STANDARD OPERATING PROCEDURES

Determination of Fine Particulate Matter Mass Concentration on PTFE® Filters using Gravimetric Analysis

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1.0 SCOPE AND APPLICATION

The method described is used for the pre- and post-weighing of all PTFE® filters used in the SPARTAN Network. The pre-weighed filters are loaded into a sampling cartridge, sealed inside 2 plastic bags, and then 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. Filters are weighed in triplicate in an ISO level 4 clean room environment with controlled temperature and humidity. Following sampling, the cartridges are sealed inside 2 plastic bags and shipped back to Dalhousie University for analysis, which begins with post-weighing. Following the disassembly of the cartridges inside a HEPA-filtered environment, the filters are allowed to equilibrate inside the clean room for at least 24 hours prior to weighing. Weights are taken in triplicate for each filter and a standard deviation of < 10 μg for pre-weights and < 15 μg for post-weights, is required or the filter is reweighed. All weights for each filter is recorded based on the filter ID in a site-specific spread sheet that is backed-up on cloud storage.

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
2.0	General reorganization and clarification	July 3, 2018	Paul Bissonnette
2.1	Addition of data validation information	August 7, 2018	Crystal Weagle
2.2	Addition of rotameter calibration procedures	March 12, 2019	Crystal Weagle

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. The pre-sampling masses are compared to the post-sampling masses to infer the mass of $PM_{2.5}$, PM_{10}, or PM_{coarse} collected during sampling. All filter weighing is conducted in a temperature and humidity controlled clean room in the Health and Environment Research Center (HERC) in the Life Sciences Research Institute at Dalhousie University.

3.0 CONTAMINATION CONTROL

Prior to pre-weighing each filter is placed into a clean petri dish and given a unique filter ID label, this label will follow the filter throughout its lifetime. All filter weighing is done in an

ISO level 4 clean room. Clean nitrile gloves are worn when working with filters, and filters are only handled using clean forceps.

All filter batches received go through acceptance testing to test for any filter contaminants resulting from the manufacturing process. During acceptance testing, the filters are tested for water-soluble ions following SPARTAN Anion/Cation SOP revision 2.0 and trace elements following SPARTAN ICP-MS SOP revision 2.0. Four filters (two for each analysis method) from each box of 100 are used for acceptance testing. The results from each method are compared to average concentrations from blank filters and if the values from a filter batch exceed 1 standard deviation of the average blank values, the batch is deemed contaminated for that component and the remaining filters in the box of 100 will not be used for sampling.

4.0 SAMPLE STORAGE AND RECORDKEEPING

Prior to pre-weighing, filters are stored in the clean room in original packaging from the manufacturer. When ready for pre-weighing, the appropriate number of filters are placed into clean petri dishes with unique filter ID labels and allowed to equilibrate in the clean room for at least 24 hours prior to weighing. The assigned filter ID labels correspond to the intended sampled location. The filter IDs are recorded in a site-specific spreadsheet along with information (date, technician, temperature, and humidity) on the clean room environment during the pre- and post-weighing sessions.

Sampled filters inside cartridges received from sampling sites are removed from the cartridge in a HEPA-filtered hood and placed into their corresponding petri dishes with unique filter IDs. The filters are then allowed to equilibrate in the clean room for at least 24 hours before post-weighing. All post-weights are recorded with the corresponding filter ID labels and information on the clean room environment during the weighing session.

5.0 EQUIPMENT

5.1 Laboratory Equipment

5.1.1 Labware

- PTFE-coated tweezers
- Petri dishes
- PTFE® filters
- Methanol
- lint-free tissue wipe (e.g. Kimwipe®)
- Anti-static spray

- Calibration weights

5.1.2 Equipment

- Sartorius microbalance
- Level 4 ISO clean room
- De-ionizing blower

5.2 Maintaining the Cleanroom and Balance

5.2.1 General

Filter weighing is at the center of SPARTAN data analysis, quality control during the weighing process is the first step to producing reliable data. The following instructions are followed to ensure that the cleanroom remains as clean as possible and that any accumulated dust is removed prior to the weighing session.

- Remove shoes prior to entering the cleanroom and put on a clean pair of socks. Use a lint brush to pull any lint off shirt, sweater and any other articles of clothing that will be reaching over workspace. Put on a pair of provided nitrile gloves.
- Replace petri dish lids of filters that were previously left out to equilibrate. Stack in a safe and convenient location.
- Spray methanol onto a lint-free tissue wipe and wipe down tables, scale, laptop and any other workspace or instrument you will be using.
- Spray anti-static solution onto a lint-free tissue and wipe down these same areas. *Note:* Do not spray solution directly onto any of the instruments and be sure to wipe down areas which are closer to workspace before areas that are less likely to encounter the filters.
- Ensure the balance is level using the indicator bubble on the top of the balance. If the bubble is not inside the indicator circle, use the leveling wheels at the base of the balance to level it.
- Thoroughly wipe the precision forceps with methanol using a small lint-free tissue wipe, being careful not to get any residue stuck on the tip of the forceps.

5.2.2 Microbalance Calibration

Proper functioning of the microbalance is essential for a successful weighing session. Therefore, at the beginning of every weighing session the microbalance is calibrated to ensure its accuracy. It is important to be sure there is nothing on the scale and that the table is not bumped during calibration. Do not rest hands on the table or move things around on the table while calibrating. The following steps are followed to calibrate the microbalance:

- On the balance, enter '202122'. This code indicates the beginning of the calibration procedure for the range of weights the balance will encounter. Then, select 'S CAL' to begin the calibration.
- Continue to press 'select' until 'set preload' appears at bottom left of the display and then press 'start'. There will be a 'C' that appears in center of display; wait until this goes away and a weight comes onto screen (i.e. 0.0000 mg) before moving to the next step.
- Press 'select' until 'SCAL: Internal adjustment' appears, and press 'start'. Wait until this procedure is finished and a weight comes up on the display.
- Press 'select' until 'SCAL: internal linearization' appears, and press 'start'. Wait until this procedure is finished and again a weight comes up on the display.
- Press the CF button, and wait until a weight comes up on screen.
- At this point, the weight displayed should be 0.0000 mg. If not, tare the balance.

5.2.3 Calibration Weights and Lab Blanks

Standard metal weights and lab blanks (blank filters that remain in the clean room) are weighed at the beginning of each weighing session to ensure the balance is working correctly and to monitor the clean room environment over time.

1. Open the "Filter blanks and calibration" spreadsheet and record the date, temperature, relative humidity, and the name of the technician conducting the weighing. The masses of the calibration weights and lab blank standards are recorded in this spreadsheet.
2. Ensure all surfaces and forceps have air-dried from the methanol and anti-static cleaning procedure.
3. Remove the 200 mg weight, 1 mg weight, and plastic forceps from the calibration kit. Begin by weighing the 200 mg and 1 mg calibration weight:
    - Pick up the metal weight with the plastic forceps.
    - Hold the weight approximately 15 cm below the de-ionizing blower for approximately 3 seconds.
    - Open scale lid and place the weight in the center of pedestal and close lid.
    - Allow weight measurement on display to remain constant for 20 seconds, before recording the final weight.
    - Repeat the steps above for the 1 mg calibration weight.
4. Repeat the measurement of each calibration weight two more times, for a total of three times.
5. The average of the three measurements for each calibration should be within ±0.0030 mg of the expected value with a standard deviation being less than 0.0020 mg.
    - If not within these guidelines, recalibrate the scale and repeat measurements.
    - If after recalibrating the balance does not allow for masses within the required range, there may be a problem with the microbalance; consult a SPARTAN manager.

6. After returning the metal weights to the calibration kit, weigh the lab blanks as follows:
    - Use the precision forceps to pick up the first lab blank from the petri dish, being sure to touch only the edge of the filter with the tips of the forceps.
    - Hold the filter approximately 15 cm below the de-ionizing blower for approximately 3 seconds.
    - Open scale lid, place the filter in the center of pedestal and close lid.
    - Allow weight measurement on display to remain constant for 20 seconds, before recording that final weight in the spreadsheet.
7. Repeat for all available lab blank standards. Weigh each lab blank filter in triplicate and in a random order (do not weigh the same filter three times in a row).
8. Confirm that the lab blank weights are reliable using the following information:
    - Compare the average of the triplicate measurements for each filter to the average obtained in the 3 previous weighing sessions; the average for each filter should be within ± 0.0010 mg of the previously found average.
    - The standard deviation of the triplicate measurements is less than 0.0010 mg
    - If these requirements are not met, ensure the microbalance is calibrated correctly.

Note: Please contact a SPARTAN Manager if measurements are not stabilizing, if they are repeatedly inconsistent, or if any other issues arise.

6.0 FILTER WEIGHING

Prior to beginning a weighing session, be sure the filters to be weighed have equilibrated in the cleanroom environment for at least 24 hours. The relative humidity and temperature of the clean room must be between 30 - 40 % and 20 – 25 °C for the weighing session. If the required temperature and humidity are not obtained, the weighing session will be suspended until the necessary conditions are met.

When the required weighing conditions are met, the steps below are followed to obtain filter masses:

1. Open the spreadsheet for the SPARTAN site corresponding to the filter ID labels and record the date, clean room conditions (temperature and humidity), and the name of the technician conducting the weighing. Create a copy of the spreadsheet prior to making changes to ensure that no mass data is accidentally lost during the weighing session.
2. Use the precision forceps to pick up the filter from the petri dish. As with the lab blanks, pick up the filter by grabbing the edge of the filter with the tips of the forceps.
3. Place filter approximately 15 cm below the de-ionizing blower for approximately 3 seconds.
4. Open the scale lid and gently place the filter in the center of pedestal and close the lid.
5. Allow the displayed weight to remain constant for 20 seconds before recording that final weight in the Excel spreadsheet.

6. Remove filter from pedestal by grabbing the edge of the filter with the precision forceps and return to the petri dish. Be careful not to grab the pedestal with the forceps.
7. After removing the filter, allow the balance to stabilize (reading 0.0000 mg) before weighing the next filter. If a mass of 0.0000 mg is not displayed, press the 'tare' button and wait until the display button reads 0.0000 mg before moving to the next filter.
8. Repeat steps 2 - 7 above for all filters to be weighed. Weigh each filter in triplicate, and in a random order.
9. After all weighing is complete, place the precision forceps back in the holder. Close all petri dish lids and use an elastic band to secure the set (one cartridge) of petri dishes for transport. Place the weighed, and secured, filters inside two sealed plastic bags.

The measurements are acceptable if the following criteria are met:

- Pre-weighing: the standard deviation of the triplicate weight measurements is less than or equal to 0.0100 mg
- Post-weighing sampled filters and field blanks: the standard deviation of the triplicate weight measurements is less than or equal to 0.0150 mg.
- If the required standard deviation is not obtained, the three measurements are repeated. If upon repetition of the three measurements the required standard deviation is not met, clean room conditions (e.g. spike or drop in humidity) are investigated as the cause and filters are reweighed once the clean room conditions are adjusted (the same day or on a subsequent day).

7.0 DATA VALIDATION

7.1 Level 1 Data Validation

The data validation procedures are performed after the return of sampled filter cartridges from the sampling site, and after the filters have been post-weighed. 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.
- For filters collected using an SS4 series sampling station with nuclepore filters, the mass of PM_{coarse} collected on the nuclepore filter must be < 160 μg, else the

nuclepore and corresponding PTFE filter is flagged as invalid due to possible nuclepore filter saturation.

- Filter masses for filters that are known not to have sampled, or sampled an unknown amount or period of time, due to a filter sampler malfunction are 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.

7.1.2 Flow Rate Measurements and Sampled Volume

Flow meters used by site operators to measure external flow rates (measured with a flow meter at the inlet by site operators, EX) are compared to a NIST-certified flow meter. The comparisons are tracked using the unique serial number assigned to each flow meter. The flow offset is used to correct measurements made in the field and are not to exceed 10% of the required flow rate, else are marked as invalid.

The internal (reported by the sampling station; IN) and external (EX) flow rates 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 start flow rate must be within 10 % of external start 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 ($\mu g\ m^{-3}$) 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 should be consistent with those around 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.
- Comparison of the mass concentration to the sum of measured chemical species