 FOR Processing Field data file.  
** Continue Processing Analysis (xms) file.  
7 FOR Running REP.  
8 FOR Merge FLD and XMS files to CHM file.  
9 FOR Calculate blank values and blank uncertainty.  
10 FOR Convert chm file to con file (ug/m3).
```

Simply follow the sequence through. Note, before going to Step 3 and beyond, you must first make sure the field and xms data are all input.

III. Continuing a Project: Batch 2 and Following.

A. The menu for batch 2 and following looks like:

**** Copying files from previous Batch \report to current \data directories**

- 1 FOR Copying Field data from Batch (prev) to (current).**
- 2 FOR Copying analysis (xms) and LAB data from Batch (prev) to (current).**
- 6 FOR Importing XMS data.**

**** Copying files from current Batch \data to \report**

- 3 FOR Copying Field data.**
- 4 FOR Copying analysis (xms) data.**

**** Continue Processing Field**

- 5 FOR Processing Field data file.**

**** Continue Processing Analysis (xms) file.**

- 7 FOR Running REP.**
- 8 FOR Merge FLD and XMS files to CHM file.**
- 9 FOR Calculate blank values and blank uncertainty.**
- 10 FOR Convert chm file to con file (ug/m³).**

This is basically the same as before, except you simply want to copy the previous Field, lab and xms files.

SVOC2 - The Sequel

Background

We have to analyze for more than just the PAH species, so a second processing program has been written. This program follows the PAH analysis program sequence with a number of exceptions.

Exceptions

The second SVOC program uses the same lab and field files as the regular program and thus these need to be finished at the same time.

The option exists in this program to define which compounds will be imported from the regular samples and which from diluted ones. This must be the same for all compounds in a project, although some adjustments can be made if necessary. In any case, all compounds must be imported the first pass through and then a sub-group can be imported from a second (called diluted) on file.

Everything is case sensitive, especially the compound names.

Steps

1. Tell the Data Processing Manager which projects need this so the OALProj database and the other necessary files can be updated.
2. Update the compound list file. This file is project-specific and it is located in the H:\db_calib\svoc\ directory in the general form xx2cmpd.dbf, where xx is the project code. The template is nf2cmpd.dbf. This needs to be filled out in the following format:

Field_name This is the mnemonic that will become the field name. Each compound must be followed by its associated uncertainty, just as in the example.

Field_type Leave alone

Field_len Leave alone

Field_dec Leave alone

Compound For the compound only (not the uncert.), insert the compound name EXACTLY as it is in the HP GC/MS calibration file. If this is not spelled EXACTLY as it is in the calibration file on the HP GC/MS nothing will work. Do not put in anything for the uncertainties.

Type Put in "c" for compounds, nothing for uncertainties. EVERY compound in the list MUST have a "c" in this field.

Dil Put in "d" for compounds that will be imported from diluted files, nothing otherwise.

3. Update the Lab database. There are five new fields in the lab database for the second SVOC files. These are:

F2_name Mass spec file name for primary analysis

F2_proc Process status for above (1= ready to import, 2= done)

Dil_f2_nam MS file name for diluted run

Dil_f2_pro Process status for above (1= ready to import, 2= done)

Date2 Analysis date for second compound list.

This should follow the conventions used in the normal data processing for PAH species.

4. Do genbatch and follow the instructions. When you select a project you will be prompted to select either SVOC or Additional SVOC compounds. Selecting the latter (option 7) will take you to the SVOC2 programs. First use the "N" option to build new files and then continue by importing the mass spec data and continuing the processing. This will create XM2 (the raw mass spec data), the CH2 file, and the CN2 (ng/m3) file.

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
1,7-dimethylphenanthrene Compound: 45 of 83 Standard Deviation: 0.028
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.800000 \text{ E}0 \text{ x}^2 + 1.269278 \text{ E}0 \text{ x} + -4.631979 \text{ E}-3 \text{ 1}$]

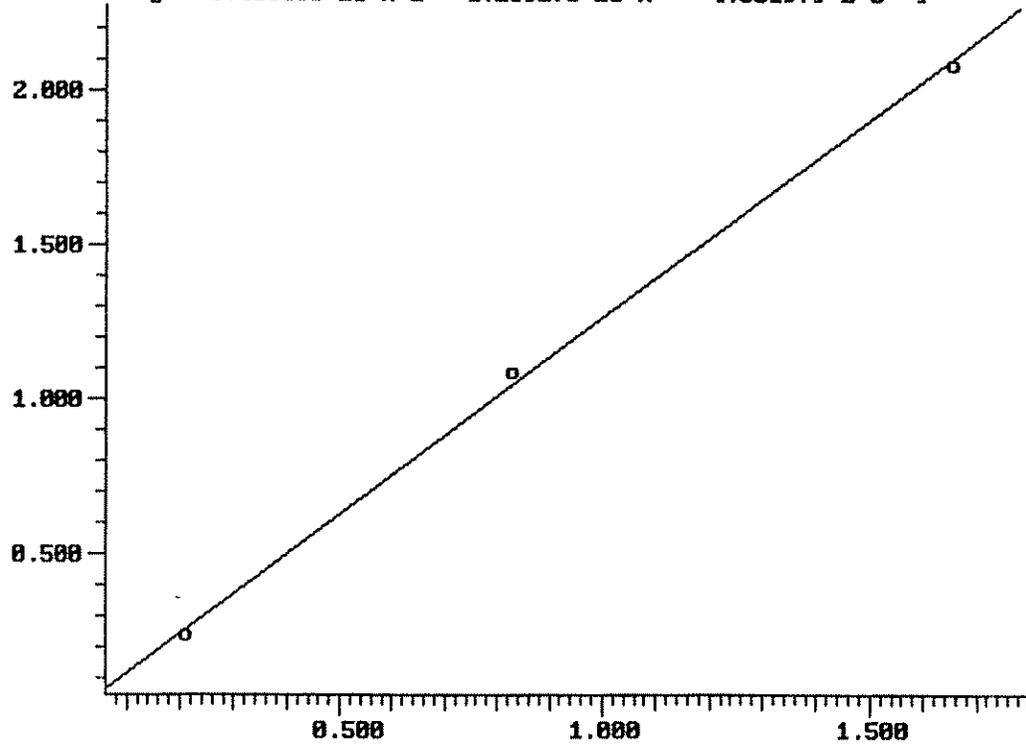


Figure 1

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
C-dimethylphenanthrene Compound: 44 of 83 Standard Deviation: 0.028
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.269938 \text{ E}0 \text{ x} + -4.550553 \text{ E}-3$]

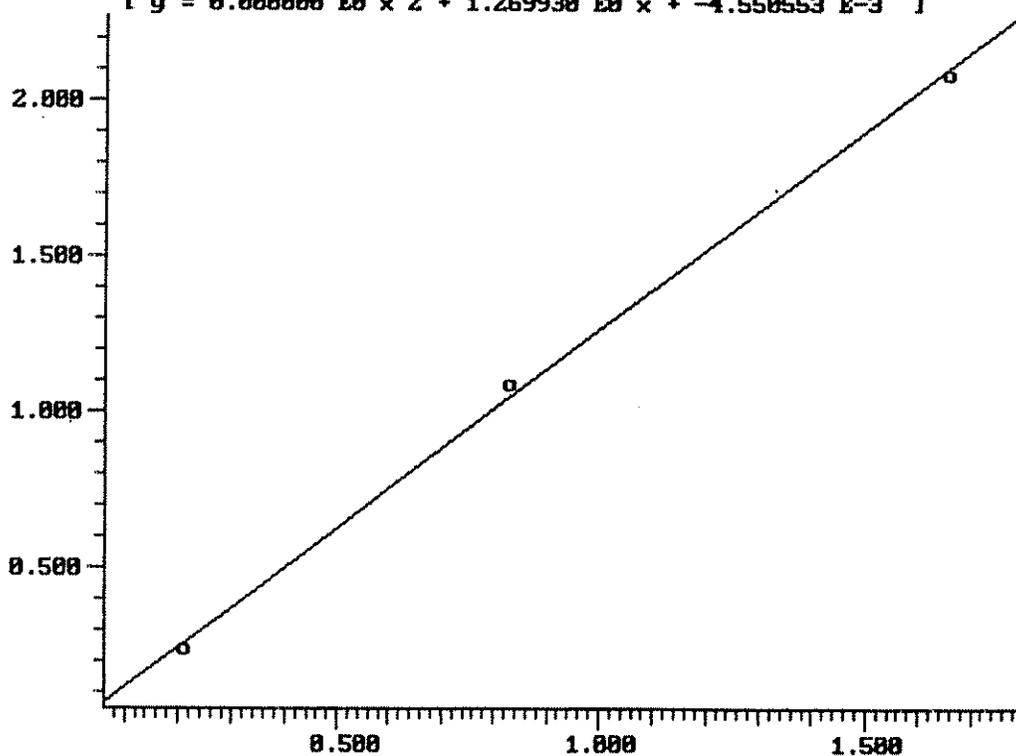


Figure 2

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
B-dimethylphenanthrene Compound: 43 of 83 Standard Deviation: 0.826
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.888888 \text{ E}0 \text{ x}^2 + 1.272932 \text{ E}0 \text{ x} + -6.577547 \text{ E}-3$]

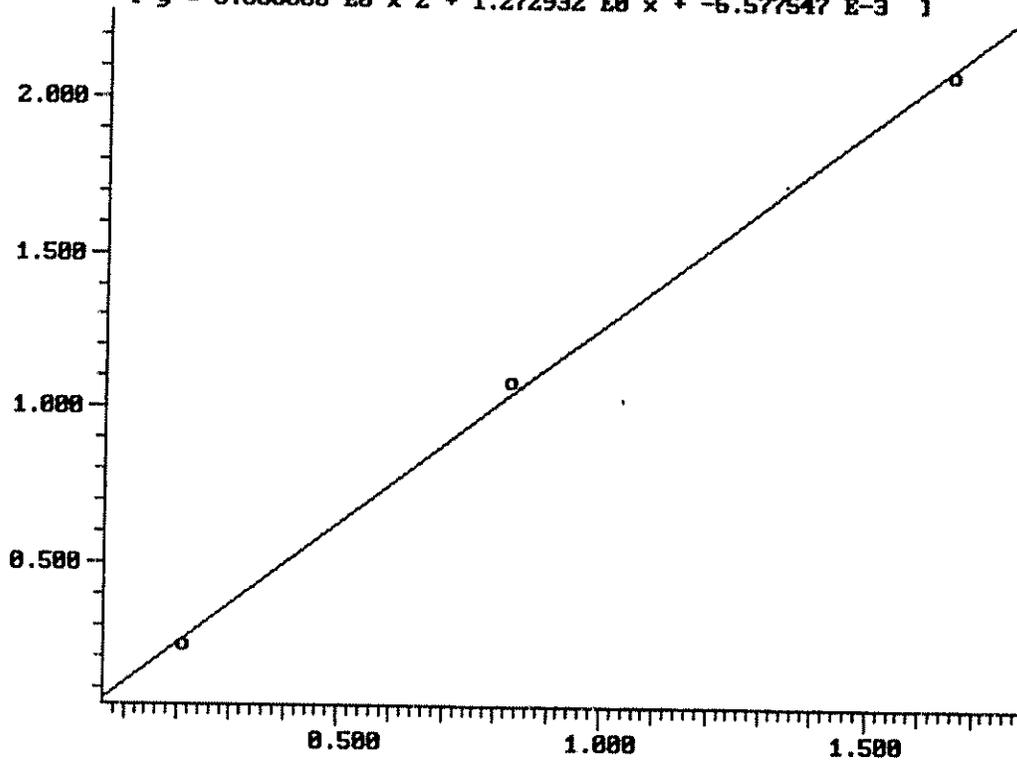


Figure 3

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.999
A-dimethylphenanthrene Compound: 42 of 83 Standard Deviation: 0.026
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) [Lin|Lin]
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 1.272866 \text{ E}0 \text{ x} + -6.185425 \text{ E-}3$]

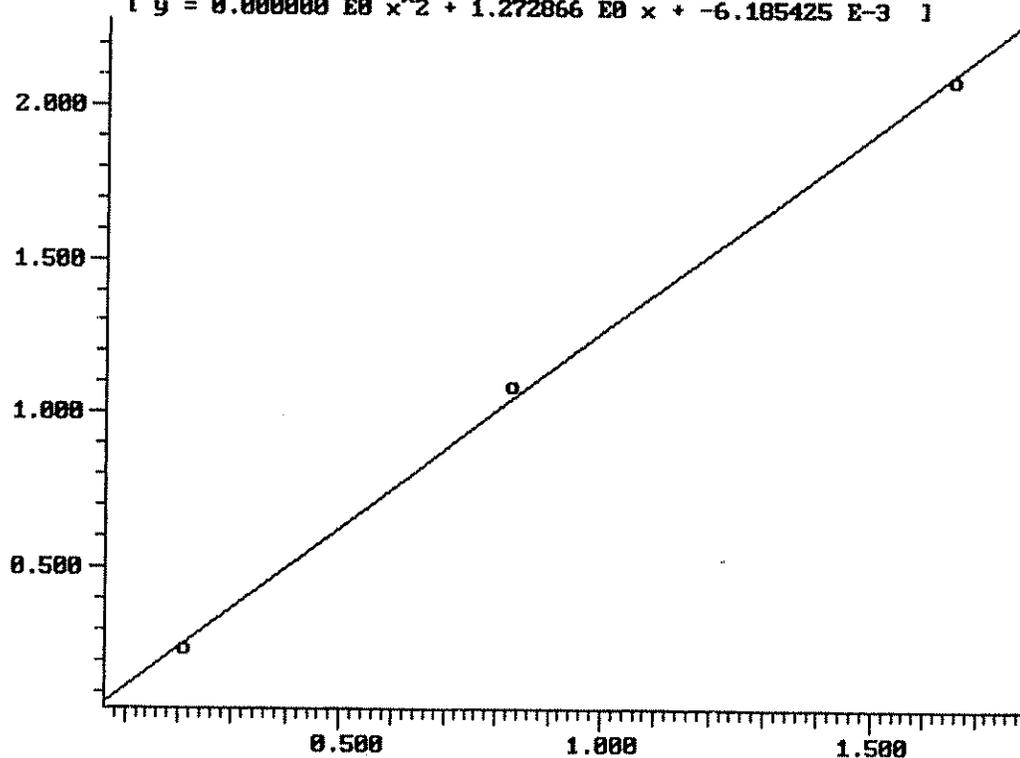


Figure 4

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.997
2,6+2,7-dimethylnaphthalene Compound: 7 of 83 Standard Deviation: 0.853
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard)) (Lin/Lin)
[$y = 0.000000 E0 x^2 + 5.571878 E-1 x + 8.442393 E-2$]

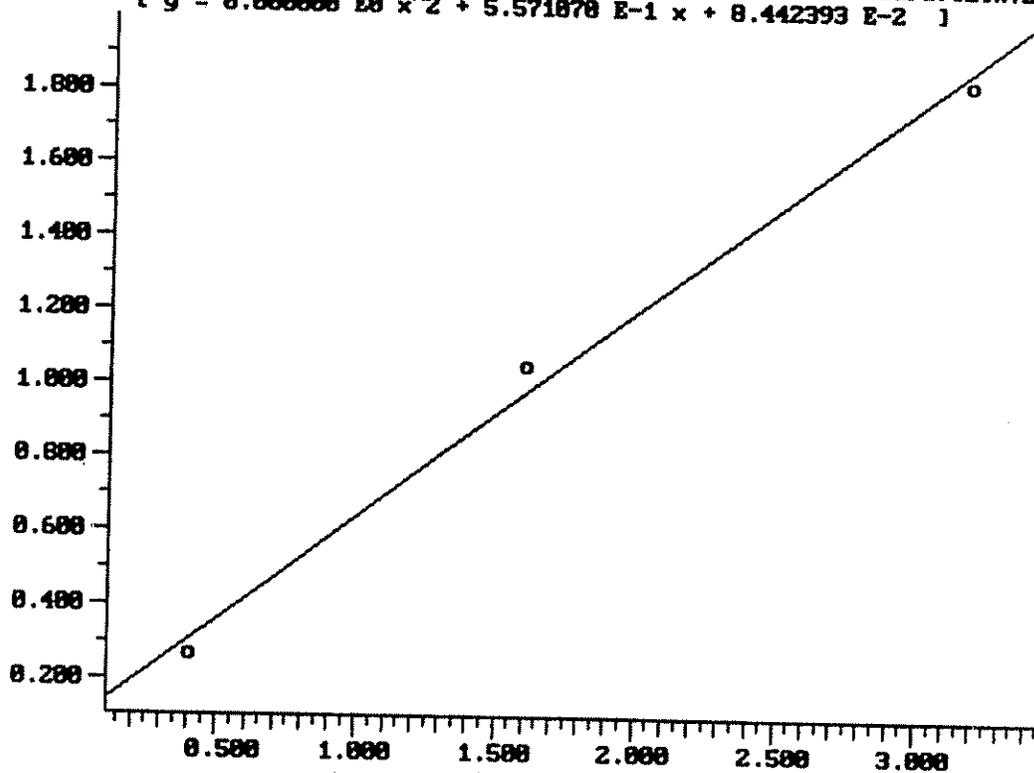


Figure 5

Calibration Plot (Int Stds) Filename: PAH Correlation Coeff: 0.996
Biphenyl Compound: 6 of 83 Standard Deviation: 0.022
(Area of Sample/Area of Standard) vs (Amount(sample)/Amount(standard))
[$y = 0.000000 \text{ E}0 \text{ x}^2 + 0.520552 \text{ E-1 x} + 3.587838 \text{ E-2}$]

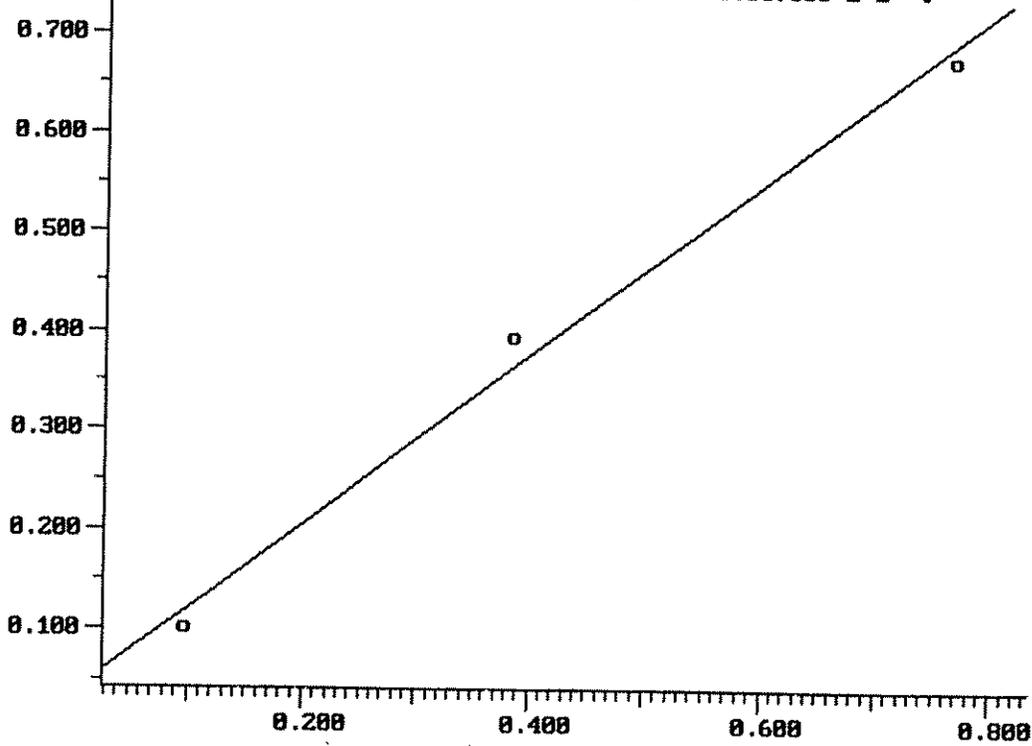


Figure 6

Standard Operating Procedure for the X-Series ICP-MS for the Analysis of Particulate Deposits on Teflon Filters

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1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) addresses the extraction and analysis of selected metals from Teflon filters using inductively coupled plasma mass spectroscopy (ICP-MS).

Table 1. Project-Specific Elements Analyzed for the PM_{2.5} Speciation Program

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.

1.1 Principle

The sample is extracted into a solution of nitric and hydrochloric acid to solubilize the material deposited on the filter. The resulting solution is aspirated into an argon plasma to generate ions, which are then accelerated through a series of focusing lenses, separated on a mass to charge basis by a quadrupole, and impacted into an electron multiplier detector that reads the resulting voltage and extrapolates the concentration against a known concentration curve.

1.2 Method Overview

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 50mL, acid-cleaned centrifuge tubes, with the loaded side facing inward. A 25mL 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 three hours to extract the metals on the filter. The samples are allowed to cool, centrifuged, and a 5mL 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.

2.0 Safety

Because the extraction solution is made from concentrated acids, proper personal protective equipment (PPE) must be worn at all times. Safety glasses, gloves, and a laboratory coat must be worn at all times to protect against spills and splashes, which can result from handling liquid samples.

3.0 Filter Sample Considerations

It is important that care be taken when handling the filters so that the deposit is not abraded in any way that would cause the loss of material. Care also needs to be taken to assure that the filters are not contaminated by metal tweezers or any other source as the whole filter, front and back, is extracted. Any contamination present would contribute to the total result for the filter.

4.0 Interferences and Intensity Corrections

The following are potential sources of error in the procedure:

4.1 Polyatomic interferences

Polyatomic interferences exist for several elements; in particular, arsenic and selenium. The polyatomic interferences are overcome using a combination of collision cell technology and kinetic energy discrimination. The collision cell introduces a mixed hydrogen/helium gas into the ion beam, and the resulting collisions break apart the polyatomic species, which have the same mass as a target analyte. Any polyatomic species that remain intact are then slowed by kinetic energy discrimination because the larger polyatomic molecule does not travel as fast as the elemental ion through the lens stack. This approach greatly reduces the impact of polyatomic species such as $^{40}\text{Ar}^{35}\text{Cl}$ on elements like ^{75}As .

4.2 Sample viscosity

The viscosity of the sample being pumped and aspirated can cause fluctuations in response. This fluctuation is negated by the use of internal standards. The internal standard response is measured on each replicate of the analysis, and the concentration of the analyte is corrected using the following formula:

$$M = A / I$$

Where M = reported concentration, A = measured concentration, and I = internal standard response.

5.0 Instruments

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, quadrupole, 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 two hours of vacuum support in standby mode
- 240 position autosampler housed in a HEPA-filtered enclosure to protect against atmospheric contamination.

6.0 Instrument Calibration

6.1 Standards

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.

6.2 Check Standard

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 ten samples, and at the end of analysis. All sample results to be reported must be bracketed by passing standard checks.

6.3 Method Set-Up

The analysis method is saved as a template that contains the analyte list, acquisition parameters, calibration standards and defined concentrations, and uptake and rinse times. The analyst will click on “create sequence from template” and save the sequence as a new name in the instrument software. The sample names will be filled in on the analysis sequence, and the sequence will be started.

6.4 Calibration Frequency

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 $\pm 10\%$ 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 $\pm 10\%$ 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.

6.5 Detection Limit and Uncertainty

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.

7.0 Filter Handling

Teflon filters are received from storage or after analysis by XRF. Custody of the Teflon filters are transferred to the ICP-MS Laboratory by the signing of the appropriate chain of custody forms. The filters are stored in plastic bags in a hood until they are ready for extraction.

8.0 Filter Preparation and Analysis

8.1 Preparation

Filters are removed from their petri dish and placed in a labeled acid-cleaned, 50mL centrifuge tube with the loaded side facing inward using acid-cleaned plastic tweezers. The tubes are gently tapped on the lab bench to settle the filter as low in the tube as possible. 25mL of an 8% HCl/3% HNO₃ extraction solution is added to each tube, and the tubes are capped. All the samples are placed in a heated ultrasonic water bath at 69°C for three hours. After removal from the bath, the samples are allowed to cool to room temperature and are vortex mixed. The samples are placed in a centrifuge at ~2800 RPM for 15 minutes to settle any insoluble particulate, and a 5mL aliquot of sample is removed for ICP-MS analysis.

8.2 Analysis

The sample identifications are typed into the autosampler table in the method, and the samples are loaded in the autosampler according to the table. The instrument is tuned, which consists of maximizing the signal at ^{115}In while minimizing cerium oxide/cerium ratio, and a system suitability check is run to show that the instrument is stable over a 10 replicate analysis. The instrument daily-use benchsheet and system suitability are posted in the instrument notebook. Once the instrument is tuned and the autosampler is loaded, the analyst will queue the experiment and monitor the analysis.

8.3 Archiving

After analysis is completed, the remaining extract will be stored in the sample custody room (Building 6, Room 205) for a period of 6 months. Samples will be stored at ambient temperature. After the 6-month storage period, samples will be discarded as acid waste.

9.0 Data Acquisition and Calculations

After all the samples have all been acquired, the software will display a message “Experiment _____ is no longer in the queue”. The analyst will click the OK button and then the Results tab in the software to display all the sample results. The analyst will confirm that the acceptance criteria in Section 10 are met. The dilution factor of 25 is built into the autosampler table, so all results are displayed in units of nanograms per filter. The analyst will transfer the CSV results file to a USB storage device. Any data that does not meet acceptance criteria will be edited out of the file, and the file will be sent for uploading into the $\text{PM}_{2.5}$ database.

10.0 Quality Control

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 the following table.

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%

11.0 Data Review and Validation

The analytical data set goes through Level 0 and Level 1 validations. These levels of validation will ensure the data set being reported will be of good quality.

11.1 Level 0 Validation

A Level 0 validation begins with the analyst. The analyst identifies any problems related to the COC, filter, or any mechanical or software problems that might have arisen during analysis of the filters. If such items are identified, validation flags will be applied to single out any problems, and these flags will be considered when using the data.

11.2 Level 1 Validation

A Level 1 validation is a more technical review of the analytical data. This review starts with the analyst, but will primarily be performed by the Technical Area Supervisor. Using the review criteria developed by the QA Manager, the Technical Area Supervisor will check to ensure that the analytical data set is complete, the data is reasonable, the QC sample results are within acceptance limits, and the procedure to analyze the filters was followed. If any discrepancies are noted and would have a direct affect on the data, the Technical Area Supervisor would apply validation flags to the data. A Level 1 checklist is presented as Figure 1. A table of laboratory flags applicable to ICP/MS in shown in Figure 2.

After the analytical data set has gone through the two levels of review, both the analyst and the Technical Area Supervisor sign off on the data set, and it is ready to be submitted for upload into the database. The data file, together with any data flags applied during the review process, will be submitted via e-mail in CSV format for uploading to the database.

Figure 1. ICP-MS Level 1 Elemental Analysis Checklist

COC Form No. _____ Report Date: _____

Data Review:

Sample Filter No. _____ Comments: _____

Quality Control Review:

Calibration Data Acceptable: Yes ___ No ___ Notes: _____

QC Data Acceptable: Yes ___ No ___ Notes: _____

Uncertainty Data Acceptable: Yes ___ No ___ Notes: _____

File Name: _____

Reviewed by: _____ Date _____

Approved by: _____ Date _____

Figure 2. Data Flags Applicable to ICP/MS

Flag Code	Description	Applicability
4	Possible lab contamination	If results can not be explained after internal investigation.
AAR	Above Analytical Range	If sample exceeds the instrument calibration.
AR	Lab Error	
AS	Poor Quality Assurance Results	Used if QC samples fail to meet specification.
LBL	Laboratory Blank values outside of limits	
LCA	Laboratory calibration out of limits	
LDU	Lab duplicates out of limits	If duplicate analysis falls outside of specified range.
LFH	Filter inspection flags* – Holes in filter	
LFL	Filter inspection flags* – Loose Material	
LFO	Filter inspection flags* – Other (wrinkling, warping, etc.)	
LFP	Filter inspection flags* – Pinholes	
LFS	Filter inspection flags* – Separation of reinforcing ring	
LFT	Filter inspection flags* – Tear	
LLI	ANALYSIS INVALID – Other	

12.0 References

- Thermo X-Series II Getting Started Guide, 1995
- Plasmalab Version 2.5.3
- CARB-MLD 061
- TID-TOP-001, Use and Maintenance of the Thermo X-Series ICP-MS

Standard Operating Procedure for Sample Preparation and Analysis of PM10 and PM2.5 Samples by Scanning Electron Microscopy

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Reviewed by: *James B. Flayn* Date: *7/10/08*

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

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Standard Operating Procedure for Sample Preparation and Analysis of PM10 and PM2.5 Samples by Scanning Electron Microscopy

1.0 Procedural Section

1.1 Scope and Applicability

The scanning electron microscopy (SEM) standard operating procedure (SOP) establishes procedures for determining the type and amount of particulate matter deposited on a Teflon filter following collection of a PM2.5 or PM10 sample. The SOP is also applicable to particulate samples collected on other filter media such as polycarbonate filters. Particles are analyzed by SEM and by energy-dispersive x-ray spectroscopy (EDS) to determine size, morphology, and particle chemistry.

1.2 Summary of Method

PM2.5 filters are examined by microscopy by first evaporating a thin layer of carbon onto the surface of the sample. The carbon-coated filters are stored for subsequent examination by SEM and EDS. Particles on the sample filter are found using SEM; upon locating a particle, its size and morphology are recorded. The spectrum of the particle is then obtained using EDS. The EDS spectrum is used to determine the elemental composition of the particle. This procedure is repeated for a minimum of 100 particles per filter.

1.3 Definitions

SEM: A microscope which creates an image of a sample by scanning the sample with an electron beam. Secondary electrons are subsequently emitted from the sample, collected in the microscope detector, and reconfigured at various magnifications on a computer screen as an image of the sample.

EDS: An instrument which collects x-rays emitted from a sample that has been bombarded by an electron beam. The x-rays are sorted by energy level, and a spectrum of x-ray energy vs. frequency is plotted, which is indicative of the elements present in the sample and of the concentration of each element present.

1.4 Health and Safety Warnings

Operators must use care around the vacuum evaporator to avoid hazards inherent in high vacuum devices (e.g., implosion of glassware under high vacuum). Because the SEM instrument employs high voltages, the operator should avoid touching conductors and should observe and report any damage to the electrical insulation or other damage to the instrument. The SEM must be checked regularly for x-ray leakage.

1.5 Cautions

Items used during sample preparation such as petri dishes, forceps, scalpels, stubs, and glassware are critically cleaned prior to use, and prior to contact with subsequent samples. Reagent aliquots used for any given sample preparation must not be used for subsequent samples. The area in which the filters are prepared must be kept as contamination-free as possible, facilitated by the use of a laminar flow clean bench, the use of a fume hood during prep stages requiring volatile chemicals, and the wet-wiping of all countertops prior to sample preparation. All prep instruments and tools must be quarantined from other areas of the laboratory, particularly where particulate samples are analyzed or stored.

1.6 Interferences

Interferences include particulate contamination that exists on the Teflon filters prior to sample collection, contamination of the filter subsequent to sample collection, and the inherent particulate appearance on the Teflon filter. Filter lots must be characterized prior to use to determine the type and concentration of particulate on the filter. Analysis of field blanks will assist with determination of the potential level of post-collection contamination.

1.7 Personnel Qualifications

Operation of the SEM/EDS instrument requires a high degree of training and skill. The laboratory supervisor will typically have a master's degree in chemistry, mineralogy, surface science, or in a related area. At a minimum, analysts should have a bachelor's degree in chemistry or in a related area, and must also receive extensive hands-on training from RTI SEM personnel. All RTI personnel performing SEM/EDS analyses for the PM2.5 program will receive necessary on-the-job training from the laboratory supervisor. Graduate-level coursework and/or continuing education relevant to the analytical technique is strongly encouraged.

1.8 SEM Apparatus and Materials

- FEI Quanta 200 variable pressure scanning electron microscope
- Oxford-INCA energy dispersive x-ray spectrometer
- Aluminum SEM specimen stubs
- Double-sided carbon adhesive specimen mounts

1.9 Calibration

EDS energy levels are calibrated each day of use by checking copper $L\alpha$ and aluminum $K\alpha$ peaks prior to use. Minor variation (± 10 eV) requires calibration; variations greater than 10 eV may require major service. The magnification of the SEM must be calibrated quarterly using a magnification calibration stub to determine that magnification settings are accurate at the magnification ranges used for PM analysis.

1.10 Sample Collection

Samples received from a client are checked to be sure the shipment is complete and includes all identification data. Sample identifications are recorded in the project file and the laboratory notebook. In any situation where data is missing or sample validity is in question, the client is contacted before proceeding.

1.11 Handling and Preservation

No special preservation considerations apply. See the next section for a description of sample handling during preparation and analysis.

1.12 Sample Preparation and Analysis

The sample housing is cleaned with a damp wipe, and a SEM substrate (stub) is prepared for receiving a filter by applying a double-sided, sticky conductive carbon pad to the stub surface. The underside of the stub is labeled with the sample number using a permanent marker. The filter is removed and placed on the stub, and the stub is placed in a vacuum evaporator for carbon coating. A thin layer of carbon is evaporated onto the surface of the sample at a vacuum of 5.0×10^{-5} torr. The filter is then removed and placed in a clean polycarbonate storage box for transfer.

Examination in the SEM involves the use of variable voltages due to the beam-sensitive nature of the Teflon filter. Morphological examination is conducted at 5 KV, and EDS spectrum collection is conducted at 15 KV. When examining the sample, randomly located areas are selected for higher magnification scanning. Specific areas are scanned for particulate matter. Upon locating a particle, size and morphology are recorded, and a spectrum is collected with the EDS. This procedure is repeated for a minimum of 100 particles encountered, regardless of size, morphology, or chemistry. Representative micrographs and spectra are stored digitally and later transferred to project digital file systems.

1.13 Troubleshooting

Because of the highly technical nature of the SEM and EDS measurements, the analyst is directed to the FEI SEM Operations Manual for troubleshooting advice. All troubleshooting should be done by qualified personnel.

1.14 Data Acquisition, Calculations, and Data Reduction

Report the size distribution of the particles measured, any notable morphological characteristics of the particles, and the chemical characteristics of the particles. The report does not need to include a spectrum for each particle, but it should include spectra representing each general type of particle found. Size distribution is reported using a table of particle sizes and a histogram of particle size versus frequency.

1.15 Computer Hardware and Software

The Oxford-INCA EDS will assist with the identification of elemental peaks on the spectrum, but it does not automatically assign identities to peaks. There are no software decisions made in the analytical process or automated functions performed by the SEM or EDS. Size distribution graphs included in the report are generated by inputting data into a spreadsheet software program, which automatically plots a graph of the size frequency distribution.

1.16 Data and Records Management

Each project is kept in duplicate electronic storage systems in chronological order in a secure office location. All records are retained for a minimum of seven years.

2.0 Quality Control

Various quality control (QC) checks are performed to ensure analytical quality. These checks are performed on sample preparation equipment, supplies, laboratory areas, and analytical instrumentation. The chief ongoing QC check is related to instrument calibration, as described in Section 1.9 above. Field blanks submitted with project batches will be prepared and analyzed as standard samples.

3.0 References

FEI Quanta 200 Operation Manual

Standard Operating Procedure for Database Operations

Environmental Health and Safety Division
RTI International*
Research Triangle Park, North Carolina

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

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Standard Operating Procedure for Database Operations

1.0 Introduction

1.1 Scope

This operating procedure covers database operation activities performed by program data processing staff. Data entry activities, such as Sample Handling Analysis Laboratory (SHAL) sample processing, are included in the SHAL standard operating procedures (SOPs).

1.2 Requirements

This procedure assumes a familiarity with general database concepts and the use of Microsoft (MS) Access and MS SQL Server programming tools, such as the Query Analyzer and Enterprise Manager. General MS Windows Server management skills are also assumed for supervisory personnel.

1.3 Hardware/Software Environment

Internal Server—RTI maintains an internal database server for use with the PM_{2.5} Chemical Speciation Program. This server runs MS SQL Server version 2000 on the MS Windows Server 2003 operating system. Only internal RTI personnel are allowed access to this internal server (individual accounts are set up as described below).

External Server—An external server (i.e., on that is accessible from outside RTI's private network) is used to store monthly reports for review by the U.S. Environmental Protection Agency (EPA) and site data reviewers.

Note: The names of specific forms, queries, reports, and programs to be run are italicized throughout this SOP.

2.0 Create Data Contact Account on the External Server

2.1 Summary of Task

This procedure describes the steps necessary to create a data contact account on the external server (geos1.rti.org). This procedure requires that the user have administrative rights on the external server.

2.2 Procedure

2.2.1 Use User Manager and select domain of geos1.rti.org.

2.2.2 Add user account and set password. Set password to not expire, not change on initial login, and not be changed by user.

- 2.2.3 Add the user to the PM_{2.5} group.
- 2.2.4 Create a directory for user's data under the correct EPA directory.
- 2.2.5 Set security for the directory. Grant read/list access to the user, the Delivery Order Project Officer (DOPO), and the overall Project Officer (EPA01).
- 2.2.6 Send the data contact's account, directory, and password to the appropriate DOPO for transfer to data contact.

3.0 Request Domain Account for a New Non-RTI Temporary Employee

3.1 Summary of Task

Domain accounts can only be created by Information Technology Services (ITS) domain administrators. This procedure describes how to make a request to have a domain account created for a new temporary service employee (e.g., SHAL temporaries). Note that all RTI employees have a domain account created as part of the hiring procedure; therefore, this procedure is only required for non-RTI temporary workers.

3.2 Procedure

- 3.2.1 The Laboratory Supervisor goes to ITS Web site and completes an *Account Request Form*. Request ONLY NT Domain Account. Be certain to mark the employee as temporary on the form. The Laboratory Supervisor adds a notation to ITS to add the employee to appropriate groups (typically RCC_NT/PMSHALUsers).
- 3.2.2 ITS returns (rejects) the Account Request Form to Laboratory Supervisor, requiring the Center Director's approval.
- 3.2.3 The Laboratory Supervisor forwards returned e-mail to the Center Director for approval.
- 3.2.4 The Center Director approves the new domain account and forwards this approval to ITS.
- 3.2.5 ITS creates a new domain account and notifies the Laboratory Supervisor by e-mail.
- 3.2.6 The Laboratory Supervisor forwards account information to the Center Information Management Systems (IMS) Supervisor and the Database Supervisor.

4.0 Request Deletion of Domain Account for Terminated Non-RTI Temporary Employee

4.1 Summary of Task

Domain accounts may only be deleted by ITS domain administrators. This procedure describes how to make a request for deleting the domain account of a non-RTI temporary worker after his or her termination. Note that domain accounts for RTI workers are automatically deleted as part of their termination process; therefore, this procedure is only needed for non-RTI workers.

4.2 Procedure

- 4.2.1 The Laboratory Supervisor notifies the ITS Department, the EISD IMS Supervisor, and the Database Supervisor about the appropriate domain account to be deleted. Because all file and MS SQL Server access is through this account, this effectively removes their file and MS SQL Server access.

5.0 Add Employee to the SHAL Database Users Group

5.1 Summary of Task

This task is performed for employees who need database access. This procedure requires administrative and MS SQL administrative rights on RTI's internal server. Only people who have domain accounts may be added to the database users group. New non-RTI temporary workers must have their domain account assigned (see Section 3.0) before they can be added to the users database group.

5.2 Procedure

- 5.2.1 Provide the ITS Department with the name and domain account of the person to be granted access to the SHAL database and the NT domain group(s) that he or she should be placed into (typically RCC_NT\PMSHalUsers).

6.0 Process Delivery Order and Schedule Associated Sampling and Analysis Events

6.1 Summary of Task

This procedure describes the operations necessary to process an incoming delivery order and to schedule the associated analytical and sampling requests.

6.2 Procedure

- 6.2.1 Get delivery order information from the EPA DOPO.
- 6.2.2 Determine the information needed for delivery order processing from information provided by the EPA DOPO.

- 6.2.3 Enter information for delivery order into the database.
- 6.2.4 Run *delivery order form* (as a report) from the database.
- 6.2.5 Prepare the file folder for delivery order paperwork. Place the delivery order form into folder.
- 6.2.6 Identify each site on the delivery order and determine if it appears on RTI's list of sites with sampler and Air Quality System (AQS) information.
- 6.2.7 Determine if the site is listed on RTI's list of sites with sampler and AQS information.
- 6.2.8 Enter sampler and AQS information for the new site into the database, if necessary.
- 6.2.9 Determine the sampler type and analysis list needed for each site listed on the delivery order. (This assumes that the same type is required throughout the delivery order).
- 6.2.10 Use the lookup list to determine the sampling configuration needed for the selected sampling type and analysis list.
- 6.2.11 Determine the beginning and end dates for each site. Use the measurement request generation program to create measurement requests for each site and date combination.
- 6.2.12 Print the sampling request forms for the location and file them in processing folder(s).
- 6.2.13 Review the sampling forms to verify that scheduling is correct.
- 6.2.14 After all samples have been scheduled, set the delivery order status to requests scheduled.
- 6.2.15 Select delivery order for proofing.
- 6.2.16 Compare the summary report to delivery order and make changes, if necessary.
- 6.2.17 Update the SHAL schedule calendar to reflect additional workload.

7.0 Receive Data from Laboratory

7.1 Summary of Task

This procedure describes the receipt of data (in spreadsheets) from the analysis laboratories for direct import into the database.

7.2 Procedure

- 7.2.1 Receive the spreadsheet that contains analytical results from the laboratory.
- 7.2.2 Move spreadsheet data onto server into the appropriate laboratory file.
- 7.2.3 Review laboratory files to ensure that they are in the correct format for import. Make corrections to format as necessary for automatic import into database.
- 7.2.4 From the database, use the *import analytical data* form to automatically import analytical results into the database.
- 7.2.5 If errors occur during import, do not commit the transaction and identify and correct any problems with analytical data before importing the data.
- 7.2.6 Move imported laboratory results files into the added to database folder within each laboratory folder on the server.

8.0 Prepare Monthly Analytical Data Report

8.1 Summary of Task

This procedure describes the preparation of the analytical data report, which is sent to the EPA DOPO each month.

8.2 Procedure

- 8.2.1 Perform preliminary duplicate data check by running the *DignoseDuplicateRows* program.
- 8.2.2 Correct any duplicated data, as necessary.
- 8.2.3 Make a copy of the main database for use in report checking by running the *Transfer to QC Draft* program using the MS SQL Server Data Transformation Services.
- 8.2.4 Select the last sample for delivery date by setting the correct value for the last sampling date and by editing the date in the *ForceApproveTestBatch.sql* program.

8.2.5 Batch approve samples by running the SQL script by running the *ForceApproveTestBatch.sql* program.

8.2.6 Fix problems with reported uncompleted samples (in main database). Rerun everything to this point if any unaccounted sampling events remain.

The New_Export_Report_Data procedure performs the following calculations:

1. Ambient concentration = analyte mass/sampler volume (for appropriate sampler channel), where sampler volume is from the Field Custody Chain of Sampling form. If no sampler volume was supplied, but an average flow and elapsed time were supplied, then sampler volume = average flow * elapsed time.
2. Sample concentration uncertainty = sample mass uncertainty/sampler volume (for appropriate sampler channel).
3. Sample mass uncertainty = greater of
 - a) lab blank uncertainty and
 - b) square root of $(s_analytical^2 + (M * sr_volume)^2)$.

where:

s_analytical = laboratory analysis uncertainty,

M = sample mass

sr_volume = volume uncertainty (relative) for appropriate sampler channel.

Notes:

1. Concentrations and concentration uncertainties are not defined for field and trip blanks because there are no sample volumes.
2. The sampler volume uncertainty (sr_volume) is currently assumed to be 5% for all sampler channels.

8.2.7 Generate Analytical Report Data in a draft database by running the program *New_Export_Report_Data*.

8.2.8 Check report data for duplicate rows by running the program *Check_for_Dups* with the argument of the latest batch number. Correct any problems and regenerate all steps to this part, if necessary.

8.2.9 Open the report generation program (Report.mdb) and verify that its tables are linked to the database copy used for quality assurance (QA) review. Re-link to the correct database with the linked table manager, if necessary.

8.2.10 Run the report program to generate draft copies of the output reports.

8.2.11 Notify the RTI QA Officer that the draft reports are ready for review.

- 8.2.12 After approval from the RTI QA Officer, repeat the procedures previously completed on the copy of database on the main database. Copy the final version of reports to the external Web site.
- 8.2.13 Remove any old reports from the Web site.
- 8.2.14 Notify the DOPOs that reports are ready.
- 8.2.15 Make CD copies of the Web site for the EPA Project Officer and for the RTI master project file.
- 8.2.16 Deliver CD to the EPA Project Officer.

9.0 Prepare results for AQS

9.1 Summary of Task

This procedure describes the preparation of the monthly AQS data report.

9.2 Procedure

- 9.2.1 Copy the current database over training database in preparation for the trial generation and review.
- 9.2.2 Run the *New_Fill_AIRS_Table* stored procedure with the argument of the batch to be delivered (this generates all data in the batch).
- 9.2.3 Using the main data entry application, set the event's delivery status to 5, AQS reprocessing needed, for all events that must be regenerated due to state reviews, etc.
- 9.2.4 Remove any data that needs to be reprocessed from the internal AQS processing table by running the *Delete_Challenged_Data* stored procedure with the argument of the AQS batch to be delivered.
- 9.2.5 Perform any needed recalculations by running the *New_Update_Challenged_Report_Data* stored procedure with the argument of the AQS batch to be delivered.
- 9.2.6 Check for any duplicate records by running the *Check_for_Dups* stored procedure with the argument of the batch to be delivered and fix any duplicates found.
- 9.2.7 Now that all records have been reprocessed, the AQS output file is generated by using the menu in the *AIRSApp.adp* program

- 9.2.8 Import the AQS file into the *AQSFile* table in *AIRS_File_Checks.mdb* using the Import Text Wizard and choosing Delimited text format with vertical bar (“|”) as the delimiter.
- 9.2.9 Run QA procedures, as described in Section 10, AQS QA Procedures.
- 9.2.10 Correct any errors and restart the process up to this step. Make note of any changes on the *QA review* form.
- 9.2.11 Send the file to the QA Officer to review the AQS data. Make any necessary corrections.
- 9.2.12 The QA Officer reviews and approves file.
- 9.2.13 Rerun procedures on main database.
- 9.2.14 Update the delivery status by running the *SetAIRSDeliveryStatus* program with argument of the AQS batch to be delivered.
- 9.2.15 Subdivide the approved AQS file into subfiles (typically two) to get files small enough for posting in the AQS.
- 9.2.16 Submit each sub-file to the AQS (see EPA’s AQS documentation for procedures).
- 9.2.17 Notify the EPA WAM and Delivery Order Project Officers (DOPOs) that results have been posted.

10.0 AQS QA Procedures

10.1 Summary of Task

This procedure describes the steps needed to review and approve AQS data before posting them to the AQS.

10.2 Procedure

The overall procedure involves making a trial version of the AQS output file and reviewing the file for errors and inconsistencies (e.g., two results at the same site and date). The database is then corrected and a new AQS output file is generated and reviewed. This cycle is repeated until no errors are found in the AQS output file. The AQS output file is then posted to AQS. The procedure is described in more detail, below.

- 10.2.1 Run the AQS file. Make a copy of the current database for use in the QA review.

- 10.2.2 Generate a draft AQS file using the *AIRSApp.adp* database application. Make sure the application is connected to the database copy before file generation.
- 10.2.3 After the AQS file has been generated, import the file into the *AQSFile* table in the *AIRS_file_checks.mdb* QA software using the Import Text Wizard and choosing Delimited text format with vertical bar (“|”) as the delimiter.
- 10.2.4 Check the data from the AQS file (now imported into the database) for errors by running the queries listed in the appropriate Quality Control Summary Sheet (Appendix A for routine samples and Appendix B for blanks). Query names for each check appear in italics on the *Quality Control Summary Sheet*.
- 10.2.5 Perform the first four steps in the *AQS Batch File Quality Control Summary Sheet* (Appendix A [or Appendix B for blanks]) to check for duplicates, modify records, new sites, and null start hours. If there are any new sites, check for complete monitor information. If the monitor information is incomplete, generate pdf files that show the monitor information for transmittal through the EPA DOPOs to request information from the appropriate agencies. After all monitor information is received, post monitor records in the AQS. Also add the AQS code, the POC, and the expected record count to the *Expected_AIRS_Counts* table in the *AIRS_file_checks.mdb* database. After the new sites are added to the expected counts table, the *Check_Record_Count2* query can be run to check the record counts. Also update the *Check_StartHour1* query batch number to the current batch number, and then run the *Check_StartHour3* query to check for odd start times.

Any errors found at this point must be corrected in the main database and marked for reprocessing. If events with duplicate dates cannot be resolved by reviewing the data in the database, send off a request to appropriate SHAL personnel so that they can review the hard copy paperwork and send inquiries to the site operator if necessary.

- 10.2.6 Subsequent Runs of AQS File. After all of the corrections have been made from the first run of the AQS file, an updated AQS file is prepared (by using the *AIRSApp.adp* program) and used to verify that all of the changes have been correctly made and to check that all of the state-requested changes have been correctly made.

To check the state-requested changes, run the *Temp_Trog13* query on the main database to get a list of all of the events in the current batch that are marked for reprocessing. Check in the appropriate batch folder for copied request change e-mails. Also check in the personal inbox for any other e-mails that may have requested that data changes be made. Make sure that all events marked for reprocessing have a requested change associated with them, as well as verify that

all e-mails with requested changes have the events marked for reprocessing in the database. If anything is missing, contact the person responsible for making the changes. If there is any question about the interpretation of changes, contact the QA Officer.

After all of events marked for reprocessing are verified, copy over the database and follow the procedures to generate an updated AQS file and import it into the *AIRS_file_checks.mdb* QA database. Run all of the queries that were previously run to verify that all errors were corrected. Because of the large datasets, the remaining queries are run on smaller static batch-specific tables, but these must be refreshed for each report batch. To perform this task, delete the data from the previous batch by running the *Delete_New_AIRS_Data* and *Delete_New_Report_Data* queries. Now refill the tables with the current batch's data by updating the batch number to the current batch number in the *Convert_Report_Data1* query, then, to append the new data, run the *Append_New_AIRS_Data* and *Append_New_Report_Data* queries. Now all of the queries specified on the Quality Control Summary Sheet (Appendix A) should be run to check the AQS file and to verify all of the changes. Note that the *Check_Delivered_Records1* query requires that the data from the previous AQS batch be appended to the *AIRS_Posted* table using the *Append_AIRS_Posted* query. This will verify that no events that were in a previous AQS file will appear in the AQS file.

If errors still remain in the AQS file, corrections should be made in the main database, and the AQS file should be reprocessed. Any manual changes to the AQS file, as well as any data withheld from the AQS file, should be noted in the Quality Control Summary Sheet.

After the final AQS file is generated, a completed Quality Control Summary Sheet, the printout results of all of the queries and printouts of all state-requested changes are submitted to the project's QA Officer for review. After the QA Officer has approved this quality control packet, the file can be loaded into EPA's AQS. Typically, the AQS file is split into 6 separate files of approximately 15,000 records to minimize loads on the AQS.

- 10.2.6 After all of the AQS data have been posted to AQS, run the AQS processing on the main database and mark events as delivered to AQS.

11.0 Database Backup

11.1 Summary of Task

Database backups are now provided by RTI's Information Technology (IT) server staff as part of their normal nightly back-up procedures. Procedures are covered in *SOP S0011-01: NT Server Data Backup and Storage of Backup Media*, which is available on RTI's internal Web site.

Appendix A

PM_{2.5} Speciation AQS Batch File Processing Quality Control Summary Sheet for Report Batch _____

Basic AQS File Checks (Required for AQS Update or by Format)

1. No duplicate rows in AQS file.

Check_Duplicates1

2. No modify records that are not appropriate. Explain any re-deliveries of AQS events or manual modification to correct modifies.

Check_Modifies1

3. Null data codes only occur when values are null; null data codes are null when values are not null. Also qualifiers do not occur without values or do not occur with null data codes.

Check_Null_Value_Codes1

4. No sample values without Minimum Detection Limits (MDLs) and uncertainties (excluding the ambient temperature and barometric pressure parameters). No MDLs and uncertainties without sample values.

Check_MDL_Uncertainty1

5. Added new locations or modifications of current locations. Please explain any changes.

Check_New_Sites3

6. No records delivered in previous batches for the same date that are not modify records.

Check_Delivered_Records1

7. Problems found during the AQS edits, which require manual edits in final the AQS file, please explain.

AQS File Checks Against Original Report Batch Data

1. Odd start times, if any, please explain.

Check_StartHour3

2. Minimum and maximum sample dates for this AQS batch. If either date is not in the range for the current batch, please explain.

Check_MinMax_SampleDate

3. Records in the AQS file that were not in original report, if any, please explain.

Check_Not_in_Report1

4. Records in original report that are not in the AQS file, if any, please explain.

Check_Not_in_AIRS1

5. Duplicates in original report (used only to rectify difference in counts).

Check_Report_Duplicates

6. Rectify the number of records in the AQS file versus the original report to verify that all appropriate records in the report made it into the AQS file and that no spurious records were created in the AQS file that were not in the original report.

7. Record counts in the AQS file versus the expected record counts for each AQS code/POC. Explain any counts that do not match.

Check_Record_Count2

8. Compare the values in the AQS file to those in the original report. Check 100% of those with an absolute difference of ≥ 1 . Spot check those that are different by 10% or more, but with an absolute difference < 1 . Spot check any differences between 1% and 10% to ensure that differences are only caused by rounding. Explain any differences not caused by rounding.

Check_Reprocessing

9. Compare null data codes in the AQS file to those in the original report. Explain any differences.

Check_NullDataCode

10. Compare AQS validity codes in the AQS file to those in the original report. Explain any differences.

Check_Validity

11. Compare MDL and uncertainty values in the AQS file to those in the original report. Check 100% of those that are different by 10% or more. Spot check any differences between 1% and 10% to ensure that differences are only caused by rounding. Explain any differences.

Check_MDLs

Check_Uncertainty

Verification of AQS Reprocessing Changes

1. Summarize changes made at the request of the states (check with person responsible for making the changes) and verify that these changes were updated with reprocessing.
2. Summarize changes made in response to problems found during the AQS processing and verify that these changes were updated with reprocessing.

Events in This Report Batch That Were Withheld from Update in the AQS

**PM_{2.5} Speciation AQS Batch File Processing Quality Control Summary Sheet
for Report Batch _____**

Basic AQS File Checks (Required for AQS Update or by Format)

1. No duplicate rows in the AQS file.

Check_Duplicates1

2. No modify records that are not appropriate. Explain any re-deliveries of AQS events or manual modification to correct modifies.

Check_Modifies1

3. Null data codes only occur when values are null; null data codes are null when values are not null. Also qualifiers do not occur without values or do not occur with null data codes.

Check_Null_Value_Codes1

4. No sample values without MDLs and uncertainties (excluding the ambient temperature and barometric pressure parameters). No MDLs and uncertainties without sample values.

Check_MDL_Uncertainty1

5. Added new locations or modifications of current locations. Please explain any changes.

Check_New_Sites3

6. No new records for site and date that were posted in a previous batch. However, update records (Action Code = U) for earlier events are acceptable.

Check_Delivered_Records1

7. Problems found during the AQS edits that require manual edits in final AQS file, please explain.

AQS File Checks Against Original Report Batch Data

1. Odd start times, if any, please explain.

Check_StartHour3

2. Minimum and maximum sample dates for this AQS batch. If either date is not in the range for the current batch, please explain.

Check_MinMax_SampleDate

3. Records in the AQS file are not in original report, if any, please explain.

Check_Not_in_Report1

4. Records in original report are not in the AQS file, if any, please explain.

Check_Not_in_AIRS1

5. Duplicates in the original report (used only to rectify difference in counts).

Check_Report_Duplicates

6. Rectify the number of records in the AQS file versus the original report to verify that all appropriate records in the report made it into the AQS file and no spurious records were created in the AQS file that were not in the original report.

7. Record counts in the AQS file versus the expected record counts for each AQS site code/POC. Explain any counts that do not match.

Check_Record_Count2

8. Compare values in the AQS file to those in the original report. Check 100% of those with an absolute difference of ≥ 1 . Spot check those that are different by 10% or more, but with an absolute difference < 1 . Spot check any differences between 1% and 10% to ensure that differences are only caused by rounding. Explain any differences not caused by rounding.

Check_Reprocessing

9. Compare null data codes in the AQS file to those in the original report. Explain any differences.

Check_NullDataCode

10. Compare AQS validity codes in the AQS file to those in the original report. Explain any differences.

Check_Validity

11. Compare MDL and uncertainty values in the AQS file to those in the original report. Check 100% of those that are different by 10% or more. Spot check any differences between 1% and 10% to make sure that differences are only caused by rounding. Explain any differences.

Check_MDLs

Check_Uncertainty

Verification of AIRS Reprocessing Changes

1. Summarize changes made at the request of the states (check with person responsible for making the changes) and verify that these changes were updated with reprocessing.
2. Summarize changes made in response to problems found during the AQS processing and verify that these changes were updated with reprocessing.

Events in this Report Batch Withheld from AQS Update

Summarize any events in the current report batch that had to be withheld from updating in AQS (e.g., the state has not yet added the site to AQS, and thus we can not add monitors). Indicate what action will be needed to allow the withheld records to be posted in the future.