MODEL STANDARD OPERATING PROCEDURES (SOPs)
FOR
SAMPLING AND ANALYSIS

AIR QUALITY MONITORING, EMISSION INVENTORY & SOURCE APPORTIONMENT STUDIES FOR INDIAN CITIES

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This document is prepared for use in 'Air Quality Monitoring, Emission Inventory & Source Apportionment Studies' being carried out for six Indian cities viz. Bangalore, Chennai, Delhi, Kanpur, Mumbai & Pune. The objective of preparing this document is to provide model standard operating procedures (SOPs) for sampling & analysis components of the source apportionment studies. This document is a guiding model for reference to all the project executing agencies, which are required to develop their own detailed SOPs for various parameters considering their QA/QC requirements. The changes made in this document (if any) should not compromise with the data quality. Document is based on information on similar studies conducted in the past, literature on various issues, specific project objectives, available infrastructure, resources, technical know-how, time frame, etc. Users are advised to keep in mind the above facts & limitations, while referring the document.

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CHAPTER – I

Standard Operating Procedures (SOPs) and Quality Control

1.0 Introduction to SOPs and Quality Control

Each measurement consist a value, precision, accuracy, and validity. Therefore, Quality Assurance/Quality Control (QA/QC) is backbone of good quality acceptable data. Quality Control (QC) and quality auditing establish the precision, accuracy, and validity of measured values. Quality Assurance (QA) integrates quality control and quality auditing to determine these four attributes of each environmental measurement.

QA integrates quality control, quality auditing, measurement method validation, and sample validation in to the measurement process. The results of assurance are data values with specified precisions, accuracies, and validities. Personnel who are independent of those performing the procedures perform quality auditing. A separate quality assurance officer performs these audits.

In this study QC has been identified as the responsibility of respective participating organization. QC is intended to prevent, identify, correct, and define the consequence of difficulties, which might affect the precision and accuracy, and or validity of the measurements. The QC activities include: (1) modifying standard operating procedures (SOPs) to be followed during sampling, chemical analysis & data processing by the respective organization; (2) equipment overhaul, repair, acceptance testing & spare parts; (3) operator training, supervision & support; (4) periodic calibrations and performance tests which include blank (including field blanks) & replicate analysis; and (5) quality auditing.

The following section describes the requirements for SOPs and gives examples on quality auditing. For detailed quality assurance activities and requirements 'U.S EPA's Quality Assurance Handbook' may be referred.

1.1 Standard Operating Procedures (SOPs)

No chemical analysis method, no matter how accurate or precise, can adequately represent atmospheric concentrations if the filters to which these methods are applied are improperly selected or handled. $PM_{2.5}$ or PM_{10} filter mass deposits are usually measured in micrograms (one-millionth of one gram). These are very small quantities, and even the slightest contamination can bias these mass measurements. Most chemical species that constitute PM_{10} fall in nanograms (one-billionth of one gram) range. The risk of sample contamination when measuring these chemical components is 10 to 1,000 times greater than mass measurement. Small biases in chemical concentrations can greatly affect the decisions that are made with respect

to source apportionment; so extra precautions are warranted during selection, handling and analysis of filter deposits. Therefore, Development of Standard Operating Procedures (SOPs) is most important to ensure proper quality control and quality assurance.

In order to ensure proper QA/QC process *Standard operating procedures* (SOPs) is recommended to be developed which delineate the procedures, step-by-step, to be followed for sample collection, analysis, substrate preparation, analysis or other activities critically related to the study objectives. It is normally expected that the SOPs will accurately reflect laboratory practice and the document shall be located where the measurement is being performed.

During the development of SOPs, attempt must be made to identify all possible sources of artifacts and incorporate adequate *performance checks* to ensure that errors are effectively minimized.

1.2 Quality Control (QC)

Quality control activities begin with the design of the sampling and measurement strategy and continue through the final validation of the database. Quality control has in fact been identified as responsibility of the laboratory conducting the work. These activities include:

- The development of standard operating procedures with comprehensive measurement performance checks to ensure the quality of the measurements are within established tolerance levels;
- Proper training and certification of operators/analysts to ensure data quality;
- The inclusion of measurements for the estimation of accuracy, precision, and detection limits to crosscheck analytical performance needed to ensure data quality;
- Verification of comparability with related measurements between operators/analysts;
- Documentation of field and analytical activities; and
- Data validation

1.3 Quality Assurance (QA)

Quality assurance is the responsibility of Laboratory management to satisfy the queries of an independent auditor. The task of the auditor is to satisfy the following questions:

- Is the Documented procedure complete and technically sound?
- Are the performance checks adequate for data quality control?
- Are the methods being followed properly and deviations, if any, properly documented?

- Do the reported measures of data quality hold up to scrutiny?
- Is the Method Detection Limits (MDL), Measurement Uncertainties reported properly?

2.0 Responsibilities

2.1 Laboratory Managers

The Laboratory Manager shall:

- Oversee and maintain records of all activities related to filter paper.
- Record maintenance of stock, procurement, issuance, inspection, labeling, pretreatment, dispatch to field, receiving of exposed filter paper and final distribution of different filters for respective analysis.
- A filter track sheet should accompany each filter with detailed information of state of analysis. The track sheet should be returned to Lab manager along with analytical data.
- Supervise and train lab technicians to maintain Good Laboratory Practices (GLP).
- Review all log sheets for completeness, and to check the validity of the samples prior to downloading of the samples by lab technicians.
- Resolve any inconsistencies on the log sheets or in the samples
- Oversee filter handling procedures
- Clean and maintain the analysis laboratory

2.2 Lab Technician/Scientist

The lab technician shall:

- Inspection of each filter paper through pinhole testing for holes/cracks on filter paper.
- Pre-conditioning of each filter papers following the guidelines for respective analysis.
- Pre weigh and individually identify filters for use at sampling sites.
- Load filters into sampling cassettes.
- Mail cassettes in shipping containers to sites.
- Receive exposed cassettes.
- Post-conditioning of each filters following respective methodologies.
- Post weighing the exposed filter papers.
- Preparation of datasheet for mass concentration.
- Segregation and dispatch of different filters to respective labs for further analysis.

CHAPTER – II

Standard Operating Procedures for Filter Inspection and Pre-Treatment for Sampling

1.0 Purpose and Applicability

This chapter on Standard Operating Procedures (SOPs) describes the laboratory procedures for initializing and processing aerosol filter papers in preparation for sampling. Preparation of filters for sampling or analysis is the responsibility of the lab manager and lab technicians. Processing includes procurement, inspection, pre-conditioning, pre-weighing and dispatching of filters for field sampling.

2.0 Guidelines for Selection and Procurement of Filters

The quality of filter papers to be used for source apportionment studies should technically meet the desired specifications. It is preferable to prepare the estimate for whole requirement and order the same in bulk with a request to supply the same batch/lot of filters to control analytical quality and blank values.

During the selection of filters following points should be considered:

- Mechanical stability;
- Chemical stability;
- Particle or gas sampling efficiency;
- Flow resistance;
- Loading capacity;
- Blank values;
- Artifact formation;
- Compatibility with analysis method; and
- Cost and availability.

2.1 Teflon Filter Paper for Elements and Ions

47 mm (dia) Teflon (PTFE) filter paper with Polypropylene support ring manufactured by M/s Whatman or M/s Pall Life Sciences or equivalent having 2 µm pore sizes. The filter papers should have very low background concentrations for ion and elements.

2.2 Tissue Quartz Filter Paper for OC/EC and Molecular Markers

47 mm (dia) Tissue quartz filters made of pure quartz without any binder manufactured by M/s Whatman or M/s Pall Life Sciences or equivalent

having 1-2 µm pore sizes. The filter papers should have very low background concentrations for carbons and organics.

2.3 Nylon Filter (Optional) for Ions

47 mm (dia) Nylon filter with 1µm pore size having low background for Sulphates and nitrate. The filter should have very little absorption potential for PAN. The filter is optional because the question of acid rain and PAN formation in atmosphere is rare in India.

2.4 Petri Dishes

Suitable unbreakable Petri dishes like Analyside Petri dish of Pall Life sciences or equivalent to keep and transport the filter papers.

3.0 Guidelines for Conditioning of Filter Papers

Filter papers selected for different analytical objectives should be conditioned by following steps:

- Inspect all the filter papers for holes or cracks. Reject, if any deformity is found.
- Note down the batch/lot in log sheet.
- Label all the filters following a general lab coding technique, which should be unique to represent a sample.
- Put the marked filters in petri dishes.
- Use always proper (blunt) twizers/forceps (made of non-reactive material) to handle the filter papers in lab and field as well.
- Prepare a sample-tracking sheet for each filter paper or a batch of filter paper.

3.1 Filter Inspection and Stability

To equilibrate, the filters are transferred from their sealed manufacturer's packaging to a filter-handling container such as a plastic petri-slide. The filters are handled with non-serrated forceps. Lab personnel must wear vinyl gloves as secondary when filters are being prepared for conditioning and weighing. Before any filter is placed in a filter-handling container, it must be inspected for defects. This is done be an examination of the filter on a "light table". A filter must be discarded if any defects are identified. Specific defects to look for are:

- **Pinhole** – A small hole appearing as a distinct and obvious bright point of light when examined over a light table.
- **Separation of ring** – Any separation or lack of seal between the filter and the filter support ring.

- **Chaff or flashing** – Any extra material on the reinforcing ring or on the heat-seal area that would prevent an airtight seal during sampling.
- **Loose materials** – Any extra loose materials or dirt particles on the filter.
- **Discoloration** – Any obvious discoloration that might be evidence of contamination.
- **Other** – A filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

4.0 Filter Conditioning

4.1 Pre-firing of Quartz-Fiber Filters

Quartz-fiber filters absorb organic vapors over time. Blank quartz-fiber filters should be heated for a lot at least three hours at 900°C. If lower temperature (550°C) is used the duration of conditioning should be at least 12 hours. One sample of each batch of 100 pre-fired filters is tested for carbon blank levels prior to sampling, and sets of filters with carbon levels exceeding 1µg/cm^3 are re-fired or rejected. All pre-fired filters should be sealed and stored in a freezer prior to preparation for field sampling.

4.2 Equilibrating Teflon-Membrane Filters

A one-month storage period in a controlled environment, followed by one week equilibration in the weighing environment, found acceptable deviations in reweighing. Sets of Teflon-membrane filters, which exceed XRF detection limits for elements, are rejected.

Gravimetric measurement is the net mass on a filter by weighing the filter before and after sampling with a balance in a temperature and relative humidity controlled environment as described in SOPs. To minimize particle volatilization and aerosol liquid water bias, $PM_{2.5}$ reference methods require that filters be equilibrated for 24 hours at a constant (within ±5%) relative humidity between 30% and 40% and at a constant (within ±2°C) temperature between 20°C and 23°C, which is a more stringent requirement than for PM_{10} filter equilibration. PM_{10} filters are required to be equilibrated at 20% to 45% relative humidity (±5%) and 15°C to 30°C temperature (±3°C).

These filter equilibrium conditions are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH and 20°C best conserve the particle deposits during sample weighing. Accurate gravimetric analyses require the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapor and other gases.

4.3 Washing Nylon-Membrane (Optional) Filters:

Nylon-membrane filters absorb nitric acid over time. Blank nylon-membrane filters should be soaked for four hours in 0.015 M sodium carbonate, then, rinsed in deionized distilled water (DDW) for 10 minutes, soaked overnight in DDW, rinsed three times in DDW and dried in vacuum oven at 60^0C for 5 to 10 minutes. Extraction efficiency tests have shown that the sodium carbonate IC eluent is needed to remove nitrates from the active sites of nylon filter. Sets of washed nylon filters with nitrate levels exceeding 1 µg/filter should be rejected. Pre-washed nylon filters should be sealed and refrigerated to prior preparation for field sampling.

5.0 Record Maintenance

The results of all filters treatments, chemical analyses, and visual inspections should be recorded in a data sheet with the lot numbers. A set of filters IDs is assigned to each lot so that a record of acceptance testing can be associated with each sample. Complete the Track sheet and transport the filters properly to field.

CHAPTER – III

Standard Operating Procedure for Sampling

1.0 Purpose

Purpose of this SOP is to delineate the steps and requirements for PM_{10} sampling with Speciation sampler. The SOPs for a few activities (e.g selection, conditioning and pre & post weighing of filters) related to sampling will be dealt separately.

2.0 Sampling Network Design

The methods recommended for different parameters are available in the document on **'**CONCEPTUAL GUIDELINES AND COMMON METHODOLOGY FOR AIR QUALITY MONITORING, EMISSION INVENTORY & SOURCE APPORTIONMENT STUDIES FOR INDIAN CITIES'. The required design and matrix is presented in Table – 3 of the document. It was emphasized in document that chemical analysis of PM_{10} and $PM_{2.5}$ (limited) samples must be closely coupled with the appropriate sampling methods and filter handling procedures are mandatory to satisfy the requirements to use CMB8 receptor model.

3.0 Sampling Equipment Selection

Particle filtration samplers consist combination of size-selective inlets, filter media, filter holders, and flow movers/controllers. In the design of these field samplers the aerodynamic diameter at which 50% of the sampled particles penetrate an inlet is termed the 50% cut-point (d_{50}). The ratio of the particle diameter for which 16% of sampled particles penetrates the inlet to the diameter at which 84% penetrate the inlet (d_{10}/d_{84}) is termed the slope. A smaller slope indicates a sharper cut-point, resulting in a better distinction between particles that are larger and smaller than $d_{50.}$ A slope of unity indicates that 100% of the particles with aerodynamics diameter less than the cut-point pass through the inlet to the filter.

In view of specific requirements of sampling system and monitoring methods in this study, it was decided to use the best suitable sampler to collect simultaneous samples in different filter matrix essentially required for characterization of particulate matter with PM_{10} inlet.

4.0 Description of Sampling Equipment

The Partisol Model 2300 Speciation Sampler is a high quality flexible sampling platform for the collection of particulate matter from ambient air. $PM_{2.5}$ and PM_{10} inlets are provided as required by the user. The device contains the

same user interface and is built upon the same hardware platform as the popular Partisol Model 2025 Sequential Air Sampler.

The Partisol Model 2300 Sequential Speciation Sampler was conceived from the ground up as a sequential sampling platform. Both the 4- and 12-channel versions of the device provide sequential sampling capabilities. Four-channel samplers can be upgraded at a later date to the 12-channel configuration if user needs. 4-channel speciation sampler is recommended in Source Apportionment study.

4.1 Applications

4-channel Speciation sampler is useful to collect PM_{10} on different filter paper to facilitate further analysis of Ions, elements, Molecular markers and Carbons (OC/EC). The built in hardware, flow controller, temperature-humidity sensors and field data recorder help in acquisition, storage and transfer of field data to data base management.

4.2 Technology

The Partisol Speciation Sampler satisfies the design criteria required for USEPA speciation sampling network. The versatility of this instrument is that it may be upgraded to simultaneously use denuders and filters to arrest both volatile and particulate phases. Special ChemComb cartridges designed by Harvard School of Public Health help in stripping gases and collect particulate fraction on desired filters.

4.3 Flow Control

Both the 4- and 12-channel configurations of the sampler contain four flow independent mass flow controllers. These provide active flow control by using information from ambient temperature and pressure sensors to maintain a constant volumetric flow rate. Flow rates are generally maintained at either 16.7 l/min, with a user-selectable range of 5 to 18 l/min. The device reports sampled volumes in either standard or volumetric terms.

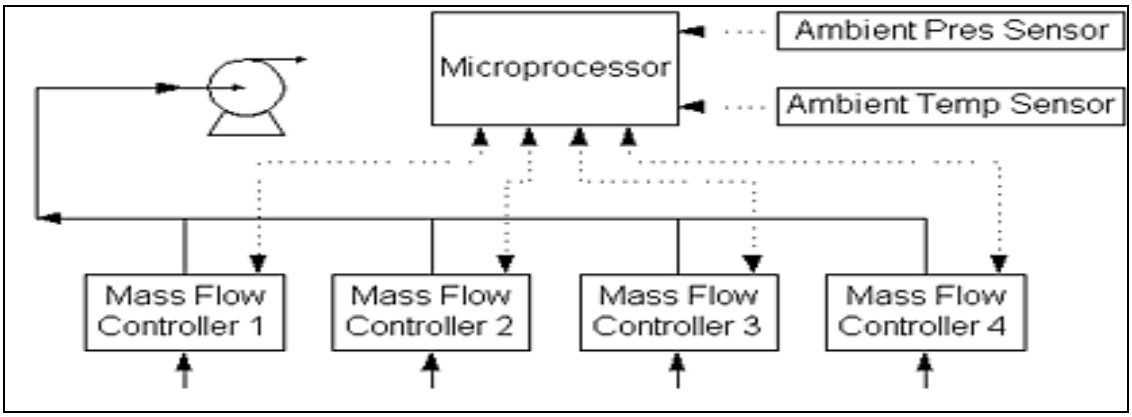

Fig. 3 (a): Flow Control

Built-in software support provides straightforward flow audits using the innovative Streamline FTS Flow Transfer Standard as well as leak checks using a leak check plug. Leak check plugs are available for insertion in the input ports of the Partisol Speciation Sampler, as well as for $PM_{2.5}$ ChemComb Cartridges configured with a greased inlet.

5.0 Pre Sampling Activities

Pre sampling activities involve Site selection, Preparation of monitoring plan, Installation of sampler, Calibration, Selection of appropriate filter media, Pre-conditioning of filters, etc. The criteria for site selection & monitoring plan for respective cities have been provided in the document on 'CONCEPTUAL GUIDELINES AND COMMON METHODOLOGY FOR AIR QUALITY MONITORING, EMISSION INVENTORY & SOURCE APPORTIONMENT STUDIES FOR INDIAN CITIES'. This SOP deals with calibration, operation, filter paper handling and data handling in field.

5.1 Potential Field Sampling Artifacts and Checks

Bias PM_{10} mass and chemical concentrations data may be generated due to several sampling artifacts. These must be taken care and evaluated at the time of sampling if the integrity of the data is to be preserved. The potential artifacts and methods to avoid them are as follows:

5.1.1 Passive Depositions of windblown dust on the filter prior to and following sampling can positively bias PM_{10} measurements. This bias can be minimized by more frequent sample changing and by use of a "Sample Saver", a device that covers the filter inside the sampler until the pump blowers starts.

5.1.2 Re-entrainment of large particles collected in the size-selective inlets can positively bias PM_{10} measurements. As noted above, impaction inlets may become saturated. Frequent cleaning and greasing of inlet impaction surfaces will minimize re-entrainment biases to physical and chemical concentrations.

5.1.3 Recirculation of pump exhaust can positively bias PM_{10} measurements. Every flow mover contains fragments of its brushes and armatures in the exhaust. Moat high vacuum pumps have outlet filters, which should be installed and changed at least quarterly. A piece of clothes-dryer duct can be attached to the high-volume exhaust plenum to direct pump exhaust away from the sampler inlet.

5.1.4 Volumetric Flow Rate errors may be caused by infrequent performance tests and calibrations of flow controllers. This is especially true of mass flow controllers, for which the set point is temperature dependent. In one of the studies, the observations indicated that flow rate biases of

10% to 20% would occur when flow measurements are taken during the winter using a calibration representative of summertime temperatures. Frequent flow meter calibration and performance tests are required to ensure that the sampled volume is accurate.

5.1.5 Volatilization of chemical compounds (ammonium nitrate and certain organic compounds), which are in equilibrium with their environment, cause losses. The most accurate monitoring of these species involves denuder-type sampling systems. However, this bias can be minimized by removing samples soon after sampling, storing them in sealed containers under refrigeration, and keeping them in coolers for transport between the sampling site and laboratory and proper preservations should follow in lab.

6.0 Leak Check & Calibration

The operator should perform leak check after every re-installation, cleaning and re-assembling operation of instrument. Inner filter holder, volume-flow meter, vacuum gauge, and vacuum pump may have leakages. Using plug provided with the system can perform leak check.

Flow calibrations and flow audits are also critical to the accurate collection of air samples. Ideally, air sampling equipment should be calibrated (multi-point) in the configuration in which it will be in the field, and the sampler flow rate is validated with an independent meter in the field. Built-in software support provides straightforward flow audits using the innovative *Streamline FTS Flow Transfer Standard* in Partisol Speciation sampler. Frequency of calibration should satisfy the QA/QC requirement.

7.0 Sampling

- Ensure proper installation and safety of equipment.
- Switch on the instrument.
- Perform Leak check.
- Calibrate the instrument one day before the monitoring starts.
- Programme the instrument and enter all relevant data.
- Set the flow of all individual channels to 16.7 LPM.
- Properly mark the channels.
- Place two pre-conditioned and pre-weighed 47 mm Teflon filters with supporting ring in two channels connected by Teflon inner coated cartridge. One is for Ions and other is for elements.
- Place pre-conditioned and pre-weighed 47 mm tissue quartz filter in third channel connected by anodized cartridges. This filter will be used for OC/EC and organic markers.
- 4^{th} channel is planned to be plugged. It may be used with appropriate filters and cartridges, if needed.
- Prepare data log sheet and filter tracking sheet.

- Care should be taken in coding and decoding of each and every filter paper. Use separate and marked petri dishes to keep and transport filters.
- Start the instrument; allow it to run for 24 hours.
- Collect the exposed filters and replace them in same petri dishes or cassettes.
- Manually note down the flow data, complete field data sheet.
- Insert new filters in same manner and follow the guidelines for next day sampling.
- Transport the exposed filter to lab along with field data sheet and sample tracking sheet to lab. Take necessary actions to follow guidelines of sample transportation.

R & P Speciation Sampler Module Disassembly/Assembly – Manufacturer's Recommendation

Summary of Task

This procedure describes how the R & P speciation sampler modules (cartridges) are handled in the SHAL. In this procedure, the order of disassembly of components is:

1st Filter pack cap with filter pack
2nd PM_{10}/ PM_{25} inlet with impactor plate
3rd Interior components of cartridge body (if any are present).

Modules (cartridges) are assembled in the reverse order.

Materials

Gloves, latex or vinyl
Jig for disassembly/assembly of module
High vacuum grease (Dow Corning, silicone) in a tube
Single-edge razor blade
Small spatula or disposable wooden sticks (to remove impactor grease)
Artist's brush, stiff (small stencil brush)
Laboratory tissues wet and dry
Plastic work tray lined with laboratory tissues
Forceps to handle filters
Prepared quartz, Teflon and nylon 47 mm diameter filters, each in a plastic Petri slide
Zero air or nitrogen gas source

Teflon Filter Module: Disassembly Procedure

1. Inspect the ChemComb™ cartridge to ensure: bar-code component ID label number matches the number on the data sheet; both ends are capped; all four retaining clips are securely fastened; the inlet is black Teflon-coated with an indented ring around the base of the inlet, indicating it is for the 16.7 liters per minute channel; and the color-coded dot is correct for the Teflon filter channel (green).
2. Inspect the filter pack outlet port for looseness. Remove the plastic cap from the inlet and inspect for damage or obstruction of the inlet jet.
3. Hold the cartridge assembly by the cartridge body with one hand encircling it. Place the assembled cartridge in the jig by sliding the collar of the filter pack outlet into the

jig opening. This positions the cartridge with the inlet up and the filter pack and outlet port down.

4. Place a strong rubber band around the cartridge so that the band covers the upper part of the clips which hold the filter pack outlet to the cartridge body.
5. While holding the middle of the cartridge body with one hand and pressing down firmly, loosen the filter pack clips with the other hand. A small cloth or piece of rubber tubing can be placed on the clip to relieve any stress on the fingers or thumb during this process. Ensure the clips are clear of the lip of the filter pack outlet port (the rubber band should hold them clear).
6. While still grasping the middle of the cartridge body with one hand and holding the top of the firmly with the other hand, exert a slight twisting and rocking motion on the cartridge and, at the same time, pull it upward gently. Remove the cartridge and place it on its side in the work tray.
7. Examine the sample filter. Make notes on the data sheet if the filter is torn, the deposit is very light, very heavy, irregular, etc. Use ling tweezers to lift the top-most filter holder (containing the filter) up and out of the filter pack cap "well." Set the filter holder on a clean surface in the work tray. Use forceps to grasp the plastic ring at the edge of the filter, lift the filter from the holder, and transfer it to a labeled Petri Slide. Take care not to split or tear the filter during this process. (The Teflon filter must be handled by its plastic ring only. The nylon filter must be handled by its edges. The quartz filter is particularly fragile.)
8. Use a deionized water wet wipe to wipe the filter holder and the rim of the aluminum cartridge that touched the filter. Note: oftentimes small pieces of the quartz filter adhere to the filter holder; if so, use a stiff artist's brush to gently dislodge them prior to wiping the holder. Set the filter holder and cartridge aside to air dry before re-assembly. Remove the filter pack outlet from the jig and set it aside.
9. Grasp the cartridge with one hand and hold it perpendicularly to the work bench so that the inlet is at the top. Detach the retaining clips that hold the inlet.
10. Remove the inlet from the cartridge body by carefully and slowly rocking, twisting, and pulling directly upward. Set the cartridge aside.
11. Remove the impactor plate from the interior of the inlet using your fingers. Do not touch the greased area during removal. Inspect the impactor plate to be sure the high vacuum grease has remained in the indented reservoir area and that a darkened spot of impacted particles is present. Note any unusual observations. Set the impactor aside.
12. Wipe the interior of the inlet and the jet with a deionized water tissue. Set the inlet aside to dry. Alternatively, a blast of clean air or nitrogen can be used to remove dust.
13. Refurbish the impactor. Use a small spatula or disposable wooden stick to scrape out the center of the vacuum grease layer to remove the accumulated particles. Wipe the spatula on a small tissue and discard the tissue. Squeeze a small amount of high vacuum grease into the depression created where the grease was removed. Use a single-edge razor blade, held at a 450 angle, to gently smooth the grease so that its surface is level with the top of the reservoir area. Do not bear down with the razor blade; to do so will damage the impactor, surfaces. Wipe the razor blade clean on a small tissue, discard the tissue, and store the razor blade safely. Use a laboratory tissue to remove any grease that is outside the impactor reservoir area. NOTE If the impactor plate is very dirty or has been used for 12 sampling events, remove all grease from the indented reservoir area using laboratory tissues and cotton swabs. It

may be necessary to gently wash the impactor with hot water and laboratory detergent and swab with tissue to remove the last traces of the grease. Rinse the impactor plate with distilled water and allow to dry. Then re-grease the impactor as described above.

14. Reinstall the impactor plate in the inlet. The greased side of the impactor must face the inlet jet. Set the inlet assembly aside.
15. Clean the interior of the empty cartridge body. Wipe the interior of the smaller diameter end with a dry, lint-free laboratory tissue. Make a wad from the tissue and push it through the interior of the cartridge. Blast clean air or nitrogen through the cartridge interior to remove remaining dust or fibers.
16. Apply a very thin coating of high vacuum silicone grease to any O-ring needing lubrication. Wipe off excess grease with a laboratory tissue.
17. Re-install the plastic caps on the inlet and outlet components. Send the disassembled, cleaned Chem Comb cartridge to the assembly area.

Teflon Filter Module: Assembly Procedure

18. Attach the black inlet with indented ring (containing the refurbished impactor plate) to the larger end of the cartridge, press it flush against the O-ring, and secure it in place by closing the clips. The ends of the clips must be fully seated in the slightly beveled rim of the inlet. Set the assembly aside.
19. Use smooth forceps to grasp the plastic ring edge of a new Teflon filter and place it in a filter holder. The numbered side of the filter must face upwards. Put the loaded filter holder aside.
20. Ensure the filter pack outlet stage is tightly seated in the filter pack outlet. If it is not, grasp the outlet fitting and pull the filter pack outlet stage into the outlet until it bottoms out and is surrounded by the Viton O-ring. Add two unloaded filter holders and check to see they are level and seated. It not, use the forceps to maneuver the filter holders until they are tightly in place. Then install the filter pack outlet, oaded with the filter pack outlet stage and two empty filter holders, on the jig.
21. Place the filter holder containing the filter just loaded in the "well" of the filter pack outlet, so that it nests with the filter holder beneath it. Be sure the holder containing the filter is level and seated. If it is not, use the forceps to maneuver the filter holder (do not touch the filter) until it falls into place.
22. Lower the cartridge (assembled in a previous step) onto the filter pack outlet and firmly and evenly press it straight down into the filter pack outlet. Do not twist the cartridge during this step. Remove the rubber band. Affix the ends of the clamps to the beveled rim of the filter pack outlet. While holding the cartridge down firmly to prevent lateral motion, close the retaining clips one at a tome to hold the filter pack outlet in place.
23. Remove the Chem Comb sampling module from the jig. Close both ends with plastic caps.
24. Store the assembled Chem Comb sampling module in a plastic bag in the designated bin until ready for documentation, packing, and shipment.

Nylon Filter Module: Disassembly Procedure

1. Inspect the sampling module (cartridge) to ensure: the bar-code component ID label number matches the number on the data sheet; both ends are capped; all four retaining clips are securely fastened; the inlet is coated with black Teflon and does not have an indented groove around it, to indicate it is used with a 10 liters per minute flow channel; and the color-coded dot is correct for the nylon filter channel (red).
2. Follow steps 2 through 9 for the Teflon filter module disassembly procedure.
3. Remove the inlet from the cartridge body by carefully and slowly rocking and twisting while pulling upwards. ***Take great care to keep the inlet and cartridge in line as they becomes detached! A glass spacer tube protrudes slightly into the inlet interior; the spacer tube can be chipped or shattered if the inlet or cartridge is tilted!***
4. Follow steps 11 through 14 of the Teflon filter disassembly procedure.

Nylon Filter Module: Cartridge Components Removal and Reinstallation

5. The nylon filter module cartridge body will contain seven components when the Chem Comb is used in its normal Trends Network configuration to collect nitrate and other ions. As viewed looking downward from the inlet end of the cartridge, these seven parts are: glass spacer, HDPE plastic spacer, glass honeycomb denuder (numbered on the side), HDPE plastic spacer, glass spacer, HDPE plastic spacer, and metal spring. To remove and clean these parts, proceed as follows. Lower the cartridge until it is just above the laboratory tissue on the work tray. Hold the cartridge in one hand and tilt it so that the parts can slide out into your other hand. As the parts slide out, catch them and place them on the laboratory tissue in the same order and orientation as they were packed in the cartridge. If needed, use a deionized water laboratory tissue to swab the interior of the glass spacers and the HDPE plastic spaces. Replace any broken or chipped glass spacers with new ones. Place all components on the laboratory tissue to dry. Examine the glass honeycomb denuder for cracks or other damage and place it on the tissue in the same orientation it was taken from the cartridge. *However, if the honeycomb denuder is scheduled for replacement, put a fresh denuder in its place and send the used denuder to the denuder laboratory, marked for refurbishment.* Clean the interior of the empty cartridge body. Wipe the interior of the smaller diameter end with a dry, lint-free laboratory tissue. Make a wad from the tissue and push it through the interior of the cartridge. Blast clean air or nitrogen through the cartridge interior to remove any remaining dust or fibers. Reinstall the cleaned (or replaced) parts in the cartridge in the reverse order of removal by allowing the parts to gently slide down the cartridge. If the metal spring or a HDPE spacer does not slide to the bottom and position properly, remove it and try again or use a length of clean polyethylene tubing to position the part. When all parts have been properly reinstalled, the top-most glass spacer will protrude above the rim of the cartridge approximately five millimeters. Place the reassembled cartridge on its side on the tissues in the work tray.
6. Apply a very thin coating of high vacuum silicone grease to any O-ring needing lubrication. Wipe off excess grease with a laboratory tissue.
7. Reinstall the plastic caps on the inlet and outlet components. Send the partially reassembled Chem Comb cartridge to the assembly area.

Nylon Filter Module: Assembly Procedure

8. Attach the black Teflon-coated inlet (containing the refurbished impactor) to the larger end of the cartridge and secure it in place by resting the end of each clip on the beveled edge of the inlet and then closing it. This inlet will not have an indented ring, indicating it is to be used with a 10.0 liters per minute channel. Be very careful not to tilt the inlet during installation; t do so may break the glass spacer that protrudes slightly from the cartridge.
9. Use smooth forceps to grasp the edge of a new nylon filter and place it in a filter holder.
10. Follow steps 20 through 24 of the Teflon filter assembly procedure.

Quartz Filter Module: Disassembly Procedure

1. Inspect the sampling module (cartridge) to ensure: the bar-code component ID label number matches the number on the data sheet; both ends are capped; all four retaining clips are securely fastened; the inlet is shiny anodized aluminum and does not have an indented groove around it, indicating it is for a 10 liters per minute channel; and the color-coded dot is correct for the quartz filter channel (orange)
2. Follow steps 2 through 17 for the Teflon filter module disassembly procedure.

Quartz Filter Module: Assembly Procedure

3. Attach the anodized aluminum inlet (containing the refurbished impactor) to the larger end of the cartridge and secure it in place by positioning the ends of the clips in the beveled ridge of the inlet and then closing the clips. Be sure the inlet does not have an indented groove around it, which indicates it is used with 10.0 liters per minute flow channel.
4. Use smooth forceps to grasp the edge of new quartz filter and place it in the filter holder. The smooth side of the quartz filter must face upwards.
5. Follow steps 20 through 24 of the Teflon filter assembly procedure.

CHAPTER – IV

Standard Operating Procedures for Sample Reception and Storage

1.0 Purpose

The following procedures ensure that the sample integrity is maintained from sample reception to final analysis in the lab and that all necessary documentation pertaining to sample traceability is readily available. Removing samples that do not meet the acceptance requirements for elapsed time or flow rate, and contacting site operators, as necessary, to repair damaged equipment or correct faulty collection techniques.

2.0 Sample Reception

2.1. All samples received are accompanied by the corresponding sample tracking sheet containing all necessary information such as, sample ID, sample description, field ID, project ID, sample prep, batch number (where applicable), tracking sheet number, type of analysis required, final volume. All samples, controls and method blanks processed, as a batch should have a common ID.

2.2 Upon receipt, the analyst immediately verifies sample integrity as well as the information provided on the sample-tracking sheet. Any discrepancies are immediately noted and reported to the supervisor.

2.3 All necessary information is entered in the 'Sample Analysis Log'. The Log sheets are used to record the following information: date of receipt, TS No., Batch No., number of samples, analytes, analysis date, instrument ID, analyst name and date reported.

2.4 Sample tracking sheets are stored in the appropriate section of the binder entitled "Sample Tracking Sheets".

2.5 Samples are processed by TS No. on a first in - first out basis unless otherwise specified (i.e. priority samples).

2.6 As samples are processed, all necessary information is recorded in the Sample Analysis Log and on the corresponding Tracking Sheet by the responsible analyst.

2.7 When sample analysis is complete, a copy of the corresponding TS is stored in the appropriate section of the binder, which is subdivided to analyte group, and the original TS is submitted to the Supervisor along with test results for approval.

2.8 The date reported that is recorded on the Sample Analysis Log is the date for which all samples results for a given TS are forwarded to the Supervisor.

2.9 The analyst reporting test results is responsible for logging the corresponding results into the appropriate work lists.

2.10 A copy of the results reported are stored in the "Results" binder under "Preliminary Results" until approved by the supervisor, whereby the

reports are transferred to the appropriate section of the binder (Approved Results).

3.0 Sample Storage

3.1 Upon reception, samples are stored on the appropriate shelf in fridge #1 according to sample status (i.e. samples in process, archives).

3.2 Each batch of samples is clearly identified by way of TS No., target analyte group and batch No. until processed.

3.3 All aspects of sample handling are documented daily in the appropriate log books as well as on the corresponding comments (i.e. procedures used, observations, problems, deviations from the method, etc.)

3.4 A record of all archived samples is maintained up-to-date in the appropriate logbook located next to the refrigerator.

3.5 All archived samples are kept for at least during the study period and then disposed off following specific instructions from the supervisor.

CHAPTER – V

Standard Operating Procedures for Filter Weighing and Mass Measurement

1.0 Purpose and Applicability

This standard operating procedure (SOP) describes the laboratory procedures to weigh the filter papers for mass. Weighing of filters for gravimetric mass analysis is the responsibility of the lab manager and lab technicians. It includes calibration of balance, pre-weighing of filters after respective conditioning, receiving of filters after field exposure and final weighing after conditioning. For QA/QC purpose, record maintenance of calibration and weighing of control mass with every run are also included.

2.0 Laboratory Conditions for Weighing

Gravimetric analysis of the filters needs to be performed with a microbalance. The sensitivity and reliability of the electro-balance is about + 0.001 mg or 1 µg. Though tolerances on re-weights of Teflon-membrane filters are typically ± 0.010 mg, these sensitive balances require isolation from vibration and air currents. Balances placed in laminar flow hoods with filtered air minimize contamination of filters from particles and gases in laboratory air. Electrostatic effects contribute another main interference in gravimetric analysis of filters. It is established that residual charge on a filter could produce an electrostatic discharge between the filter on the pan and the metal casing of the electro balance, which induces non-gravimetric forces. This charge can be removed from most filter media by exposing the filter to a low-level radioactive source (500 Pico curies of polonium^{210}) prior to and during sample weighing.

3.0 Requisitions for Balance Room

Followings are the basic requisitions for a standard Balance Room:

- Standard Electronic microbalance with a minimum resolution of 0.001 mg and a precision of $\pm$ 0.001 mg, supplied with a balance pan. The microbalance must ideally be positioned on a vibration-damping free balance support table.
- Calibration weights should utilize Mass Reference Standards (non-corroding type) with a tolerance of 0.025 mg. range in weight from 1 mg to 2 mg, and be certified as traceable to standards. Two sets are needed, one set as a working standard and one set as a primary standard.
- Radioactive (alpha particle) Polonium-210 ("Static Master") antistatic strips for static charge neutralization. At least five strips are needed per balance.
- Non-serrated forceps for handling filters and weights.

- Digital timer/stopwatch.
- Relative humidity/temperature recorder.
- Certified hygrometer for calibration of relative humidity readings.
- Certified thermometer for calibration.
- Antistatic powder free vinyl gloves.
- Zip-lock plastic bags.
- Disposable laboratory wipes.

4.0 Electro Balance Controls and Calibration

Gravimetric mass analysis is performed using single pan electronic balance. If possible, polonium strip ionization units are used to reduce electrostatic effects in the weighing cavity and on individual filters. A segregated laboratory area is used to control human traffic and to stabilize the temperature and relative humidity of the weighing environment. The area is cleaned with a high efficiency vacuum cleaner, and a tacky floor covering is installed at the entrance to the sample handling room to minimize dust artifact. Gravimetric analysis of filters currently uses the difference method to determine the mass of the collected aerosol. The pre weight of each filter is measured prior to being sent into the field for sampling. Once exposed and returned to the sample handling room, the filter is removed petri dishes and the post weight of the filter is measured after conditioning. The mass of the aerosol is determined by calculating the difference between the pre and post weights.

4.1 Cleaning and Maintenance of the Sample Handling Room

The requirements for a sample handling room include a reduced dust environment, and, over the twenty-four hour period prior to analysis of exposed filters, temperature in the range of 25° C with variation less than ± 3° C, and relative humidity 45% ±5%.

Every last working day, the sample handling room should be thoroughly cleaned, after insuring that all filters have been protected against contamination. To reduce fugitive dust levels, all surfaces are cleaned with a high efficiency vacuum. The floors are cleaned with a mild cleaning solution, if necessary. Finally, all work surfaces are cleaned with reagent grade alcohol (or another reagent grade solvent, if necessary) and Kimwipes™. This procedure reduces the possibility of contamination if a filter falls to the work surface. Following the Friday cleaning, no analysis shall occur for at least twenty-four hours to reduce the potential for contamination of filters by compounds used in the cleaning process.

4.2 Calibration and Maintenance of balance

The balance is cleaned and calibrated every day for ranges at the start of operation. It is also recalibrated if the balance fails a "zero" test that is

performed periodically. A calibration log database is maintained for each balance. Significant events concerning the balance and any balance maintenance other than routine procedures are recorded in the log of the lab manager.

4.2.1 Cleaning

Regular cleaning should be performed as following:

- Clean the metal and plastic forceps with ethanol and a Kimwipe™.
- Clean the work surface around the balance with ethanol and a Kimwipe™.
- Clean the top surface and the strips of the anti static ionizing units by gently rubbing with a Kimwipe™ wetted with ethanol. Do not neglect to clean the ionizing unit in the electro balance.
- Replace the clean ionizing unit in the center back of the balance cavity, and close the door on the weighing chamber (if polonium strip is used).

4.2.2 Thorough Calibration (Once in 3 Months)

- Allow the balance to stabilize with no weights on the pan. The computer will automatically record the mass to the screen when the balance has stabilized; this is the "zero" mass. It should be within 0.010 mg of 0.000. If not, contact the lab manager (see step 3, section 4.3.2.1 for lab manager procedures).
- Set the zero on the balance by pressing the tare button on the balance. This forces the "zero" mass to be exactly 0.000.
- Calibrate the balance. Momentarily ground yourself by touching the balance casing. Use nylon forceps to remove the certified calibration weight from its container. Gently place it in the center and allow the mass reading to stabilize and stop decreasing. Take readings.
- Use a 200.000 mg or suitable mass of graded Calibration weight.
- Use a 20.000 mg or suitable mass graded Calibration weight.
- Remove the calibration weight from the bail, using the nylon forceps, and replace it in its storage container.
- Check the calibration of the balance using the test weight. Momentarily ground yourself by touching the balance casing. Use the nylon forceps to remove the test weight from its container.
- Place the test weight in the center of the balance pan and allow the mass reading to stabilize and stop decreasing. The computer will record a reading to the screen when the balance has stabilized. The test weight is an old 50.000 gm calibration weight.
- Allow the balance to return to "zero." Compare the zero value and the value determined for the 50.000 mg mass to the expected values posted on the balance. If they exceed 02 micrograms, repeat the procedure. If variations greater than 10 micrograms are observed, report to the

laboratory manager so that he/she can take appropriate action (section 4.3.2.1 step 3).

- On a random basis, but at least semiannually, the laboratory supervisor shall request a comparison of the normal calibration standards with a master set of reference standard masses maintained by the laboratory supervisor. After calibration, measure these 200.000, 50.000, and 20.000 mg standards and report their masses to the supervisor. The results are used to verify the integrity of the electro balance and the standard masses used in daily calibrations.
- The electro balance is available to run controls or for routine determination of mass.
- Linearity checks (Once in a year otherwise after every repair/shifting of balance). To run a linearity check on the balance (if the balance is suspected to be damaged), utilize the series of four standard weights stored in the lab manager's desk. The four weights, 200 mg, 100 mg, 50 mg, and 20 mg, must be weighed and a regression line developed. Take following steps for performing Linearity checks:

  (i) Use the nylon forceps to remove a weight from its container and place it on the weighing pan.
  (ii) Wait until the balance has stabilized (approximately one minute). Then, record the displayed weight as the 'y' value and the certified mass as the 'x' value.
  (iii) Remove the weight from the pan, using the plastic forceps, and replace it in its protective container.
  (iv) Repeat steps (i) through (iii) for the other three weights.
  (v) Linearly regress the 'y' value versus the 'x' value. Calculate the r^2 value.
  (vi) If the r^2 is not better than 0.995, the balance requires maintenance.

4.2.3 Stability Check (Once in Month)

To check the stability of the balance, reweigh the last 20 archived control filters, and develop a regression line comparing the re-weight values to the original values. Use following steps:

(i) Reweigh the series of 20 old controls filters on the suspect balance.
(ii) Plot the re-weights versus the original weights.
(iii) Derive the best line fit equation correlating the original weights to the re-weights.
(iv) Calculate the standard deviation and the r^2 of the line fit.
(v) If the standard deviation is greater than ±3 micrograms, and the r^2 is not better than 0.995, the balance should be carefully inspected and submitted for maintenance.

4.2.4 Daily Calibration

Internal and external Calibration should be performed daily before any Pre- or Post sampling weighing.

Internal Calibration: Open the draft shield door for at least one minute to allow the balance-weighing chamber to equilibrate to room temperature, then, close the draft shield door. Press the "TARE" key when readout has stabilized to ensure zero-readout. The liquid crystal display (LCD) should display "0.000 mg". Press the key for ensuring the internal calibration.

External Calibration: Open the draft shield door. Place a 100 mg working reference standard calibration weight onto the microbalance pan with non-metallic forceps. Close the draft shield door. Record the date, temperature and relative humidity of the balance room, and mass readout in the quality control logbook assigned to the microbalance. Remove the calibration weight and tare the microbalance as described above. Enter the calibration data into logbook records and assign to the calibration session in the quality control logbook assigned to the microbalance. External calibration must be performed for each day on which filters are pre-weighed and/or post-weighed.

5.0 Weighing of Filters

- Take out pre-conditioned filters by forceps one by one and weigh properly. Record the mass in data sheet and log books against respective filter numbers or code.
- Replace and close the filter container (Petri dishes). Weigh one Control Filters (Archived one) with each batch of ten weighing. Keep separate controls for Pre (Blank filter) and Post (Exposed) sampling filters.
- Put the values of all control measurement in Quality Control Charts against dates.

6.0 Calculation and Reporting of Mass Concentrations

The equation to calculate the mass of fine particulate matter collected on a Teflon filter is as below:

M_{10} / $M_{2.5}$ = (M_f – M_i) x 10^3 µg

Where,
M_{10} / $M_{2.5}$ = total mass of fine particulate collected during sampling period (µg)
M_f = final mass of the conditioned filter after sample collection (mg)
M_i = initial mass of the conditioned filter before sample collection (mg)
10^3 = unit conversion factor for milligrams (mg) to micrograms (µg)

Field records of PM_{10}/$PM_{2.5}$ samplers are required to provide measurements of the total volume of ambient air passing through the sampler (V) in cubic meters at the actual temperatures and pressures measured during sampling. Use the following formula if V is not available directly from the sampler:

$V = Q_{avg} \times t \times 10^{-3}\ m^3$

Where,

V	=	total sample value (m^3)
Q_{avg}	=	average flow rate over the entire duration of the sampling period (L/min)
t	=	duration of sampling period (min)
10^{-3}	=	unit conversion factor for liters (L) into cubic meters ($m^{3)}$

The equation given below can be used to determine PM_{10} or $PM_{2.5}$ mass concentration:

$PM_{10} = M_{10} / V$

Or

$PM_{2.5} = M_{2.5} / V$

Where,

PM_{10} / $PM_{2.5}$	=	mass concentration of $PM_{2.5}$ particulates (µg/m^3)
M_{10} / $M_{2.5}$	=	total mass of fine particulate collected during sampling period (µg)
V	=	total volume of air sampled (m^3)

8.0 Reporting

Data reporting should be done in prescribed Format. The Format shall contain all information including calibration. The data sheet must be accompanied by Sample Tracking sheet.

FIELD LOG SHEET FOR $PM_{2.5}$ / PM_{10} SAMPLING

Site ID: _____Site Name: _____ Sampler No.: _____

Name and Designation of Operator:

Date of Last Calibration:
Date and Time of Leak check:
Date and time of cleaning of Sampling Head and Path:

Pre-Sampling Checks (Please mark ✓):

1. Clean the sampler and its head as scheduled.
2. Renew its quartz Teflon filters.
3. Adjust the initial flow rates to 16.7 LPM.
4. Program the timer
5. Record initial flow rates and sampling time as below:

Sample ID#	Filter ID	Initial Flow	Starting Date/Time (YYYY/MM/DD, hh:mm)	Stopping Date / Time (YYYY/MM/DD, hh:mm)

e.g. Q for Quartz, T for Teflon.

Post-sampling Checks:

Operation Procedures (Please mark ✓)

1. Retrieval and storage of all exposed filters into transport container.
2. Crosschecking of flow was performed.
3. Record the end time and final flow rates into the following table.

Sample ID# (Description)	Filter ID	Final Flow	Average Flow	Actual Sampled Air Volume (m^2)	Valid Elapsed Time (hh:mm)

Checked By: _____
Date of Visit: _____ Arrival Time: _____ Departure Time: _____

SAMPLE TRACKING SHEET

Filter Paper Nos.					Sender's or Operator's Signature	Received by (Signature)
F.Paper Type						
Lot/Batch No.						
Site Description						
Date of Sampling						
Inspection	Date of inspection	Inspection done by		Certified by		
Lab Code						
Pre-conditioning	Nature	Date and Time	Done by	Certified by		
Pre-weighing	Date and Time	Weighed by	Balance Calibration (Y/N)	Control weight Status		
Dispatch detail	Date	To (Specify Sites)				
Filter Receiving	Date & Time	Sites	Sampling date & time	Condition of filters		
Post Conditioning	Nature	Date and Time	Done by	Certified by		
Post-weighing	Date and Time	Weighed by	Balance Calibration (Y/N)	Control weight Status		
Dispatch Detail	Date & time	To (Specify Lab)	Parameters	Results Expected by the date		

REPORT FORMAT

Name of the Project :

Name of Executing Agency :

Sampling Location ID and Name :

Monitoring Season :

Date and Time of Monitoring :

ID of Instrument used :

Last date of Calibration :

Field Sampling Done by :

Analysis Done By :

Filter Type :

Filter ID :

Start time	Closing time	Initial Weight (mg)	Final weight (mg)	Flow rate (LPM)	Air Volume (m^3)

Calculation:

Volume of air passed (V) = Sampling Duration (Min) X LPM (Average)
Dust collected on Filter (M) = (Final weight – Initial weight) * 1000 µg
Concentration = M / V µg/m^3

Remarks:
Meteorological conditions: Temperature – (Min & Max)
% RH – (Min & Max)
Rain fall –

Sampling Stoppage time (if any) with reason:

Name & Signature of Field Operator

Name & Signature of Analyst

Report Checked by (Supervisor)

Report Approved by
(Officer in charge)

CHAPTER – VI

General Guidelines on Standard Operating Procedures for Chemical Analysis of Ambient PM_{10} & $PM_{2.5}$

1.0 Standard Operating Procedures

Standard Operating Procedures (SOPs) codify the actions, which are emphasized to implement a measurement process over a specified time period. Ideally state-of-the-art scientific information should be incorporated into the SOP and should include the following basis elements:

- A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions, which must be met for it to be valid. A list of materials, equipment reagents, Specifications and suppliers are to be given for each expandable term.
- Designation of the individual to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and schedule for transfer standard verification.
- Start-up, routine, and shutdown operating procedures and an abbreviated checklist.
- Copies of data forms with examples of filled out forms.
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- Internal calibration and testing procedures and schedules.
- External performance auditing schedules.
- References to relevant literature and related operating procedures.

In the light of prevailing conditions the following section gives typical design of SOP required in this study for characterization of particulate matter (PM_{10} & $PM_{2.5}$).

Typical of minimum detectable limits for elemental, ionic, and carbon analysis methods that are commonly applied to aerosol filter samples should be mentioned in SOPs. The MDL values given in SOPs are nominal, and actual detection limits should be supplied by the laboratory performing the analysis prior to sampling.

The commonly applied aerosol analysis methods can be divided into the categories of mass, elements, ions, and carbon. For additional information to identify and quantify source/receptor relationships, organic compound, individual particle, and isotopic analyses methods have been recorded.

2.0 Filter Handling and Storage

Filter handling starting from procurement through inspection, pre-conditioning, weighing, field exposure, post weighing and data reporting should be followed as guided in respective SOPs for defined purposes. There are certain general precautions required for filter handing and storage before any chemical processing, which are as follow:

Often excessive blank levels and filter interferences put substantial impact on study results. At least two filters from each lot (typically 100 filters) or a minimum of 2% of the filters purchased from the specified manufacturers should be analyzed for all species to verify that the pre-established specifications have been met. Lots are rejected for chemical analysis when blank levels for individual species exceed 1µg/filter.

Each filter should also be individually examined prior to labeling for discoloration, pinholes, creases, separation of ring, chaff or flashing, loose materials, or other defects. For ringed Teflon filters, the diameter of the exposed areas should be measured and should not deviate by more than $\pm$ 1 % of 40.538 mm.

Testing of sample media should continue throughout the course of a monitoring project. In addition to 2% to 5% of laboratory blanks, approximately 10% of all samples are designated as field blanks; those should follow all handling procedures except for actual sampling.

The SOPs for the further chemical analysis for the following four different types of methodologies are described in this document. These are model SOPs and respective executing agencies are responsible to develop and rewrite their own SOPs for all the parameters.

CHAPTER – VII

Standard Operating Procedures for Elemental Analysis

1.0 Elemental Analysis Methods

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), atomic absorption spectrophotometry (AAS), inductively coupled plasma with atomic emission spectroscopy (ICP- AES) or with mass spectroscopy (ICP-MS), photon- induced x-ray fluorescence (XRE), and proton induced x-ray emission (PIXE) have all been applied to elemental measurements of aerosol samples for atomic numbers ranging from 11 (sodium) to 92 (uranium).

Since air filters contain very small particle deposits (20 to 100 g /cm^2), preference is given to methods like XRF that can accommodate small sample sizes and that require little or no sample preparation or extensive operator time after the samples are loaded into the analyzer.

2.0 A Model SOP for Elemental Analysis of Air Particulate by Energy Dispersive X-Ray Fluorescence (EDXRF)

Elemental Analysis of Air Particulate by Energy Dispersive X-ray Fluorescence (EDXRF). This method applies to the analysis of ambient air particulate collected on 47mm diameter Teflon Filters.

This method describes the quantitative determination of elements in ambient air particulate collected on Teflon membrane filters. The elements that are determined by this method include many of the elements with atomic numbers 11 (Na) through 82 (Pb). (Note: both Na and Mg are reported as only estimates.

The method assumes that the particulate is collected as a surface deposit on top of the filter media, that the particulate loading level is less than approximately 100 µg/cm^2, and that the filter matrix is relatively uncontaminated with elements over Z=9.

2.1 Principle of Detection

An X-ray source removes electrons from the inner shells of atoms by exciting the atoms to energy states above the stable configuration. As electrons move to refill the ground state energy levels, the atomic system maintains its fundamental energy balance by emission of electromagnetic radiation. The emitted radiation is an x-ray whose energy is characteristic of the excited element. The samples are quantitatively analyzed by counting the number of

observed x-rays over a set period, as compared with the number of fluoresced x-rays from similarly analyzed standards.

2.2 Detection Limits

The detection limits and reporting limits are calculated approximations based on several of the known uncertainties of both the sampling and analytical methods. Limitation with determining detection limits based on replicate low level standard analysis is that the detection and reporting limits for any particular element are dependent on the concentrations of other elements in that particular sample. The uncertainty equals the propagation of the MDL for that sample plus a calibration/sampling error (estimated at 8%). The uncertainty is rounded to 5 significant figures.

An example list of MDLs for blank Whatman Teflon filters is given in Table below, if we assume of sample volume of 9.68 M^3 for unit conversion purposes. These are relatively interference free samples: Therefore MDLs will increase on samples with particulate loading.

Table 7 (a): Minimum Detection Limits (MDLs) of Element in ED-XRF Analysis

Element	Z	MDL (ug/M3)	MRL (ug/M3)
Na	11	0.1567	0.47
Mg	12	0.0367	0.11
Al	13	0.0033	0.010
Si	14	0.0018	0.0053
P	15	0.0012	0.0035
S	16	0.0050	0.015
Cl	17	0.0033	0.010
K	19	0.0023	0.0068
Ca	20	0.0016	0.0049
Sc	21	0.0021	0.0062
Ti	22	0.0063	0.019
V	23	0.0022	0.0067
Cr	24	0.0011	0.0032
Mn	25	0.0020	0.0059
Fe	26	0.0017	0.0051
Co	27	0.0013	0.0040
Rb	27	0.0009	0.0026
Ni	28	0.0013	0.0040
Sr	28	0.0011	0.0032

2.3 Interferences

Peak overlap interference results when the energy of the fluoresced photon for one element overlaps the range of energies used to determine the

concentrations of another element. This overlap results from the limited resolution of the analyzer. The "peak overlap correction" is quantified by measuring the counts in the analyte range of interest when analyzing a thin-film standard that contains the interfering element but not the analyte element.

Both the particle size and composition affect the degree of attenuation of both the excitation and the fluorescence X-rays. X-ray attenuation is most significant for lower energy x-rays. Corrections can be made for these attenuations based on an average particle size and the composition of particulate, but particle size and composition can only be estimated. The use of Elemental Analysis of Air Particulate (EDXRF) Department of Environmental Quality the attenuation corrections also assume that the filter loading is low enough that the particles are deposited as a virtual mono-layer. The approach to particle size/matrix attenuation correction also assumes that the particulate is deposited on the surface of the filter, not within the depth of the filter.

Self-absorption (matrix effect) occurs in standards just as it does in samples. With standards, mass absorption coefficients and spectrometer geometry are used to calculate the infinitely thin concentrations upon which the calibration factors are based.

X-rays other than fluoresced x-rays reach the detector. Both the filter matrix and the particulate loading scatter x-rays to the detector. If not removed from the spectrum, these scattered x-rays are positive interferences. The amount of scatter is dependent upon the mass thickness (i.e. the mass per unit area) of both the filter and the particulate. The scatter background is corrected for by subtracting the average spectra (for blank filters) from the samples' spectra. (The shape of the scatter actually varies depending upon the average atomic number of the scattering material.)

The Toolbox software is also used to calculate an additional "automated background" correction based on the shape of the spectrum, basically drawing a background from "valley to valley". Because the software finds even the "random noise valleys", the background can be modeled at too low a level.

Secondary fluorescence occurs when fluoresced photons from one element more efficiently (as compared to the original excitation x-rays) excite another element. This would normally lead to a positive interference. Secondary fluorescence is a relatively insignificant interference at the concentration levels found in air particulate.

Escape peaks and sum peaks are artifacts of the detector and are corrected for by the software.

The x-ray tube flux changes over time (weeks or months). Conditions with low voltage and high current cause the greatest drift in the x-ray tube output. To

maintain the same calibration factor over time, the current must be increased as the x-ray tube output decreases. The change in x-ray tube output is monitored by analysis of at least one check standard during each run.

The monitor ratio can correct for change in the x-ray tube output. The height of the sample relative to the plane of the sample tray holder changes the intensity of both the excitation and fluorescence x-ray beams. The edges of the sample holders used for the standards are recessed so that both the thin-film standards and the loaded filters are presented to the instrument in the same vertical plane.

Sample holder geometry can increase scatter. For both secondary target excitation and direct excitation, the area of the filter being analyzed is a region centered on the openings of the 2" by 2" squares in the sample tray. The sample holders used for the filters are low profile with an offset 33 mm sample presentation hole. (Ideally, the sample holders would have a centered ~40mm hole.) The analyzed region of the surface is within the 33mm hole. Under the configurations used for air particulate analysis, both excitation modes analyze a region approximately 1.5 cm^2. (Changing the collimators' sizes would change the sizes of the areas of analysis.) The analysis results, however, are weighted to the center of this region. That is, a particle contributes more counts to the spectra if it is at the center of the analyzed region than if it is at the edge of the analyzed region. This should not cause an error as long as the particulate is deposited homogeneously over the surface of the filter.

Changes in the environmental temperature of the environment may cause drifts in the constants used in the analog to digital conversion operation: The exact location of peaks may drift if the instrument is operated when the room temperature has recently drifted. In practical terms, the most likely time that the room environment changes are when the instrument's nitrogen Dewar has been recently filled. Therefore, do not calibrate the unit (i.e., run the CALADC procedure) or analyze samples until at least 3 hours after the Dewar has been filled.

2.4 Safety

For general laboratory safety procedures, consult the DEQ Laboratory Safety Manual) supplied by manufacturer.

3.0 Equipment Standards and Reagents

3.1 Instrument

A typical set of equipment and supplies are highlight for one type of EDXRF mode. A Kevex 771-EDX Spectrometer with the following features is used for analysis:

An X-Ray tube with:
A Rhodium anode
A 127 µ thick Be window
0 to 3.3 mA current
0 to 60 kV voltage
0.25% RSD stability for any 8-hour period in 24 hour duration with tube current from 0.01 to 3.3mA and voltage from 5 to 60 kV.

A primary excitation configuration that can utilize any of 4 sets of transmission filters and collimators. The geometry in the direct mode is a 21° incidence angle and a 45° take-off angle. Angles are measured from the plane of the samples' surfaces.

A secondary excitation configuration that can utilize any of 6 targets. The geometry in the secondary mode is a 45° incidence angle and a 45° take-off angle. Angles are measured from the plane of the samples' surfaces.

A 0.05mm thick tungsten baffle has been installed between the x-ray tube and the detector so that direct excitation of detector collimator is reduced. (This baffle is attached to the detector "snout" and should not touch any other portion of the instrument because the detector should be electrically and mechanically isolated.

A sample chamber with sixteen positions for 2" by 2" sample holders. The sample chamber is evacuated with a 200 L/min vacuum pump.

A beryllium windowed, Si (Li) detector that is cooled with liquid nitrogen. The detector has an energy resolution of 165 ev FWHM for 5.9-keV (using Fe55 test source) at 1000 cps, 32 shaping index. The detector is collimated with a tantalum collimator. (A silver detector collimator is also available.)

A 4665 Pulse Processor, which is normally operated with 40 keV gain, 32 µsec shaping index, and 0.8 µsec pulse pair resolution. (For condition 6, the processor is operated at a gain of 80 keV and a shaping index of 32 µsec). Gain, shaping index, and pulse pair resolution are all selectable by software control.

A multi channel analyzer that is normally operated within preset lifetime acquisition mode with up to 2 K channels and ranges from 10 to 40 keV. The System controller is a Pentium3 with MS Windows 98 and with Kevex WINXRF software V2.41.

3.2 Reagents

There are no reagents used in this analysis.

3.3 Standards

- Typical standards recommended for the equipments supplies (given earlier as an example) are as under:
- NBS SRM 1832 (Thin Glass Film on Polycarbonate for X-ray Fluorescence Spectrometry)
- NBS SRM 1833 (Thin Glass Film on Polycarbonate for X-ray Fluorescence Spectrometry)
- NIST SRM 2708 (Zinc Sulfide Thin Film on Polycarbonate for X-ray Fluorescence
- Spectrometry)
- NIST SRM2783 (Air Particulate on Filter Media: Simulated $PM_{2.5}$ air particulate matter deposited on polycarbonate filter membrane)
- Dzubay polymer film standards each of which contain two non-interfering elements. These are referred to by the two atomic symbols: e.g., CrCu.

- **Quality Control standard (QCS).** The NBS/NIST SRMs are used as quality control standards. Only NIST SRM2783 is used solely as a QCS.

- **Calibration (Working) standards**: Both thin films and SRMs are used in the calibration, to determine both calibration factors and inter-element correction factors. See the attachment with specifics of which standards are used in each case.

4.0 Sample Collection, Preservation, Shipment, and Storage

- The samples are collected using sequential sampler.
- The samples are shipped and stored properly at room temperatures or conditioned environment.
- The FRM samples (collected on the R&P Partisol samplers) are collected within 4 days of the end of sampling, are shipped and stored at < 4°C prior to analysis (except during equilibration and weighing).
- The Speciation samples are retrieved from the samplers within 2 days of the end of sampling, are shipped and stored at less than <4°C until analysis (except during equilibration and weighing).

5.0 Calibration and Standardization

The XRF instrument analog to digital converter (ADC) energy levels are calibrated weekly using the software function based on spectra of a multi-element film containing layered titanium and tin foils.

The more traditional calibration, the determination of calibration factors and inter-element interference correction factors, is conducted annually, after modifications have been made to the instrument set up (either physical or ramp settings), or if the monitor ratio falls outside the 90%- 110% range. The factors are determined based on analysis and processing of spectra from Micro matter standards, for example NIST SRMs and Dzubay polymer

standards. Standards used in determining calibration factors are analyzed at reduced X-ray tube current (33% of normal) to maintain counting dead times closer to those associated with the samples. The reduction in tube currents are reflected in the monitor ratios that are associated with all calibration standard data, besides calibration requires the following:

One standard is used for each element to determine its calibration factor, although when multiple standards are available and analyzed, the results for all the standards analyzed under a condition are graphed against the atomic number to determine which standard fits best to the smooth curve. The calibration factor for each element is calculated from the infinitely thin standard concentration, the net intensity in the analyte's region of interest, and the monitor ratio. The calibration factors have the units of counts per second per ug/cm^2. The infinitely thin concentrations are determined based on the excitation source, the instrument geometry, the concentrations of elements in the standard, and mass absorption coefficients (from reference sources) of both the excitation and fluoresced x-rays. The correction of actual concentration to infinitely thin concentration is described in detail in the calculation section of this SOP. This correction is most significant for the lighter elements.

The inter-element correction factors are based on the net counts in a region interest for a standard that contains the interferent but that does not contain the analyte. The units of the interferent factors are: (net interferent counts in the analyte's region)/(net interferent counts in the interferent's region of interest). It is essential to find an interferent standard that is not contaminated with the analyte. (The purity of the interferent standard can be investigated by examining the interferent spectra for several of the analyte peaks.) If a correction factor involves comparing regions of interest from 2 different conditions, it is especially important the monitor ratios of all conditionals do not drift excessively.

In analyzing any of the standards, it is important to present them to the instrument at the same height as the samples. To accomplish that, special holders have been made to account for the thickness of the rings that hold the standard materials.

For consistent results, when standards are analyzed, they are placed a dot along their edge closest to the outer edge of the sample tray.
However suppliers in operation manuals provide the detailed calibration procedures.

6.0 Quality Control

Data assessment and QC acceptance criteria are of primary importance in assessing the quality of data resulting from analytical batch. Both negative

and positive biases are a concern. The following data assessment and QC data are required for all analyses:

Listing of required Quality Control (QC) elements, including frequency and acceptance limits.

Quality Control Element	Frequency	Acceptance Limits
Lab blanks	At least 1 per 20 samples, or one every batch.	The concentration for all analytes should be less than the MRL.
Quality control sample (QCS)	1 for each batch	± 20% of the reference value, if the value is >5 time the MRL
Laboratory duplicates	1 in every 20 samples	The uncertainty ranges overlap.
Continuing Calibration Verification (CCV)	1 per 15 samples. The monitor ratio results are used for this purpose.	± 10% of the initially determined value

6.1 Corrective Actions for Out-of-control Data

It is at the analyst's discretion on how to handle out-of-control or unacceptable data. If the CCV (or monitor ratio) of any condition is outside the range of 90-110%, the reason for the drift is investigated and corrected prior to repeating the analysis of all samples. When the ratio is simply changing due to the aging of the tube (as mostly occurs in low voltage/high current conditions), the current can be adjusted in the procedure and matrix files to bring the monitor ratio within specifications.
If the precision of the lab duplicates does not meet the acceptance criteria, the following steps can be taken:

(a) Examine the spectra to determine if there was an obvious problem with the analysis, such as sample ID error.
(b) Reanalyze the samples and determine if the analysis conducted on one day is suspect. If the results from one day appear significantly different from 2 other days, re-analyze all samples analyzed on the "outlier" day.
(c) Examine the programs used to process of the spectrum, and if imprecision is occurring due to normal baseline noise, adjust the uncertainty and reporting limits for the analyte in future sample processing.

If lab blanks have reportable values for any analyte, investigate the source and/or run additional blank filters to determine if the blank spectrum for that lot of filters needs to be replaced. If no other satisfactory explanation and solution can found, investigate the handling of the filters during weighing.
If the results of repeated analysis of the quality control standards show a change
Greater than a 10% drift, rerun the standard and the samples, investigate the source of the drift if it remains, and recalibrate if necessary. Reanalyze sample that have been analyzed after the last in-control QCS.

6.2 Contingencies for Handling Out-of-control Data

If none of the corrective actions brings the QC elements under control, the data may be reported as estimates or not reported at all, as decided by the analyst and the section manager.

7.0 Procedure

The analyst must be familiar with operation and troubleshooting of the XRF system and the files that used in the calculation steps. This procedure will only serve as an outline of the steps that must be performed. Understanding the software and hardware are the responsibility of the chemist who is performing the analysis.

To understand the steps described in this section, the reader must understand the several of the terms used to describe the software. The front-end interface software that controls the XRFsystem is referred to as "WinXRF", with the underlying language and file structure referred to as "Toolbox". The front-end interface software that displays the spectra is referred to as the "SDP" (Spectral Display Program). The following is a list of most of the file types used in setting up and conducting the analysis, and in processing and calculating the results:

Excel spreadsheets: These files contain the calculations to convert the net and gross counts for each sample into reportable numbers in the unit's ug/M^3 at LTP. The files also contain the macros that perform the importing of PRN files and formatting of the output. There are separate excel files for each sample type (e.g., PM_{10}, $PM_{2.5}$, NBS2708 standard, etc.)
Library file: Basically, the library files are the folders used to collect related toolbox files that are recognized by the Kevex software. Each toolbox file has a very limited size (1.1MB).
Matrix files: Toolbox files that set the conditions (e.g., current, target, vacuum, monitor ratio, etc.) under which the samples are being analyzed.
Names files: Toolbox files that list the sample IDs.
Procedure files: Toolbox files in command language that controls the x-ray instrument and the processing of data found in the toolbox files.
PRN files: Translations of Toolbox U1 files that is output in a delimited format that can be imported by Excel. These are used to transfer from toolbox to Excel the gross, net, and error counts for all analytes. Each file contains the data for only one sample.
Spectrum files: Toolbox files that can be display in the "SDP". These contain the raw results of fluoresced spectral acquisition.
Window files: Toolbox files that describe the boundaries of the regions of interests, as used for integration and background corrections.
U1 files: Toolbox files containing the net and gross counts for a sample that result from the processing of spectra.

U2 files: Toolbox files containing constants (e.g., regions of interest channels) used in extracting net and gross counts from the spectrum.

7.1 Sample Tray Loading

Handle the filter holders and the filters (by their edge ring) using only stainless steel forceps Never touch the filter, even on the edge, as it may be extracted for ion analysis.

Select the proper sample holder type for each sample or standard: Routine holders are used for all samples but standards and reference material have modified holders to present the filter at the correct height.

Never leave the samples or standards in the sample tray outside of the XR front-end cabinet for longer periods than necessary.

Load the monitor standard in the sample position 1, the CALADC standard—if it is being used—in sample position and any samples or control standards in the remainder of the positions.

A sample from the previous run and a QC standard are usually analyzed with every tray of samples.)

- Make small labels for each of the samples.
- Clean the bench space being used for the sample handling.
- Remove the sample tray from the instrument and place it on a stand to elevate the tray several inches above the counter.
- Turn on the x-ray tube to 10kv and 0.05ma when the tray is removed.
- Place a new 6" glassine weighing paper on the counter to use as the surface upon which the sample holders are placed during loading.
- Remove the filter from its Petrie dishes and place it in the filter holder, with the loaded surface facing down. (If it is difficult to determine which side is loaded in case the particulate loading is very light, the loaded side is the side with the filter ID number printed on the edge ring.)
- Place a small label on the edge of the filter and place in the sample tray.
- Continue load sample into the tray and then record the loading positions and sample IDs in a blue book.
- Turn off the X-ray tube, place the tray in the sample compartment, and turn on the x-ray tube again.

The other following components of procedures are to be observed as per directive given 'Manual' supplied with equipment:

- Instrumental Analysis
- Spectra Processing
- Method Performance
- Maintenance
- Pollution prevention
- Waste Management

- Preventive measure of Job Hazardous

7.2 Calculation & Data Reporting

Collect all the PRN files from the samples of interest in one folder.

Add information about the samples (date, site, filter ID, RPN file name, sample volume in M3 at LTP, and loading area in cm2) to the appropriate spreadsheet. Separate spreadsheets have been created which include calibration factors, interelement correction factors, and attenuation correction factors. These factors are specific to the instrument calibration and the particulate size (or standard thickness).

Run the macro "Samples": it calculates, prints an individual report each sample, and transposes/copies the data into a single table that includes all the data being processed. This excel file is saved with a unique name.

7.3 Data Reporting

Import the excel file into an access table in the database: PMChemExport. The form PMChemExportForm in this database provides macros and documentation of the process for creating a table that meets the needs of the analytical supervisor for transferring the data to the Central system.

7.4 Calculations

These calculations are typical & pertinent to a particular mode of EDXRF.
Infinitely thin standard concentration calculations are based on the equations presented in Dzubay's paper "Evaluation of Polymer Films as Standards for X-ray Fluorescence Spectrometers".

A = {1-e (-x)}/x =X-ray attenuation factor

Where,

x = M (μ1secY1+μ2secY2)/ðr2
M = mass of disk
r = radius of disk
μ1 = total mass absorption coefficients for incident X-rays.
μ2 = total mass absorption coefficients for outgoing X-rays.
Y1 = angle between the path of the incident X-rays and the line normal to the film.
Y2 = angle between the path of the outgoing X-rays and the line normal to the film.
"sec" = secant = 1/cosine

Total mass absorption coefficients (either μ1 or μ2) equal the sum of individual mass absorption coefficients (located in standard tables such as the CRC Handbook) times the individual weight fractions. That is, μ= μ i * w i
Where μ i and w i are elemental mass absorption coefficients and weight fractions.

For the Kevex 771, the geometry of the instrument is as follows:

Secondary target excitation incidence angle = 45°.
Direct excitation incidence angle = 69°.
Outgoing angle for both modes of excitation = 45°.

Excitation energies are as follows:

Cond. 1: Direct, Incident E=2.7
Cond. 2: Ti target, Incident E=4.5
Cond. 3: Fe target, Incident E=6.4
Cond. 4: Ge target, Incident E=9.9
Cond. 5: Direct with Rh foil filter, Incident E=20
Cond. 6: Direct with W foil filter, broad excitation range

The infinitely thin concentration of the standard equals the concentration of the standard (μg/cm2) times the X-ray attenuation factor. The infinitely thin concentration of each standard is specific to the condition under which it was analyzed.

Calibration factors

Calibration factor calculations are described by the following equation:

Cf = Cnts/Lt/(Infconc)

Where,

Cf = calibration factor in counts/second per μg/cm^2.
Cnts = net counts in the region of interest.
Lt = Lifetime for which counts were collected (seconds).
Infconc = Infinitely thin concentration of the standard under these conditions (μg/cm2).

Overlap interference factors

Overlap interference factors calculations are described by the following equation:

Intf = Acnts/Icnts

Where,

Intf = Overlap interference factor.
Acnts = Net counts in the analyte's region of interest in a standard, which contain interfering element but no analyte element.
Icnts = Net counts in the interferent's region of interest in the same standard as used for Acnts determination.

Particle size corrections

Calculations for particle size correction are based on the calculations described by Criss.

Sf = (1+biai) 2 = Size factor
where *b* is values from the Criss table referenced and *a* are estimated particles diameter (see table VII (b) for values that we are using).

Table 7 (b): Estimate of Size of particulate containing specific elements (with attenuation factor used in parenthesis)

Element	$PM_{2.5}$	PM_{10}	TSP
Na	2 μm (1.300)	5 μm (1.823)	7.5 μm (2.326)
Mg	2 μm (1.309)	5 μm (1.850)	7.5 μm (2.372)
Al	2 μm (1.259)	5 μm (1.703)	7.5 μm (2.124)
Si	2 μm (1.232)	5 μm (1.626)	7.5 μm (1.995)
P	2 μm (1.145)	5 μm (1.381)	7.5 μm (1.594)
S	1 μm 1.042)	1.5 μm (1.064)	1.5 μm (1.064)
Cl	2 μm (1.069)	5 μm (1.177)	7.5 μm (1.271)
K	1 μm (1.034)	2 μm (1.069)	3 μm (1.105)
Ca	2 μm (1.061)	5 μm (1.156)	7.5 μm (1.238)
Sc	1 μm (1.030)	2 μm (1.061)	3 μm (1.092)
Ti	2 μm (1.061)	5 μm (1.156)	7.5 μm (1.238)
V	0.5 μm (1.010)	1 μm (1.020)	2 μm (1.04)
Cr	0.5 μm (1.018)	3 μm (1.111)	4 μm (1.149)
Mn	0.5 μm (1.019)	2 μm (1.077)	3 μm (1.117)
Fe	0.5 μm (1.017)	4 μm (1.141)	6 μm (1.214)
Co	0.5 μm (1.020)	2 μm (1.082)	3 μm (1.124)
Ni	0.5 μm (1.024)	2 μm (1.098)	3 μm (1.149)
Cu	0.5 μm (1.018)	2 μm (1.073)	3 μm (1.111)
Zn	0.5 μm (1.017)	2 μm (1.069)	3 μm (1.105)

Concentration of analytes

Concentration of analytes per volume of air sampled calculation:

Rconc = (((Cnts*Sf)/Cf/Lt/MR)-Rb)*(Area/Vol)

Or

= ((Cnts*Sf/(Cf*Lt*MR)-Rb)*(Area/Vol)

Where,

Rconc = Reported concentration in ug/M^3 LTP.
Cnts = Net counts (Net counts for each analyte's region of interest are reduced by the overlap counts from the interfering elements. The overlap count for each interfering element is determined sequentially in the order of average significance.)

Sf = Particle size attenuation factor for this element, this condition, and this sampling size cutoff.
Cf = Calibration factor in counts/second per µg/cm^2.
Lt = Lifetime for which counts were collected (seconds)
MR = monitor ratio for this day for this condition.
Rb =Average residual blank concentration (µg/cm^2)—normally close to zero.
Area = Surface area of filter on which particulate is collected (cm^2).
Vol = Volume of air from which the particulate was collected (M^3 in LTP).

Uncertainties

Calculation of uncertainties are described by the following equation:

$$Uconc = [\{Ucnts^2 + ModelingU^2 + (Serr*Cnts)^2 + (Cnts*SfU)^2\}*\{Sf/(Cf*Lt*MR)\}^2]^{0.5} *(Area/Vol)$$

where:
Uconc = Uncertainty of report concentration in ug/M3 LTP.
Uconts = uncertainty of counts based on counting statistics = (2*GrossCounts-NetCounts)$^{0.5}$)), plus Interferent Uncertainty Factor * Interferent Counts, where the Interferent Uncertainty Factor is 0.1 to 0.3, depending on the type of overlap.
ModelingU = modeling Uncertainty counts (estimated)
Serr = Sampling error and calibration uncertainty (estimated to be equal to 8%, or 0.08).
Cnts = Net counts in the region of interest.
SfU = Uncertainty of Particle size attenuation factor =15%*(Sf-1))
Sf = Particle size attenuation factor for this element, this condition, and this sampling cutoff size.
Cf = Calibration factor in counts/second per µg/cm^2.
Lt = Lifetime for which counts were collected (seconds).
MR = monitor ratio for this day for this condition.
Area = Surface area of filter on which particulate is collected (cm^2).
Vol = Volume of air from which the particulate was collected M^3

MDLs

The MDL is calculated the same as uncertainty but without the sampling/calibration error counts included (i.e., excluding the (Serr*Cnts) 2 addition)

MRLs

The MRL = 3*MDL.

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CHAPTER – VIII

Standard Operating Procedures for Water-Soluble Ion Analysis in Pm_{10} & $Pm_{2.5}$

1.0 Preparation, Extraction and Ion (Anions & Cations) Analysis

Aerosol ions refer to chemical compounds, which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and non-soluble fractions, as in the case of soluble potassium. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter materials. Samples are generally extracted in DDW, which is filtered to remove suspended particulate matter prior to analysis. Polyatomic ions such as sulfate, nitrate, ammonium and phosphate must be quantified by other methods such as ion chromatography (IC) and automated colorimetry (AC).

2.0 Purpose and Applicability

This document outlines procedures for the filter preparation and extraction, and the subsequent determination of ions in filter extracts.

3.0 Summary of Method

Teflon filters for collection of ions do not require pretreatment. Exposed filter samples are extracted by a method appropriate for the analyte(s) of interest. Filters are extracted with deionized water. Extraction with deionized water makes it possible to analyze for both anions and cations. Sample extracts are passed through a column of ion chromatographic resin consisting of polymer beads coated with quaternary ammonium active sites. During passage through the column, ion separation occurs due to their different affinities for the active resin sites. Following separation, the ions pass through a suppressor column, which exchanges all cations for OH- ions and anions for H+ ions. An eluent, which yields a low conducting acid/base, is used. Species are detected and quantified as their acids/alkalies by a conductivity Detector.

4.0 Cautions

Laboratory personnel should always wear clean clothes and wash hands thoroughly before performing filter handling and analysis procedures. The use of clean room gloves is required and will minimize the potential for laboratory contamination.

5.0 Interferences

Large amounts of cations or anions eluting close to the ions of interest will result in interference. No interferences have been observed in Teflon/nylon filters 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 columns.

6.0 Laboratory Requirements

6.1 Apparatus and Materials

- Filters (Teflon/Nylon)
- Volumetric flask, 1000 mL, 500 mL, 250 mL, 100 mL and 50 mL
- Tweezers
- Glass rod drying racks
- Tweezers
- Adjustable Eppendorf or equivalent micro-pipettes
- Ultrasonic bath
- Syringe filter with 13 mm Nylon filter holder and filter discs
- 250 mL glass beakers

6.2 Reagents

Stock Standards for Cations:

Use high purity graded chemicals for the preparation of all solutions. Dry chemicals used for the preparation of calibration standards salts of sodium, potassium and ammonium at 105 °C for 2 hours and cool in desiccators immediately before weighing. The stock solutions containing (Cation) = 1000 mg/L can be prepared by dissolving the appropriate amount of a suitable salt (purity standard.) in ultra pure water. The sample weight required per liter ultra pure water is shown in the table below (Table VIII (a)). To prepare the cation standard, these stock solutions are then diluted to the desired concentrations with ultra pure water.

Table 8 (a): Required weight of salts to prepare 1000-ppm stock individual standards

Cations	Salt	Weights in (g)	Final Volume	Concentrations
Sodium	NaNO3	3,6971	1000 mL	1000 mg/L
Ammonium	NH4Cl	2,9654	1000 mL	1000 mg/L
Potassium	KNO3	2,5858	1000 mL	1000 mg/L
Calcium	Ca $(NO_3)_2$,4H_2O	5,8920	1000 mL	1000 mg/L
Magnesium	$Mg(NO_3)_2$ x 6 H_2O	10,5467	1000 mL	1000 mg/L

Commercially available high purity individual liquid stock standards (1000 ppm) are also useful. Mix standards should be chosen carefully considering the difference in responses of individual ions in a chromatogram.

Calibration Standards preparation

Prepare Standard Mix - A Solution containing 100 ppm each Na^+ and NH_4^+ from 1000-ppm stock by diluting the same.

Prepared Standard Mix – B solution containing 100 ppm each K^+, Ca^{++} and Mg^{++} by diluting the stock. Final calibration standards for 5 levels are prepared following the Table VIII (b) given below. Prepare fresh working calibration standards weekly and refrigerate when not in use. Stock Standards may be used for 6 months if refrigerated properly.

Table 8 (b): Calibration Standards (in ppm) preparation guidelines (Final volume 100 mL)

Ions	Level I	Level II	Level III	Level IV	Level V
	0.50 ml A + 1.0 mL B	1 ml A + 2 mL B	2 ml A + 4 mL B	4 ml A + 8 mL B	5 ml A + 10 mL B
Sodium	0.50	1.0	2.0	4.0	5.0
Ammonium	0.5	1.0	2.0	4.0	5.0
Potassium	1.0	2.0	4.0	8.0	10.0
Calcium	1.0	2.0	4.0	8.0	10.0
Magnesium	1.0	2.0	4.0	8.0	10.0

Eluent for Cations: Specific for brand and make to instrument and columns being used. For concentration and composition of eluent please refer to the application notes. Generally for cation analysis Weigh 600 mg of **Tartaric Acid** and 167 mg Dipicolinic **Acid** and dissolve in 100 ml of ultra pure water (HPLC/Milli-Q Grade). Heat on Hot Plate / Heating Mantle until dissolved. Make up the volume to 1 Liter with Milli-Q Water. Eluents are required to be filtered through 0.22 µm nylon filter.

Suppressor for cations: Dionex system has inbuilt ionic suppressor system but Metrohm system does not require suppressor for cations.

Stock Standards for Anions: Use high purity graded chemicals for the preparation of all solutions. Dry chemicals used for the preparation of calibration standards at 105 °C for 2 hours and cool in a desiccator immediately before weighing. The stock solutions containing □ (anion) = 1000 mg/L can also be prepared by dissolving the appropriate amount of a suitable salt (purity standard.) in ultra pure water. The sample weight required per liter ultra pure water is shown in the table VIII (c) below. To prepare the anion standard, these stock solutions are then diluted to the desired concentrations with ultra pure water.

Table 8 (c): Required weight of salts to prepare 1000-ppm stock individual standards

Anions	Salt	Weights in (g)	Final Volume	Concentrations
Fluoride	NaF	2.2100	1000 mL	1000 mg/L
Chloride	NaCl	1.6484	1000 mL	1000 mg/L
Bromide	NaBr	1.4998	1000 mL	1000 mg/L
Nitrite	$NaNO_2$	1.2877	1000 mL	1000 mg/L
Nitrate	$NaNO_3$	1.4330	1000 mL	1000 mg/L
Phosphate	KH_2PO_4	1.3707	1000 mL	1000 mg/L
Sulphate	Na2SO4	1.4790	1000 mL	1000 mg/L

Commercially available high purity individual liquid stock standards (1000 ppm) are also useful. Mix standards should be chosen carefully considering the difference in responses of individual ions in a chromatogram.

Calibration Standards preparation

Prepare Standard Mix - C Solution containing 100 ppm each Cl^-, NO_3^- and $SO_4^=$ from 1000 ppm stock by diluting the same.

Prepared Standard Mix – D solution containing F^- (5 ppm) and Br^-, NO_2^-, PO_4^{-3}, 20 ppm each by diluting the stock. Final calibration standards for 6 levels are prepared following the Table VIII (d) given below. Prepare fresh working calibration standards weekly and refrigerate when not in use. Stock Standards may be used for 6 months if refrigerated properly.

Table 8 (d): Calibration Standards (in ppm) preparation guidelines (Final volume 100 mL)

Ions	**Level I**	**Level II**	**Level III**	**Level IV**	**Level V**	**Level VI**
	0.5 C + 0.5 D	1 C + 1 D	2 C + 2 D	5 C + 5 D	10 C + 10 D	15 C + 1 5 D
Fluoride	0.025	0.05	0.1	0.25	0.5	1.0
Chloride	0.5	1.0	2.0	5.0	10.0	15.0
Bromide	0.1	0.2	0.4	1.0	2.0	3.0
Nitrite	0.1	0.2	0.4	1.0	2.0	3.0
Nitrate	0.5	1.0	2.0	5.0	10.0	15.0
Phosphate	0.1	0.2	0.4	1.0	2.0	3.0
Sulphate	0.5	1.0	2.0	5.0	10.0	15.0

Note: All the aliquot volume is in ml

Eluent for Anions: Specific for brand and make to instrument and columns being used. For concentration and composition of eluent please refer to the application notes. Generally for anion analysis $NaHCO_3$ - Na_2CO_3 eluent is

used. Eluents are prepared by dissolving prescribed amount of chemicals in high purity nano-pure distilled water. Eluents are required to be filtered through 0.22 µm nylon filter.

Suppressor for Anions: Dionex system has inbuilt ionic suppressor system but Metrohm system chemical suppression for anions with 2.8 mL concentrated (98%) pure H_2SO_4 diluted in 1 liter is used for regeneration of suppressor cartridges. Pure water (DI) is used for washing of suppressor during run.

7.0 Sample Handling

Laboratory shall provide chain-of-custody documentation with all sample shipments to track and ensure that filter 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 project co-coordinator.

7.1 Filter Extraction Procedure

7.1.1 Teflon / Nylon Filters

Filters to be analyzed for cations are extracted with water. Extraction with deionized water makes it possible to analyze for both cations and cations. Due to hydrophobic nature of Teflon/Nylon filters soaking with 100-µL iso-propan-ol are necessary before extraction. This treatment enhances the solubility of particles entangled in between the pores of filter and prevents bacteriological degradation of some soluble ions in the extract.

- Remove filters to be extracted from the freezer and allow them to equilibrate to room temperature.
- Using gloved hands and tweezers, place each filter in cleaned glass beakers (250mL) that has been labeled with the sample I.D.
- Add measured 50-100 mL of deionized water. The extraction volume will depend upon the quantity of dust accumulated on filter paper.
- Place the batch of beakers in ultrasonic bath, expose them to ultrasonic energy in a bath for 60 minutes at 60 °C, and then allow them to sit at room temperature overnight. Refrigerate at least one additional night prior to analysis.
- Record the date of extraction on the Sample Filter Processing Form. Allow the samples to warm to room temperature just prior to analysis.
- Filter all the samples by syringe filter using 13 mm 6.6 µm nylon filter disc. Ensure no particle should pass through in samples to be injected. Injection may be done manually or through auto sampler.

7.2 IC Procedure

- Fill the eluent reservoirs with the eluent.

- Fill the suppressor reservoir and distilled water reservoir in case of chemical suppression technique (Metrohm instrument)
- Start the eluent flow, activate the self-regenerating suppressor in case of (Dionex instrument), and allow the baseline to stabilize.
- In case of Metrohm instrument ensure baseline determination until stable baseline is achieved.
- Inject two pure distilled water blanks to flush the system and to ensure that the system is operating properly.
- Using the calibration schedule, perform the monthly multipoint calibration over the range.
- Inject middle level calibration standards daily to know the status of performance. If the observed value for any ion differs by more than 10 percent from the known values, identify and correct the problem before analyzing samples.
- Load the sample extracts into the auto sampler vials according to the schedule prepared for that day. Typically, fifty field samples are analyzed per day. The daily schedule includes, at a minimum, 3 duplicate samples, 2 spiked samples and 5 QA/QC samples.
- Begin the analysis run, occasionally checking to ensure that the system is operating properly.
- 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.

7.3 Calculations and Data Reduction

In-built software will always give some results, which may not be acceptable all the time. Study each and every chromatogram and perform manual integration of peaks if necessary. Proceed to report format and copy the results in Excel data sheet. All the information related to sample ID, Air volume, Extraction volume are already fed to the Excel sheet and instrumental reading may be converted easily to concentration in $\mu g/m^3$.

8.0 Quality Assurance and Quality Control

The analyst should be familiar with the terms and use of following parameters for QA/QC

Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.

Field Blanks: These are filters that are treated in all ways as a normal sample (including installation on the sampler) except that no air is sampled on them. (These are also referred to as equipment blanks in LIMS.)

Continuing Calibration Blank (CCB): a "zero" standard analyzed along with the CCV standard to verify that the lower end of the calibration curve remains valid during the analysis of the batch of samples. A CCB is analyzed at the beginning of each batch, at the end of a batch, and at least every 20 samples during a batch.

Continuing Calibration Verification Standard (CCV): a standard analyzed after the initial calibration to verify that the instrument calibration remains valid. The concentration of this standard is varied over the calibration range during each run. A CCV is analyzed at the beginning of each batch, at the end of a batch, and at least every 20 samples during a batch.

Laboratory Duplicate: aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. In this SOP, extracting equal portions of the loaded filters creates laboratory duplicates.

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of Target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. In this SOP, a matrix spike consists of adding a known concentration of analyte(s) to a separate aliquot of the filter.

Lowest Detection Limit (LDL): the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. The estimation of MDL should be done applying any suitable statistical method.

Lowest Reporting Limit (LRL): the minimum concentration of an analyte that is reported. Generally, this will be 3 to 5 times the concentration of the MDL.

9.0 Calculations

Preliminary Raw Value (PRV) µg/m^3 rounded to 5 decimal digits

PRV = (Result * V_{EXT}) / (Filter Fraction) * (VAIR)
Reported value = PRV but not reported below LRL and rounded to no more than 3 significant figures (and no more than 2 decimal digits)

Method Detection Limit (MDL) µg/m^3 rounded to 5 decimal digits

(MDL) = (LDL * V_{EXT}) / (Filter Fraction) * (V_{AIR})

Method Reporting Limit (MRL) µg/m^3 rounded to 5 decimal digits
(MRL) = (LRL * V_{EXT}) / (Filter Fraction) * (VAIR)

Uncertainty rounded unto 5 decimal

Uc =[{(MRL / 3)^2 + (Result * 0.08)^2} $^{0.5}$ * V_{EXT}] / (Filter Fraction) * (VAIR), where 0.08 = sampling and calibration uncertainty

Where,

Result = analytical result for extract in mg/L

V_{EXT} = volume used in extraction (ml)

Filter Fraction is 1 if full filter is used.

V_{AIR} = Volume of air sample passed through the filter in m^3

If correlation coefficient for all the multipoint calibration curves does not exceed 0.998, stop the analysis and identify the problem.

Analyze QC samples 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.

10.0 Reference

DRI Document No. 8068.1F4, Appendix D, Section 4.2

CHAPTER – IX

Standard Operating Procedures for Elemental and Organic Carbon (OC/EC) Analysis

1.0 Purpose and Applicability

Two classes of carbon to be measured in ambient aerosol samples collected on quartz-fiber filters: (1) organic, volatilized, or non-light absorbing carbon and (2) elemental or light-absorbing carbon. The TOR, TOT, and TMO methods have been most commonly applied in aerosol studies fro the analysis of organic and elemental carbon. Filter transmission analysis is often performed to estimate particle light absorption, which is proportional to the level of elemental carbon in the atmosphere. These methods are discussed in detailed in the following subsections. TOT is the seconded method is this study.

2.0 Definitions

The following terms are used in this document:

The IMPROVE_A thermal protocol derives from the Interagency Monitoring of Protected Visual Environments (IMPROVE) to quantify carbon fractions evolved at different temperature plateaus.

Calibration Injection- The injection of calibration gases, either CO_2 or CH_4, into the sample stream at the beginning and end of each workday 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 runs 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.

Organic Carbon- 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.

Elemental Carbon- Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 580, 740, and 840 °C minus any pyrolyzed OC.

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).

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.

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% O2 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.
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.

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).

3.0 Apparatus, Instrumentation, Reagents, and Forms

3.1 Apparatus and Instrumentation

The components of the DRI Model 2001 Thermal/Optical Carbon Analyzer, which is connected to a Pentium 4x compatible computer, the following items, are needed for routine carbon analysis:

- **Stainless steel punching tool-** 5/16-inch diameter, 0.5 cm^2 nominal area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is re-sharpened, the punch area must be re-verified. Verification is performed by removing 10 punches from a 47-mm quartz-fiber filter (17.35 cm^2) then calculating the punch area [= 17.35 cm2 x (average weight of 10 punches / original 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 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 Wipers and large KimWipes (EX-L).
- Small Styrofoam cooler or refrigerator.
- Blue ice (if using Styrofoam cooler).
- Butane or piezoelectric lighter.

3.2 Reagents

The following chemicals should be reagent grade or better:

- Potassium hydrogen phthalate (KHP), for calibration
- Sucrose, for calibration use
- Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxidation oven
- Nickelous nitrate [Ni $(NO_3)_2 \cdot 6H_2O$], crystalline, used to prepare the nickel catalyst in the methanator
- 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% for removing the white deposits from diversification (white deposits of SiO_2) on the quartz oven.
- Nan pure water.

3.3 Gases

The following compressed 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.
- 5% CO_2 by volume in He for calibration injections, regulated to 10 psi by a metal diaphragm regulator.
- 10% O_2 by volume in He as a carrier gas, regulated to 15 psi by a metal diaphragm regulator.
- In addition, the following gases are required:
- Hydrogen for the FID flame, regulated to 15 psi with a metal diaphragm regulator.
- Hydrocarbon-free air to supply O_2 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. The 90% He/10% O_2 mixture is typically replaced every four to six weeks; H_2 and He are replaced once a week. All gases are replaced when the cylinder pressure drops below 500 psi. Check the O_2 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% O_2, H_2, and FID air. The pneumatic drivers for the breech should have a pressure of ~25 psi to operate effectively (sealing the opening).

3.3 Forms and Paperwork

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. Figure 2-6 provides an example of the sample analysis run list. As individual samples are analyzed, entries are made in the *Carbon Analyzer Logbook*.

4.0 Operation and Maintenance

4.1 Instrument Operation

Operator concerns for correct routine operation of the instrument include the following:

- 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:
- FID (Flame Ionization Detector),
- Temperature, and
- Laser signals are behaving as expected (Section 4.1). 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 wiper is left on the sample punch, tweezers, and/or glass plate.

4.2 Maintenance

Daily check

Compressed gas supplies, Cleaning the punching tool and tweezers between each sample with dry KIMTECH, Cleanliness of Lab, and backing up data files to disc on a daily basis (unless files are automatically backed up to server).
Leak check of instrument

Monthly check

Checks of laser adjustments (physical and electrical) and leaks.

Periodic check

Temperature calibrations for the six temperature plateaus (140, 280, 480, 580, 740, and 840 °C) need to be performed semiannually.
Additional leak tests are performed with a He leak detector each time a part is replaced, and 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.

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*. 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 balance should be performed as well.

4.3 Analyzer Start-Up

If 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 the start, 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 H_2 or compressed air cylinders are changed), relight the flame by turning the H_2 rotameter to the upper limit (as posted on the flow meter) and holding 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 H_2 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 wiper, taking care not to contact the cleaned surfaces with fingers or other dirty items. Check to make sure that no fibers from the KIMTECH wiper are left on the surfaces.
- Begin the daily entry in the *Carbon Analyzer Logbook*.

- Make sure that the printer has enough paper for the day and that the toner cartridge is producing legible text and graphics.
- 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. If for some reason the program freezes, allow the sample oven to cool to below 200 °C and then close the program and restart

4. 4 Leak Checks

- Perform leak checks daily to detect leakage in the sample oven.
- To begin the manual leak check, go to C:\CarbonNet, and then double click the program icon to begin the carbon program shortcut on the computer desktop. Verify that the correct version of the software and database are being used.
- With the breech closed, flip the oven outlet toggle on the side of the analyzer down (off) and let the sample oven pressure reach ~5 psi. Most systems are working in the ~2.5 psi range, but a leak is easier to detect when the pressure is at ~5 psi. Close the oven inlet toggle, on the front of the analyzer, and watch for a decline in the sample oven pressure. 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, 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 wiper, 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*
- The pressure should be consistent with previous day's values.

4.4 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.

4.5.1 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 are run after the oven bake.

4.5.2 Automatic Oven Bake

- From the main welcome screen, select "Analysis".
- Set Type to "Sample" and select *cmdBakeOven* from the drop-down menu in the "Command table" field.
- The project name should be "SAMPLE" and the sample ID should be in the format "CxxYYYYMMDD" where "xx" is the analyzer number (e.g. C0720050715 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 are run after the auto calibration has been completed and shows an acceptable range.
- The following items should be checked and recorded on the *Daily Analyzer Checklist.*
- 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.

4.6 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 "Special Analysis".

Always execute the *cmdBakeOven* command to bake the oven before beginning analysis each day. This will ensure the system is clean (1.5 µg OC, 0.5 µg EC, and 2.0 µg TC per cm^2). Run a system blank with the IMPROVE_A protocol.

4.6.1 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 wiper.
- 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.
- Open *operating software*.
- Select "Analysis" from the "Main" submenu of the Welcome form. This will initiate the analysis protocol.
- 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*.
- 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 wiper. 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.

4.6.2 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?" 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 wiper.

4.6.3 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 to confirm that the calibration peak counts are within specifications (typically 25,000 counts).
- 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 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.
- If all aspects of the analysis appear correct, select the appropriate analysis flag from 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.

4.7 Special Analysis

4.7.1 System Blanks

System blanks are run at the beginning of each day. Follow the steps outlined in Section on oven baking with the following exceptions:

- Go through all the steps for a routine analysis, 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 an ID number derived from the current date: e.g., SB071805 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.

4.7.2 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 3.3.1 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 HCl, and then will state "Load syringe" and "XX seconds to acid injection".
- Inject 20 µl of 0.4 M HCl through the septum port to the sample.
- Prior to acidification (approximately 90 seconds elapsed analysis time), flush the 25 µl syringe with 0.4 M hydrochloric acid (HCl) into a waste beaker. When prompted to inject HCl eject 20 µl HCl onto the filter punch, 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 Nan pure 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. 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.

4.8 Analyzer Shutdown

- 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 *operating executive 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 6.5).
- 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 µl 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.

5.0 Quantification

5.1 Instrument Calibration

The calibration procedures for the carbon analyzers are of three types: 1) the end-of-run calibration peak; 2) the routine beginning and end-of-day calibration injections of He/CH_4 and He/CO_2 (you can also use the auto calibration check using the *cmdAutoCalibCheck* command); and 3) full instrument calibration, performed every six months, using KHP, sucrose, and the two calibration gases.

5.1.1 End-of-Run Calibrations (Description)

The end-of-run calibration consists of a set quantity of He/CH_4 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 operator should check the integrated calibration peak counts immediately after each run to confirm that the analyzer is operating satisfactorily. Calibration peak area counts should be greater than 20,000. Check daily records to compare and determine analyzer performance and stability.

5.1.2 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 *Carbon Network* database Command table.

5.1.3 Automated Routine Calibration (Description & Instructions)

- The automated calibration uses the Carle valve to inject the methane standard once in a He-only atmosphere, once in a He/O_2 atmosphere, and finally, the normal calibration peak at the end of analysis. The three peaks should have identical peak areas if the catalysts are in good condition and the calibration factor holds. Use the following steps to perform this automated calibration:
- From the *operating software* 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.
- The project name should be "Calib", the Batch # should be "0" 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. The three calibration peak counts (OC3, EC1, LtPyMid) should be above 20,000 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 MnO_2 or Ni catalyst is replaced, an automated routine calibration should be run to confirm that the previous calibration curve holds.

5.2 Manual Routine Calibration (Instructions)

From the Welcome screen, select "Analysis" from the "Main" submenu.
Set Type to "CALIB" and select *cmdCalib-HeO_2* (for example) from the drop-down menu in the "Command table" field.

A project name is not required. The sample ID should be in the format "MIxYYYYMMDD" for CH_4 injection or "CIxYYYYMMDD" for CO_2 injection where x is the analyzer number (e.g. MI720050710 for a CH_4 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.). Enter "1" in the Punch area, and Deposit area fields. 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 HeO_2 or He; HeO_2 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.

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 4-2. 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.

Calibration gas injections should be in the following ranges for 100-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 area 20,000 --
[1] *Calculated in a real laboratory environment. For a 5.12% CH_4 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% CO_2 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.

Note: Each time the MnO_2 or Ni catalyst is replaced, the instrument calibration should be checked to confirm that the previous calibration curve holds. This can be done by running two points from the six CH_4/He calibration volumes and two points from the six CO_2/He volumes used in the full calibration.

5.3 Full Calibration (Description)

Full instrument calibration, performed semi-annually, 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 (Section 4.1) and injecting 100 to 1500 µl of the CO_2 and CH_4 gases. Four types of standards are used to calibrate the carbon analyzers: 5% nominal CH_4 in He, 5% nominal CO_2 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 CH_4 and CO_2 semiannually to establish the calibration curve of each analyzer.

5.4 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: CH_4 (internal standard) versus µg of carbon 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% CH_4 or CO_2 standard at 760 mm Hg at 20 °C, each micro liter = 0.499 µg carbon. For a 5% standard, it will be 0.02495-µg carbon/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.

Actual µg C per µL = $(P_a/760)\{1/(t+273)\}(1/0.08206)$(% of Cal Gas * 12)
Where, P_a = Ambient Pressure in mm Hg
T = Ambient Temperature in °C

The calibration gases are traceable to NIST/equivalent standards. The gas supplier assays the calibration gases for exact concentrations; the assay value is obtained from the tag on the cylinders and is typically determined by gas chromatography (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 M concentrated hydrochloric acid (HCl) and 99.6 ml Nan pure 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:

Actual µg C per µL = {(Weight of KHP in µg)/(Volume of Solution prepared in µL)} {(Number of Carbon in KHP * 12)(Molecular weight of KHP)}

The nominal 1800-ppm sucrose solution is prepared by transferring 0.428 µg of sucrose into a glass 100 ml volumetric flask. Dilute to volume with acidified

Nan pure 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 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:

Actual µg C per µL = {(Weight of Sucrose in µg)/(Volume of Solution prepared in µL)} {(Number of Carbon in Sucrose * 12)(Molecular weight of KHP)}

To prepare a blank solution, add 0.4 ml of concentrated HCl to a glass 100 ml volumetric flask and dilute to volume with Nan pure water. This acidified Nan pure water is made fresh each time an 1800-ppm KHP stock solution is prepared. No 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.

5.5 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.

5.6 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 4.1).

5.7 Data Treatment for Calibration Data

Calibration values are plotted as actual µg carbon vs. the ratio of the integrated sample peak counts to the calibration peak counts (Figure 4-1). 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:

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. The date and version number in the *Carbon. par* file is also updated.

Calibration data and plots are retained in file folders in the file cabinet with raw analysis data.

Slope, $m = \{\Sigma(y_i * x_i)\} / \{\Sigma(x_i)^2\}$

$$\text{Standard Deviation} = \sqrt{\frac{1\Sigma\,(y_i - mx_i)^2}{n-1\ \Sigma\ x_i^{\,2}}}$$

Where, y_i = Calculated Carbon in spiked or manually injected sample
x_i = (Injected Carbon peak area) / (Calibration Carbon peak area)

6.0 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:

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 O_2 and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively, for the reflectance and transmittance optical charring correction. The EC reported includes pyrolyzed carbon.

Carbon values per punch are converted to µg C/cm^2 by:

Peak µg C / Punch = {(Integrated peak count)(Calibration slope)} / (Internal Calibration count)
µg C / Cm^2 = (µg C / Punch)(Punch area)

µg C / Filter = (µg C / Cm^2)(deposition area in filter)
Concentration = (µg C / Filter) / (Volume of air sample in m^3)

6.1 Instrument Calibration Instructions

6.1.1 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. 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, "MIxYYYYMMDD_zzz" (where "MI" is for CH_4 injection; use "CI" for CO2 injection; x is for the analyzer number and zzz 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". 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 set up screen. 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 CO_2 and CH_4 calibrations are run using the "Calibration" options from the main menu. The following volumes are injected:
- 100 µl CO_2 gas (use 1000 µl syringe)
- 250 µl CO_2 gas (use 1000 µl syringe)
- 500 µl CO_2 gas (use 1000 µl syringe)
- 1000 µl CO_2 gas (do once with 1000 µl syringe and once with 2500 µl syringe)
- 1500 µl CO_2 gas (do with 2500 µl syringe)
- Repeat for CH_4
- Record these calibration values in the logbook.
- The integrated peak counts are extracted manually from the tabular printouts and entered into the spreadsheet, which is used to determine the final calibration. 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.

6.1.2 Full Sucrose and KHP Calibrations

- To perform the full calibration, select "Analysis" from the Main menu of the *DRICarb.exe* program Welcome screen.
- Choose "Calib" under the "Type" drop down menu. Complete the information about the sample, including: Project Name, Batch #, and Sub-batch #. The Project Name should be "CALIB" and the Batch # should be "SUKHPCAL".
- 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, "SUxYYYYmmdd_zzz" (where "SU" is for sucrose spiking; use "KHP" for KHP spiking; x is the analyzer number and zzz 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 4.1.3.1 and kept at room temperature) is injected onto the punch using a 25 µl syringe. The following volumes are used:
- 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 3.1.5.1)
- 20 µl acidified Nan pure water only (check of background level of Nan pure 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 Nan pure 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 µl of solution deposited

(e.g., 5 µl=300s, 10µl=600s, 15µl=900s and 20µl=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.

7.0 Temperature Calibrations

Temperature calibrations are performed semiannually on all instruments to verify that the sample temperature is as accurate as possible.

7.1 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° G (Tempil, Inc., South Plainfield, NJ, USA), were used as temperature indicators in muffle furnaces. A Tempilaq° G set contains long-chain hydrocarbons suspended in an organic solvent, which change their appearance at 44 specific temperatures spanning 80-100 °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.

7.1.1 Standard Preparation

Temperature calibration requires two pre-fired quartz-fiber filter (#2500 QAT-UP, Pall Life Sciences, Ann Arbor, MI) punches (0.3 cm2 and 0.5 cm^2 for DRI analyzer) and a clean matching-sized quartz disk (Continental Glass Engineering, Burbank, CA). Quartz-fiber filter punches are sliced in half with a filter-slicing device (Fung et al., 2004). A thin layer of Tempilaq° G (25 µL) is uniformly applied to the 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 used for Temiplaq° G at temperatures less than 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%.

7.1.2 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. When the specified temperature is reached, the Tempilaq° G liquefies, causing a sharp change in reflectance and transmittance. The thermocouple temperature, reflectance, and transmittance as a function of thermal analysis time.

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.
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, de-vitrification (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 4.1, 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. Primary standards in the form of NIST-traceable spiked filter punches do not exist. The *cmdAutoCalibCheck* command check allows the condition of the catalysts to be monitored and verified.

7.2 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 a group of ten is completed. It is run on a randomly selected analyzer (it can be the same or a separate analyzer as the original). This practice provides a

better indication of potential differences if different laboratories analyze samples. The µg/cm2 values for OC, EC and TC are compared with the original run. The values should fall into the following criteria

Range Criteria
OC, EC & TC < 10 µg/cm2 < ±1.0 µg/cm2
OC and TC > 10 µg/cm2 < 10 % of average of the 2 values
EC > 10 µg/cm2 < 20 % of average of the 2 values

Notice that the criteria converge at 10 µg/cm2. Replicates, which do not fall within 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.

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.

7.3 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. 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 CH_4 calibration gas is changed, when the catalysts are renewed, or when extensive repairs are performed.

7.4 Analysis Flags

During Level I validation, 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.

CHAPTER – X

MODEL Standard Operating Procedures for Organic Speciation (Molecular Markers)

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. In the Los Angeles area organic compounds was reported. The most common method used for analysis of particulate matter collected on filters for speciated organic compounds is the extraction of a filter with a suitable organic solvent (or combination of solvents), followed by the analysis of the extract by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also possible but recommended technique is GC-MS in this study.

1.0 Introduction and Scope

This method describes a procedure for separating saturate and aromatic hydrocarbon compounds from solid samples. This method describes a gas chromatography/mass spectroscopy (GC/MS) technique for determination of individual petroleum hydrocarbon compounds including C_8 through C_{41} normal alkanes, the isoprenoids pristane and phytane; target polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs and dibenzothiophene compounds; and biomarker triterpanes and sterane compounds, including an important biomarker compound C_{30} 17(H), 21(H)-hopane. Table X (a) lists the analytes, which can be determined by this method.

This method is restricted to use by or under the supervision of analysts experienced in the use and interpretation of GC/FID and GC/MS.

2.0 Terminology

2.1 Definitions: for definitions of terms used in this test method, refer to ASTM Definition D1129 (Annual book of ASTM Standards, Vol. 11.01), ASTM Practice E355 (Annual book of ASTM Standards, Vol. 14.01), and ASTM Practice D3415 (Annual book of ASTM Standards, Vol. 11.02).

2.1.1 Internal Standard (IS): a pure analyte added to a sample extract in a known amount, which is used to measure the relative responses of other analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

2.1.2 Surrogate Analyte: a pure analyte that is extremely unlikely to be found in any sample, which is added to a sample aliquot in a known amount and is measured with the same procedures used to measure other

components. The purpose of a surrogate analyte is to monitor the method performance with each sample.

2.1.3 Alkanes: the total normal alkanes from n-C_8 to n-C_{41}.

3.0 Principle of Method

Organic molecular markers attached or adhered to the particles are extracted in suitable solvents. Then cleaned and pre-treated according to requirement and finally analysed using GC-MS in SIM mode.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvent reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences by analysing method blanks.

4.2 All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it. This should be followed by hot water washing and rinsing with tap water and distilled water. It should then be drained dry, and rinsed three times successively with pesticide grade acetone, hexane and methylene chloride.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample.

4.4 The silica gel clean-up procedure is useful to overcome many of these interferences.

5.0 Safety

5.1 All extraction and clean-up operations should be carried out in fume hood.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound used in this method should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by every means available.
Methylation of sample should be carried out with high precaution. The Temperature of reaction should be maintained properly.
The laboratory is responsible for maintaining a current awareness file of regulations regarding the safe handling of the chemicals specified in this method.

6.0 Apparatus

6.1 GC/MS System: The mass spectrometer is operated in both scan and SIM mode utilizing 70-volt electron energy in the electron impact

ionization mode and producing a qualified mass spectrum. A computer system, interfaced to the mass spectrometer, is used for system control as well as data acquisition, storage and data processing.

6.2 **GC Columns:** 30 m long x 0.25 mm ID, 0.25 µm film thickness capillary DB-5 MS or equivalent column will be used in GC/MS system for analyses of PAHs, alkylated PAH and dibenzothiophene compounds, and triterpanes.

6.3 Apparatus for Sample Extraction

- Glassware: All glassware is washed in an automatic washer with hot water and rinsed with deionized water. It is then manually rinsed with three portions each of acetone, hexane and DCM. Glassware is air-dried in a fume hood or oven dried and then stored in a contaminant free area.
- Ultrasonic bath and Vacuum filtration system.
- Soxhlet Extractor
- Rotary-evaporator and nitrogen blow down device.
- Analytical balance capable of accurately weighing 0.0001 g.
- Erlenmeyer flasks, 250 and 500 mL.
- Beakers, 100, 250 and 500 mL.
- Glass funnel and Buchner funnel.
- Glass wool and glass fibre filters (9.0 cm).
- Graduated cylinder: 1 liter.
- Centrifuge tube, 15 mL, graduated, with a ground-glass stopper. The tube should be pre-calibrated before use.
- Vials, 1 mL, 7 mL and 14 mL, with Teflon-lined screw cap septa.
- Pasteur pipettes: 22 cm, disposable.
- Pipettes: Electronic or mechanical pipettes with capacities from 10 to 1000 µL capacity) and appropriate condensers.

Note: The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

7.0 Reagents and Materials

7.1 All solvents should be of pesticide quality or equivalent.

7.2 **Sodium sulphate:** ACS, granular, anhydrous. The sodium sulphate is poured into a pre-cleaned column and eluted with two column volumes of dichloromethane followed by two column volumes of hexane. The dichloromethane and hexane are discarded. The clean sodium sulphate is poured into a pre-cleaned 1-L beaker, covered loosely with solvent-rinsed aluminium foil and allowed to air dry, overnight, in fumehood. The sodium sulphate is dried in an oven at

approximate 120 ^{0}C overnight and then stored in the oven at a temperature ranging from 120 to 320 ^{0}C until ready for use.

7.3 Silica gel: Silica gel (100-200 mesh, pore size 150 , pore 1.2 cm^3/g, active surface 320 m^2/g) can be obtained from chemical companies such as Fisher Scientific. Before use, place it in a large size column, serially rinse with acetone, hexane and methylene chloride. Completely dry at 50 ^{0}C and activate for at least 20 hours at 160-180 ^{0}C in a shallow glass tray, loosely covered with foil.

7.4 Glass wool: Glass wool is placed in a large column and eluted with two column volumes of dichloromethane followed by two column volumes of hexane. The dichloromethane and hexane are discarded. The clean glass wool is then placed in a pre-cleaned 1-L beaker, covered loosely with solvent-rinsed aluminium foil and allowed to air dry, overnight, in fumehood. The dry glass wool is kept in the oven at a temperature ranging from 120 to 320 ^{0}C until ready for use.

8.0 Sample Preparation & Pretreatment

Another Popular method of Particulate extraction for biomarkers is repeated extraction with hexane followed by 2:1 mixture of Benzene and 2-propanol by ultrasonication. Each composite sample was placed in a pre-baked jar first, and then 40 mL of hexane is added. After spiking with deuterated standard mixtures, sample was extracted twice with hexane and then three successively extractions by 2:1 mixture of benzene and 2-propanol. Benzene was distilled before use. About 40 mL solvent was used for each extraction. The extraction was conducted under mild sonication with ice bath under room temperature. The extracts of each sample, about 200 mL in total volume, were filtered through pre-baked glass wool and concentrated into 5-10 mL by a rotary evaporator. The volume of the extract was then 5 blown down to the volume of IS spiked (250µl) by nitrogen gas purging. It was then equally divided into three aliquots with one aliquot stored in the freezer and one injected directly to GC system for bulk analysis. The third aliquot is derivatized by freshly prepared diazomethane to convert organic acids to their methyl esters. The methylated samples were analyzed by gas chromatography/mass spectrum (GC/MS) for the first round to quantify all compounds except for levoglucosan and cholesterol, and then silylated by adding *N*, *O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) (Pierce Biotechnology, Inc.) and analyzed by GC/MS for the second round for the quantification of levoglucosan and cholesterol.

8.1 Internal standards

Two deuterated internal standard mixtures are carefully spiked into the jar, which include 16 isotopically labeled compounds, benzaldehyde-*d*6, dodecane-*d*26, decanoic acid-*d*19, phthalic acid-3, 4,5,6-*d*4,

acenaphthene-*d*10, levoglucosan-13C6 (carbon-13 uniform-labeled compound), hexadecane-*d*34, eicosane-*d*42, heptadecanoic acid-*d*33, 4,4'-dimethoxybenzophenone-*d*8, chrysene-*d*12, octacosane-*d*58, 20*R*-5á(*H*), 14á(*H*), 17á(*H*)-cholestane-*d*4, cholesterol-2, 2,3,4,4,6-*d*6, dibenz (*ah*) anthracene-*d*14, and hexatriacontane-*d*74. Their concentrations are shown in following Table I.

8.2 Sample Methylation

Diethyl ether from Sigma-Aldrich, Inc. (3 mL) is added into the outer tube of the standard diazomethane generation apparatus, and then 1 mL of diethyl ether and 1 mL of carbitol (diethylene glycol monoethyl ether, 99%) is placed into the inner tube. The lower part of the outer tube, 1-2 inches below the joint of inner and outer tube, was immersed into the ice bath. About 0.4 grams of diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 99%) is weighed and transferred carefully into the inner tube, and then about 1.5 mL of 5N KOH was injected into the inner tube by using 5 mL syringe through the cap of inner tube. The gas-phase diazomethane was then generated gradually and dissolved in the diethyl ether in the outer tube. The whole reaction was complete after 40 minutes from KOH injection (Nugan and Toofan, 1991). Freshly prepared diazomethane in diethyl ethyl (200 µL) was transferred into each extract, which contains 10 µL pre-added methanol. In about an hour, the methylated samples are then ready for the first round of GC/MS analysis.

Table 10 (a): Concentration of the deuterated internal standards

Compounds	IS Concentration (ng / µL)
benzaldehyde-*d*6	10.2
dodecane-*d*26	10.9
decanoic acid-*d*19 methyl ester	4.5
phthalic acid 3,4,5,6-*d*4 methyl ester	4.6
acenaphthene-*d*10	2.4
levoglucosan-U-13C6	31.3
hexadecane-*d*34	2.4
eicosane-*d*42	1.9
heptadecanoic acid-*d*33 methyl ester	4.4
4,4'-dimethoxybenzophenone-*d*8	9.6
chrysene-*d*12	1.8
octacosane-*d*58	4.9
20*R*-5á(*H*),14á(*H*),17á(*H*)-cholestane -*d*4	0.4
cholesterol-2,2,3,4,4,6-*d*6	9.9
dibenz(*ah*)anthracene-*d*14	4.8
hexatriacontane-*d*74	10.2

8.3 Sample Silylation

300 µL of BSTFA plus 1% TMCS is added into each extract, which is then immediately placed in an oven at 70°C for one hour (Simoneit and Elias, 2000). The extract is then blown down to about 200 µL for the second round of GC/MS analysis.

8.4 Authentic Standards

Combination of authentic standards solely depended on target analytes fixed by the analysts. For a complete range of analysis in source apportionment study huge number of standards is used even though each and every target analytes could not be analyzed directly by GC-MS analysis due to non-availability of standards in market. 6 combinations covering whole range of standards along with their required concentrations are listed in following Table J.

9.0 Calibration

Prepare calibration standards at a minimum of 5 concentration levels for each component of interest from stock standard solutions. One of the standards should be at a concentration near, but above, the minimum detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples.

Store the daily calibration standards at in the refrigerator (at <10°C). The daily calibration standards must be replaced after 2 months or sooner if comparison with checks standards indicates a problem.

Analyse each calibration standards and tabulate peak area response against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using the equation:

$$\frac{A_S}{C_{IS}}$$
$$RRF = (A_S * C_{IS}) / (A_{IS} * C_S)$$

where:
A_S = Response for the target analyte to be measured
A_{IS}= Response for the internal standard
C_{IS}= Concentration of the internal standard
C_S = Concentration of the target analyte

A five-point response factor calibration is established to confirm the linear range of the analysis.

The working calibration curve or RRF should be verified on each working day by the measurement of one or more calibration standards. If the response for any target analyte varies from the predicted response by more than 20%, the test must be repeated using a fresh calibration standard. If the response factors are constant (20% RSD over the working range), then the response factors of the daily calibration standards are used to quantitate sample analyte concentrations. Analysis is conducted within the range of concentration established by the calibration curve. Samples may need to be

further concentrated or diluted to bring concentration levels within the established working range.

Daily Calibration Check

A mid-level calibration standard (typically, 1 µg/mL for PAH standard) is analysed daily to monitor system performance. If the calculated concentrations vary by no more than 25% of the expected concentrations then the calibration response factors are updated. If the calculated concentrations vary more than 25% of the expected concentrations for any given analyte then analysis should be stopped until the problem (such like the system may require recalibration) is corrected.

GC Performance

The GC resolution is verified daily with a mid-level calibration standard. Adequate resolution is demonstrated when the valley between phenathrene and anthracene does not exceed 30% of the highest peak and the valley between benzo (b) fluoranthene and benzo (k) fluoranthene does not exceed 70% of the highest peak. The calibration check standard must demonstrate good overall peak shape for all target analytes. Chromatographic problems such as excessive peak tailing, split peak, unsymmetrical peaks and poor sensitivity should be corrected prior to further analysis.

Surrogate and Internal Standard Spiking Solutions

The sample spiking solutions must be calibrated before use. These solutions must be recalibrated periodically (at least every two months) against the daily calibration standard.

Standard Accuracy

The daily calibration standard must be verified against a certified PAH reference solution (i.e. NIST SRM 1491) at least every six months when samples are being analysed. A dilution of the certified reference solution is analysed as a sample. Calculated concentrations must be within 15% of expected results, with no more than 20% of values falling outside of this range.

GC/MS Instrument Sensitivity

A standard with a concentration near detection limit (typically 0.005 to 0.05 µg/mL) is analysed at every months to verify system sensitivity. If the sensitivity falls out of the acceptance range, some correction measures (such as column trim and cleaning of the ion source) should be taken.

10.0 GC/MS Analysis

The methylated and silylated extracts are analyzed, respectively, by GC-MS equipped with a 30 m length. 0.25 mm i.d. 0.25 µm film thickness HP-5 MS capillary column coated with 5% phenyl methyl siloxane. The GC/MS conditions were as follows: oven temperature isothermal hold at 65 °C for 10 minutes, rise to 300 °C at rate of 10°C min-1, then isothermal hold at 300 °C for

22 minutes. Other settings include should include GC/MS interface temperature as 300°C, ultrapure He as carrier gas with a flow rate of 1.0 mL min-1, split less injection mode, scan range of 50-550 amu, and electron ionization mode with 70 eV. A series of authentic standards pre-mixed with internal standards should be analysed by GC/MS along with the samples for assisting the identification and quantification of organic compounds in the ambient samples. For those compounds that are not present in the STD series, secondary standards including wax extraction (n-alkanes and branched alkanes), wood smoke standard (polycyclic aromatic hydrocarbons (PAHs) and resin acids), and picene standard may be used. Relative response factor (RRF) of each target compound to the respective deuterated internal standard, which has similar retention time and chemical structure, may be used in the quantification. For those compounds, which RRFs are not available, RRFs from other compounds with similar polarity, retention time, and chemical structure may be used instead. A Possible mode of identification and quantitation of molecular markers by GC-MS analysis is presented in following Table K.

11.0 Calculation

11.1 Calculation of Individual Analytes

When a compound has been identified, the quantitation of that compound will be based on the integration area or integrated abundance. Quantitation will be performed using the internal standard method.
Calculate the concentration of the analyte of interest in the sample using the response factor determined

$$\text{Concentration } (\mu g/g) = \frac{A_S \times W_{IS} \times D \times F}{A_{IS} \times RRF \times W_S}$$

where:

A_S	=	Response for the analyte in the sample, units may be in area counts or peak height.
A_{IS}	=	Response for the internal standard in the sample, units same as A_s.
W_{IS}	=	Amount (µg) of internal standard added to the sample.
D	=	Dilution factor. If dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
W_S	=	Weight of sample extracted, g. either a dry or wet weight may be used, depending upon the specific application of the data.
F	=	Factor if the samples are splitted in half for analyses, so the final concentration of individual analytes should multiply volume factor.

12.0 Reporting

Reporting units are µg/m^3 or pg/m^3.
Surrogate Recovery
Surrogate recovery is reported for each sample analysed. Data should be flagged if the percent recovery is outside of the 70-120% range.
In case the concentrations found below detectable limits (BDL), respective MDL should be reported in ().

13.0 Quality Control

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance.

The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within accuracy and precision limits expected of the method.
Before performing any analysis, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method.

The reliability of this method is dependent on the quality control procedures followed with each analytical batch (approximately 7-10 samples), one procedure blank, one check standard are analysed.

13.1 Initial Calibration and Continuing Calibration Check

Prior to the use of this method, a five-point response factor calibration curve must be established showing the linear range of the analysis. Each calibration standard is analysed and the response factor (RRF) for each compound at each concentration level is calculated.
A check standard at about the mid-point of the established calibration curve must be analysed before and after each set of up to 7 samples or once per working day, whichever is more frequent, in order to determine the response factors for the analytes of interest relative to the initial calibration.
The percent difference between the response factors in the check standard and those of the initial calibration is calculated using following Equation

$$\text{Difference (\%)} = \frac{RRF_I - RRF_C}{RRF_I} \times 100$$

Where,

RRF_I = Average response factor from the initial calibration
RRF_C = Response factor from continuing calibration

If the difference of response factors is within 20%, analyses may proceed. If not, a five-point calibration curve must be repeated for that compound prior to analysis of the sample.

RRF stability is a key factor in maintaining the quality of the analysis. Mass discrimination, that is the reduced response of high molecular weight compounds, must be carefully monitored. The ratio of RRF of n-C_{32} to n-C_{21}

should not be allowed to fall below 80% in the check standard. If there is a problem with mass discrimination, it can be reduced by trimming the first 10-20 cm of the capillary column and by replacing the quartz liner in the injection port.

13.2 Surrogate Compounds Analysis

All samples and quality control samples are required to be spiked with surrogate o-terphenyl (OTP). OTP will spiked into sample prior to extraction. This will measure individual sample matrix effects associated with sample preparation and analysis. Recovery of surrogate should be within 60% to 120%. If the recovery for any surrogate standard does not fall within the control limits for method performance, the following corrective actions can be taken:

(1) Check calculations to ensure there are no errors.

(2) Check instrument performance and initial standard and surrogate solutions for degradation, contamination or other possible problems.
Reanalyze the sample or extract if the steps above fail to reveal a problem. If re-analysis yields surrogate recoveries within the stated limits, the re-analysis data will be used.
If the surrogate could not be measured because the sample diluted prior to analysis, or surrogate co-elutes with a compound, no corrective action needs be taken.

13.3 GC Resolution

The target compounds, surrogate and internal standards must be resolved from one another and from interfering compounds. Potential problems may arise from the lake of baseline resolution of these compounds. Corrective action must be taken to correct resolution problem, i.e. rerun samples with a different temperature program.

Table 10 (b): Mix Standard combinations and their concentrations

Compounds	ng/µl	Compounds	ng/µl
STD#1		STD#2	
naphthalene	20.0	decane	20.5
acenaphthylene	40.0	undecane	20.5
acenaphthene	20.0	dodecane	20.5
fluorene	4.0	tridecane	20.5
phenanthrene	2.0	tetradecane	20.5
anthracene	2.0	pentadecane	20.5
fluoranthene	4.0	hexadecane	20.5
pyrene	2.0	heptadecane	20.5
benzo(*a*)anthracene	2.0	octadecane	20.5
chrysene	2.0	eicosane	20.5
Benzo (*b*) fluoranthene	4.0	tetracosane	20.5
benzoic(*k*)fluoranthene	2.0	octacosane	20.5
benzo(*a*)pyrene	2.0	dotriacontane	20.5

Compounds	ng/µl	Compounds	ng/µl
benzo(*ghi*)perylene	4.0	hexatriacontane	20.5
indeno(*cd*)pyrene	2.0	tetracontane	20.5
dibenzo(*a*,*h*)anthracene	4.0	tetratetracontane	20.5
bis(2-ethylhexyl)phthalate	20.0	3-methylnonadecane	4.9
butyl benzyl phthalate 2-	20.0	methylnonadecane	4.9
diethyl phthalate	20.0	cyclopenta(*cd*)pyrene	4.9
dimethyl phthalate	20.0	dibenzo(*a*,*e*)pyrene	1.0
di-*n*-butyl phthalate	20.0	pyrene	1.0
di-*n*-octyl phthalate	20.0	benzo(*a*)pyrene	9.8
20*R*-5α(H),14β(H),17β(H) - cholestane	1.0	methylfluoranthene	1.0
20*R*-5β(H),14α(H),17α(H)- cholestane	1.0	methylchrysene	1.0
20*S*-5α(H),14α(H),17α(H)- cholestane	1.0	retene	4.9
20*R*-5α(H),14α(H),17α(H)- cholestane	1.0	anthroquinone	11.8
20*R*-5α(H),14β(H),17 β(H)- ergostane	1.0	9-fluorenone	21.7
20*R*-5α(H),14 β(H),17β(H)- sitostane	1.0	benz(*a*)anthracene-7,12-	20.7
17 α(*H*)-22,29,30-trisnorhopane	1.0	dione	
17 β(*H*)-21 α(*H*)-30-norhopane	1.0	1,8-naphthalic anhydride	20.4
17 β(*H*)-21 β(*H*)-hopane	1.0	squalene	41.4
17 β(*H*)-21 α(*H*)-hopane	1.0	triacontane	43.0
methylfluorene	1.0	1-octadecene	38.3
octylcyclohexane	10.0		
decylcyclohexane	10.0		
tridecylcyclohexane	10.0		
nonadecylcyclohexane	10.0		
norpristane	10.0		
pristane	10.0		
phytane	10.0		
coronene	10.0		
1-methylnaphthalene	2.5		
2-methylnaphthalene	22.4		
2,6-dimethylnaphthalene	24.2		
9-methylanthracene	19.2		
squalane	20.9		
STD#3		STD#4	
oxalic acid (C2)	11.8	levoglucosan	1540
malonic acid (C3)	12.7	cholesterol	2000
maleic acid (C4=)	11.6	stigmasterol	1664
fumaric acid (C4=)	12.2	monopalmitin (C16:1)	310
succinic acid (C4)	12.5	monoolein (C18:1)	310
glutaric acid (C5)	14.8	monostearin (C18:0)	310
adipic acid (C6)	12.8	glycerine	1500
pimeric acid (C7)	12.9		
subiric acid (C8)	12.9	STD#5	
azelaic acid (C9)	11.5	guaiacol	32.8
19.2 sebacic acid (C10)	11.7	2-methoxymethylphenol	46.0
phthalic acid (1,2)	12.6	ethylguaiacol	42.1
iso-phthalic acid (1,3)	13.1	propylguaiacol	39.9
terephthalic acid (1,4)	12.4	eugenol	42.2
1,2,4-benzenetricaboxylic acid	12.3	acetovanillone	53.9
1,2,4,5-benzenetetracaboxylic acid	12.1	3,5-dimethoxy-4-	19.2

Compounds	ng/µl	Compounds	ng/µl
methylphthalic acid	12.8	hydroxycinnamaldehyde	
hexanoic acid	38.1	iso-eugenol	22.7
octanoic acid	37.8	vanillin	37.6
decanoic acid	29.9	syringealdehyde	35.3
dodecanoic acid	35.0	4-hydroxy-3-	24.1
tetradecanoic acid	30.7	methoxycinnamaldehyde	39.3
hexadecanoic acid	30.0	3,5-dimethoxyphenol	
octadecanoic acid	23.8	3,5-dimethoxy-4-	34.3
eicosanoic acid	24.6	hydroxyacetophenone	
docasanoic acid	24.9	dimethoxycoumarin	9.2
tetracosanoic acid	28.0	4-methylphenylacetone	10.6
abietic acid	36.0	octadecamide	8.4
octacosanoic acid	30.3	1-phenyl-naphthalene	8.9
triacontanoic acid	29.8		
pinonic acid	45.1	STD#6	
palmitoleic acid (C16:1)	32.1	dehydroabietic acid	54.6
oleic acid (C18:1)	33.7	isopimaric acid	57.3
linoleic acid (C18:2)	28.7	pimaric acid	45.0
linolenic acid	35.9	cholesta-3,5-diene	45.4

Table 10 (c): A Possible mode of identification and quantitation of molecular markers by GC-MS analysis

Targets	Sources
pentacosane [b]	gasoline vehicles, diesel vehicles
hexacosane [b]	gasoline vehicles, diesel vehicles
heptacosane [b]	gasoline vehicles, diesel vehicles
octacosane [a]	gasoline vehicles, diesel vehicles
nonacosane [b]	vegetative detritus
triacontane [b]	variety
hentriacontane [b]	vegetative detritus
dotriacontane [a]	variety
triatriacontane [c]	vegetative detritus
20 *S*,*R*-5*á*(*H*), 14*â*(*H*), 17*â*(*H*)-cholestanes [a]	gasoline vehicles, diesel vehicles
20R-5*á*(*H*), 14*á*(*H*), 17*á*(*H*)-cholestane [a]	gasoline vehicles, diesel vehicles
20 *S*,*R*-5*á*(*H*), 14*â*(*H*), 17*â*(*H*)-ergostanes [a]	gasoline vehicles, diesel vehicles
20 *S*,*R*-5*á*(*H*), 14*â*(*H*), 17*â*(*H*)-sitostanes [a]	gasoline vehicles, diesel vehicles
22,29,30-trisnorneohopane [b]	gasoline vehicles, diesel vehicles
17*á*(*H*), 21 *â*(*H*)-29-norhopane [b]	gasoline vehicles, diesel vehicles
17*á*(*H*), 21 *â*(*H*)-hopane [a]	gasoline vehicles, diesel vehicles
nonanal [b]	meat cooking
cholesterol [a]	meat cooking
levoglucosan [a]	wood combustion
benzo(*b*)fluoranthene [a]	wood combustion, gasoline vehicles
benzo(*k*)fluoranthene [a]	wood combustion, gasoline vehicles
benzo(*e*)pyrene [c]	wood combustion, gasoline vehicles
indeno(*cd*)fluoranthene [c]	wood combustion, gasoline vehicles
indeno(*cd*)pyrene [c]	wood combustion, gasoline vehicles
benzo(*ghi*)perylene [c]	wood combustion, gasoline vehicles

Note:
[a] may be Identified and quantified by using authentic standard (STD #1-6, IS#1, and IS#2);
[b] may be Identified by using mass spectra and quantified using authentic standard with similar structure and retention time;
[c] may be Identified by using secondary standards (picene standard, wood smoke standard, and wax extraction) and quantified using authentic standard with similar structure and retention time.

Further Readings

1. List of Reference Methods
2. Common Methodologies Recommended by CPCB for Source Apportionment Project
3. General Air Sampling Guidelines, SOP 2008, USEPA
4. Method IO-2.2 Sampling of Ambient Air for PM10 Using an Andersen Dichotomous Sampler
5. Method IO-2.3 Sampling of Ambient Air for PM10 Concentration Using the Rupprecht and Patashnick (R&P) Low Volume Partisol® Sampler
6. Method IO-2.4 Calculations for Standard Volume
7. Method IO-3.1 Selection, Preparation and Extraction of Filter Material
8. Method IO-3.2 Determination of Metals in Ambient Particulate Matter Using Atomic Absorption (AA)Spectroscopy
9. Method IO-3.3 Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence(XRF) Spectroscopy
10. Method IO-3.4 Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy
11. Source Apportionment of Atmospheric Fine Particulate Matter Collected at the Seney National Wildlife Refuge; Rebecca J. Sheesley and James J. Schauer Environmental Chemistry and Technology Program, University of Wisconsin-Madison
12. Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases Version 3.3; J.P.A. Neeft, H.A.M. Knoef, U. Zielke, K. Sjöström, P. Hasler, P.A. Simell, M.A. Dorrington, L. Thomas, N. Abatzoglou, S. Deutch, C.Greil, G.J. Buffinga, C. Brage, M. Suomalainen
13. Source Characterization Guidelines Primary Particulate Matter And Particulate Precursor Emission Estimation Methodologies For Chemical Production Facilities, Canadian Chemical Producers' Association
14. Source Apportionment of $PM_{2.5}$ in North Carolina**,** Mei Zheng, School of Earth and Atmospheric Sciences
15. Molecular characterization of smoke from campÆre burning of pine wood (Pinus elliottii) B.R.T. Simoneit, W.F. Rogge, Q. Lang, R. Jaffe