STANDARD OPERATING PROCEDURE

Determination of Fine Particulate Matter Mass Concentration on PTFE® Filters

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TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

The method described is used for the pre- and post-weighing of all polytetrafluoroethylene (PTFE®) filters used in the SPARTAN network. The pre-weighed filters are loaded into a sampling cartridge, sealed inside 2 plastic bags and shipped to the appropriate sampling site for collection of particulate matter. The precise determination of the gravimetric masses of the filters before and after sampling allows for the exact mass of collected particulate matter to be determined. The pre-sampling masses are compared to the post-sampling masses to infer the mass of $PM_{2.5}$, or PM_{10}, collected during sampling. All filter weighing is conducted in a Darwin Chambers environment-controlled room in the Center for Aerosol Science and Engineering at Washington University in St. Louis. Following sampling in the field, filters are sealed inside 2 plastic bags (still within their cartridge) and shipped back to Washington University for analysis, which begins with post-weighing. Following the disassembly of the cartridges inside a HEPA hood, filters are placed inside the environmentally controlled room to equilibrate for at least 24 hours prior to weighing. Weights are taken in triplicate for each filter and a standard deviation of < 2 µg for pre-weights and < 5 µg for post-weights, is required. If a larger standard deviation is obtained, the filter is re-weighed.

2.0 SUMMARY OF METHOD

The first step in the SPARTAN filter sampling process is pre-weighing filters to obtain their masses prior to sampling in the field. Following a 24-hour equilibration period, filters are weighed in triplicate using an automated filter weighing system (Measurement Technology Laboratories (MTL) AH500E) and microbalance (Mettler Toledo XPR6UD5) in a temperature and humidity-controlled room. The pre-weighed filters are loaded into a sampling cartridge, sealed inside two plastic bags, and then shipped to the appropriate sampling site for collection of particulate matter. Following sampling, the cartridges are shipped back to Washington University in St. Louis for disassembly and filter analysis. The assembly and disassembly of cartridges occurs under a HEPA-filtered ventilation hood. After disassembly, the filters are left to equilibrate within the MTL weighing system for at least 24 hours prior to weighing. Filters are then post-weighed, again in triplicate. A standard deviation of < 2 µg for pre-weights and < 5 µg for post-weights, and a relative humidity level of 35 +/- 1% is required, or the filter is reweighed. All masses for each filter are recorded based on the SPARTAN Local ID in a site-specific spreadsheet that is backed-up on cloud storage.

3.0 CONTAMINATION CONTROL

3.1 General Contamination Control

Prior to pre-weighing, new filters are first visually inspected for any obvious signs of contamination that could have occurred during the manufacturing process, or during shipping. Each filter's laser-etched data matrix and serial number ("MTL ID") is assigned to a unique SPARTAN ID ("Local ID"). Following label assignment, the filter is placed in a clean petri dish labeled with the Local ID. Prior to use, petri dishes are pre-cleaned with methanol and rinsed with Milli-Q water in triplicate. They are then left to dry overnight on a clean Kimwipe®.

To reduce the impact of humidity on the weighing result, all filter weighing is done within the MTL chamber with temperature set to 21.5°C +/- 1° and relative humidity set to 35% +/- 1%. The MTL weighing system and chamber is placed on a marble weighing table within an environment-controlled room with temperature and humidity settings at 21.5°C +/- 1°C and 39% +/- 1%, respectively. A cleanroom sticky floor mat at the entrance of the room helps remove and trap unwanted dirt and debris from shoes. The room is also cleaned once a week with a Swiffer® dry cloth. Prior to weighing, the work surface is wiped with methanol and a Kimwipe®. Clean nitrile gloves are worn when working with filters and open petri dishes. Filters are only handled from their outer support rings with PTFE®-coated tweezers that have been wiped with methanol. Prior to first-time use, aluminum carriers are wiped down with methanol and allowed to soak in water overnight to minimize anodized aluminum contamination.

3.2 Acceptance Testing of Filters

Each new box of blank MTL filters goes through acceptance testing to test for contamination that may have occurred during manufacturing. When a new shipment of blank filters arrives, four filters from each box of 50 are randomly selected. Two of those filters are designated as "Acceptance Testing" filters and two of those filters are designated as "Lab Blank" filters. All four filters are pre-weighed and analyzed for trace metals via x-ray fluorescence (XRF) spectrometry. Following XRF, the two Acceptance Testing filters are extracted to measure water-soluble ions via ion chromatography. The remaining two Lab Blank filters are set side to be sent to UC Davis for analysis of organics via FTIR. Upon return from UC Davis, the Lab Blanks are also extracted for analysis via ion chromatography.

The results from each chemical analysis (filter masses, ion chromatography, and XRF) are recorded in the Acceptance Testing Master File. The IC and XRF measurements are compared to the average concentrations from field blank filters. If the values from an acceptance testing filter batch exceed the mean plus 1 standard deviation of the average field blank values, the batch is deemed contaminated and the remaining filters in the will not be used for sampling.

3.2.1 Preparing Acceptance Test Filters

- Select five blank filters from each box of filters to be tested and place them in clean petri dishes. To ensure randomization, select filters stacked throughout the box, rather than only selecting the first four filters.
- Petri dishes are then labeled in the format "10093-L41659-AT". The first 5 digits uniquely identify the acceptance test filter. The blank space after the L is to be written-in by hand with the filter box number. The end of the label consists of either an "LB" or an "AT". The "AT" at the end stands for "Acceptance Test", which means those three filters will be analyzed at Washington University in St. Louis via XRF and IC. The "LB" at the end stands for "Lab Blank" which means those filters will NOT be extracted following XRF analysis and will instead be set aside for FTIR at UC Davis.
- For example, the Local Filter ID "10095-L41659-AT" identifies SPARTAN's 95th acceptance test filter which came from filter box 41659 and is destined for IC and XRF analysis. 10093-L41659-LB would be destined for FTIR at UC Davis.
- In the MTL software system's "Assign to Carriers" page, select "Assign Local Filter IDs" to assign each filter's MTL ID (the laser-etched data matrix and serial number) to its Local ID (i.e. "10093-L41659-LB"). You must use the handheld barcode scanner to make this assignment. The LocalID will show up as "10093-_____-LB" since the LotID is handwritten – leave the underscores as is.
- Under the "Test Manager" page, create a new test with the test name "L" followed by the filter box number (i.e. "L41659"). Add the four acceptance test filters to this test using the Local IDs.
- Load the acceptance filters onto filter carriers and place in the MTL weighing chamber to equilibrate for 24 hours prior to weighing. Record the equilibration start time under the "Custody Data" page of the filter weighing software.
- After equilibration the four filters can be weighed following the same procedure outlined in sections 5.0 and 6.0 of this SOP.

4.0 SAMPLE STORAGE AND RECORDKEEPING

4.1 General filter storage, labeling, and recordkeeping

Prior to pre-weighing, filters are stored in the temperature and humidity-controlled room in original packaging from the manufacturer. Each filter comes with a laser-etched serial number and data matrix (MTL ID, i.e. "E52767") from the manufacturer and will be assigned to an

analysis ID and QR code (Local ID, i.e. "AEAZ-0081-3"). For sampling filters, the Local ID includes the four-letter site code, the individual filter number for that site, and the position that filter will hold within a cartridge. For example, the Local ID "AEAZ-0081-3" is destined for the site with code AEAZ: Abu Dhabi, United Arab Emirates, will be the 81st filter sampled at that site, and will be placed in position 3 in the cartridge In the event that non-barcoded filters are to be weighed, the Carrier ID will be recorded in place of the MTL ID.

When a Test Report is generated following a weighing procedure, the Local IDs, MTL IDs, information on the room environment (temperature, humidity) during the pre- and post-weighing sessions and all weighing results for a particular cartridge is exported. This data is copied into a site-specific spreadsheet.

Each time new filters are laid out to be pre-weighed, their lot ID number must be recorded in the Acceptance Testing Summary File. The Summary File records which FilterIDs came from which box of filters. Once a week, the Acceptance Testing Summary File is automatically backed up.

5.0 EQUIPMENT

5.1 Laboratory Equipment

5.1.1 Labware

- 25 mm PTFE® membrane filters (PT25DMCAN-PF03A, 3 μm pore size with FEP support ring)
- PTFE®-coated tweezers
- Petri dishes
- ACS-grade methanol
- Lint-free tissue wipe (e.g. Kimwipe®)
- Nitrile gloves

5.1.2 Instruments

- Darwin Chambers walk-in environmental room
- Robotic autohandler and chamber, MTL AH500E
- Mettler Toledo XPR6UD5 microbalance, sensitive to +/- 0.5 μg
- Cognex DM600 handheld scanner

5.2 Maintaining the environmental room and balance

Filter weighing is at the center of SPARTAN data analysis and quality control, and the weighing process is the first step to producing reliable data. It is essential that the environmentally controlled room remains as clean as possible and that any accumulated dust is removed prior to the weighing session, therefore the following cleaning procedure should be followed to maintain appropriate conditions for weighing:

- Put on a lab coat, walk over the sticky floor mat prior to entering the cleanroom and put on a pair of nitrile gloves.
- Spray methanol onto a lint-free tissue wipe and wipe down work surfaces.
- Ensure the microbalance is level by checking the indicator on the balance tablet. If the indicator is red, click on the indicator and use the leveling aid to turn the leveling wheels at the base of the balance in the appropriate direction.
- Thoroughly wipe the tweezers with methanol using a small lint-free tissue wipe.
- Once a week, clean the Darwin Chamber floor with a Swiffer® dry cloth.
- To monitor the microbalance performance and weighing environment over time, weigh calibration weights and reference filters before and after every weighing session (see Section 6.0 Filter Weighing).

6.0 FILTER WEIGHING

6.1 Pre-weighing: Test Creation and Equilibration Start

The following describes how to prepare filters for pre-weighing and create a new filter weighing test.

- Label 8 clean petri dishes with the appropriate Local IDs. Place two matching labels on each petri dish, one for the lid and one for the dish.
- Use clean tweezers to place a new filter into each petri dish, handling each filter only by its outer ring. While placing new filers into petri dishes, ensure that none of them have holes, punctures, or any other visible sign of damage or contamination.
- In the MTL software system, assign the MTL IDs (the serial number laser etched onto the filter ring) to their Local IDs (the SPARTAN analysis ID on the petri dish).
- Prepare 8 clean filter carriers and place filters onto the carriers. If there isn't an ongoing weighing procedure in progress, place filters into Silo C or Silo E for post-weighing.
- Once filters are ready to equilibrate inside the MTL weighing chamber, create a Test Report. Add all of the filters in the cartridge you will be weighing into the test by scanning them into the Filter ID box with the handheld barcode scanner, or by manually typing in the IDs and clicking "Add Filter".

- After a test has been created, record the pretest stabilization start time on the 'Custody Data' page.

6.2 Pre-weighing: SPARTAN Weighing Procedure

- In the 'Automated Filter Weighing' page, select "SPARTAN procedure" in the procedure drop-down menu and click on "Begin Procedure". *Set the weighing date and time 24 hours in the future.* The following describes each step of the SPARTAN procedure:
    1. QC Protocol (Now and When Needed, Every 4 hour(s))
        a. Balance Calibration
        b. Weigh Calibration Weights
            i. Weigh 100 mg Calibration Weight
            ii. Weigh 200 mg Calibration Weight
            iii. Weight 400 mg Calibration Weight
        - Weighing Repetitions: 3
        - Warmups: 0
        - Weighing Method: Direct Read w/ Drift Correction

        c. Weight Reference Filters
            i. Weigh Blank 1
            ii. Weigh Blank 2
            iii. Weigh Blank 3
        - Weighing Repetitions: 3
        - Warmups: 0
        - Weighing method: Direct Read w/ Drift Correction
        - Weighing Type: Reference (Diesel)

    2. Weigh Silos
        a. Weigh Silo C, place in Silo D
        b. Weigh Silo E, place in Silo F
        - Weighing Repetitions: 3
        - Warmups: 0
        - Weighing Method: Direct Read w/ Drift Correction
        - Weighing Type: Force Initial/Pretest
        - Artifact Count: All Artifacts default)\ 10

    3. QC Protocol (Now and When Needed, Every 4 hour(s))
        a. Balance Calibration
        b. Weigh Calibration Weights
        c. Weigh Reference Filters

- Once weighing is complete, unload filters from the filter carriers and return them to their assigned petri dishes.
- In the "Custody Data" page, record the "Out of Weighing Room" date/time for that particular test.
- In the "Test Manager" page, double-check the filter masses, standard deviations and weighing room conditions for each filter
- The measurements are acceptable if the following criteria are met:

- Humidity conditions: the recorded relative humidity is between 34.0% and 36.0%
- Temperature conditions: the recorded temperature is 20.5 and 22.5 degrees Celsius.
- Pre-weighing: the standard deviation of the triplicate weight measurements is ≤ 2 μg.
- Post-weighing (including field blanks): the standard deviation of the triplicate weight measurement is ≤ 5 μg.
- If the required environmental conditions and measure standard deviation is not obtained, the three measurements are repeated.

- Generate the test report in the 'Test Reports' tab and save the test report under "Desktop" > "SPARTAN Weighing Results" and on the SPARTAN server.

6.3 Post-weighing Procedures

6.3.1 Equilibration Start

- Assign Local Filter IDs to the Carrier ID using "Assign to Carriers."
- Load filters into carriers and place inside the weighing chamber.
- Record the "Return to Weighing Room" date and time under Custody Data.
- Select the SPARTAN weighing procedure and click "Begin Procedure". Set the start time to 24 hours from now.

6.3.2 Post-weighing: SPARTAN Weighing Procedure

Follow the same weighing procedure as outlined in detail in the SPARTAN pre-weighing procedure, steps briefly outlined below.

- Calibrate the balance
- Weigh calibration weights
- Weigh reference filters
- Weigh filters
- Unload filters from carriers
- Record "Post-weigh Date/Time" under Custody Data
- Export data

7.0 DATA VALIDATION

7.1 Level 1 Data Validation

Level 1 data validation occurs immediately following the filter post-weighing and analysis of the cartridge log sheet and data files collected by the filter sampling station.

7.1.1 Filter Masses

- After sampling in the field, the mass collected on the filter (μg) is determined as the difference between the post- and pre-weighed filter masses. The collected mass must be > 0 μg, else the filter is flagged as invalid.
- If the mass collected on the PTFE® filter is > 500 μg, the filter is flagged as valid but suspect; further investigation into the validity of the collected mass is required.
- Negative filter weights for the control (Filter 7) are common and no cause of concern.
- Filters flagged with abnormally large standard deviation (> 2.5 μg) should be reweighed.

7.1.2 Flow Rate Measurements and Sampled Volume

The internal (reported by the sampling station; IN) and external flow rates (measured with a flow meter at the inlet by site operators, EX) for each filter are measured when the cartridge is installed (start flow rates, e.g. EX_i) and when all filters in the cartridge have finished sampling (end flow rates, e.g. EX_f). If continuous internal flow rate measurements from the sampling station are not available due to data recording problems, the average flow rate for each filter is taken as the average between the start and end external flow rates. When continuous internal flow rates are available, the mean continuous flow is weighted by the ratio of external to internal flow rate measurements:

$$Flow = \overline{Flow_{cont}} \sqrt{\frac{EX_i}{IN_i} \cdot \frac{EX_f}{IN_f}}$$

For the average flow rate to be used in determining the volume of air sampled for a given filter the following conditions must be met:

- The internal flow rate must be within 10 % of external flow rate,
- The external end flow rate must not have dropped by more than 10 % of the external start flow rate,
- The external start flow rate must be within 10 % of the target flow rate.

If any of the above conditions are not met the filter is flagged as invalid. The sampled volume is calculated from the mean flow rate and the time sampled.

7.2 Level 2 Data Validation

When the mass collected on the filter and the sampled volume are verified as valid, the mass concentration (μg m^{-3}) over the sampled time period is determined. Once the mass concentration is in the master data base, internal consistency checks are applied.

- The mass concentration determined for a given filter at a particular site should be consistent with the mass concentrations of filters sampled at the same site immediately before and after it, except for known cases of an event that is expected to lead to an exceptional ambient mass concentration.
- The average $PM_{2.5}$ concentration over the cartridge sampling period should be less than or equal to the average PM_{10} concentration over the same period.
- The sum of measured chemical species should be less than or equal to the total mass concentration.
- Large net weights (>8 μg) on Filter 7 indicates sampling on the control filter. This invalidates the entire cartridge.