UCD CSN Standard Operating Procedure #277

Optical Absorption Analysis of $PM_{2.5}$ Samples

Chemical Speciation Network
Air Quality Research Center
University of California, Davis

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
4/28/2020	LMK	All	Changed procedures to reflect new software for slide tray generation and analyzing samples.
4/29/2021	LMK	4, 6.4	Added end of day QC
5/7/2021	NJS	1,2	Changed Fabs to fAbs for consistency

TABLE OF CONTENTS

LIST OF FIGURES

1. PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) describes the measurement of optical absorption for $PM_{2.5}$-loaded polytetrafluoroethylene (PTFE) filters collected in the Chemical Speciation Network (CSN) using the Hybrid Integrating Plate/Sphere (HIPS) system. Readings for transmittance and reflectance of light from the sample filters are stored in an internal database. A calculated light absorption coefficient for particles collected on the filters (fAbs) is reported to the US Environmental Protection Agency's Air Quality System for public dissemination.

2. SUMMARY OF THE METHOD

The HIPS system utilizes a HeNe laser (632.8 nm wavelength) to illuminate the backside of a sample aerosol filter. Reflected light from the backside of the filter is detected by an integrating sphere, which provides the reflectance value (R) for the measurement. Light transmitted through the filter also passes through the deposit, which absorbs and scatters some of the light. The remaining transmitted light is diffused by an opal glass plate and collected by a detector (the integrating plate), which provides the transmittance value (T) for the measurement. Absorptance (A) of the sample deposit is related to the transmittance and reflectance signals by $A = 1 - T / (1 - R)$. The reflectance and transmittance detectors both read zero in the absence of light and respond linearly with increasing irradiance. Therefore, a single reading is used to register the HIPS system to previous measurements. This is done by adjusting the detector's gain to previously set values for a single registration filter. The filter's reflectance and transmittance values were assigned based on calibration with a research integrating sphere.

Once registration of the HIPS detectors is complete, a set of 15 verification filters are run (the registration filter is part of this set of 15). These 15 filters span an order of magnitude in absorption values, providing a comprehensive range of transmittance and reflectance values to verify that the HIPS detectors are performing consistently over every measurement session. Once run, a Quality Control (QC) check is performed to ensure the HIPS analysis of these filters meets acceptance criteria.

Prior to analyzing the monthly sample filters, a set of reanalysis filters is analyzed. Where the verification filters ensure consistency of T and R measurements of the HIPS system, the reanalysis filters check for consistency of the calculated absorption optical depth.

Sample filter analysis with the HIPS system is typically grouped by sampling month. It can take two to three days to complete the analysis of an entire sampling month of filters and the verification and reanalysis QC tests are run daily. Sample filters must first be prepared by scanning and transferring filters into slides. Filters mounted in slides are then organized in slide trays. Filter information for each sample is verified prior to scanning. Files used for HIPS analysis are generated during the scanning process.

3. DEFINITIONS

- HIPS: Hybrid Integrating Plate/Sphere.

- $PM_{2.5}$: particles with aerodynamic diameter equal to or less than 2.5 micrometers (mm); fine particulate matter.
- HeNe laser: Helium-Neon laser operating at a wavelength of 632.8 nanometers (nm) in the red part of the visible spectrum, used in the HIPS system.
- Field blanks: PTFE filters which travel to CSN sites and are loaded into samplers, but are not sampled. These are used mainly for blank correction of different CSN analysis methods. For HIPS they allow correction of the raw T and R values for the case of non-absorption.
- T: transmittance measurement; measured by the integrating plate in the HIPS system. Transmittance is the ratio of light passing through the filter/deposit to the incident light.
- R: reflectance measurement; measured by the integrating sphere in the HIPS system. Reflectance is the ratio of light backscattered by the filter to the incident light
- t: the field blank corrected transmittance value. Field blank correction is found by the equation, $t = T / a_0$, where a_0 is the intercept of the linear regression of the field blank results to the line, $r + t = 1$.
- r: the field blank corrected reflectance value. Field blank correction is found by the equation, $r = -a_1 R / a_0$, where a_0 is the intercept and a_1 is the slope of the linear regression of the field blank results to the line, $r + t = 1$.
- b: raw absorption optical depth, $b = ln\left(\frac{1-R}{T}\right)$.
- τ_{abs} : field blank corrected absorption optical depth, $\tau_{abs} = ln\left(\frac{1-r}{t}\right)$.
- fAbs: inferred atmospheric absorption coefficient, $fAbs \stackrel{\text{def}}{=} \frac{f}{V}\ln\left(\frac{1-r}{t}\right)$, where f is the area of the sample deposit and V is the volume (at local conditions) of air sampled. This is the calculated value in which all HIPS data is reported to CSN.
- Verification filters: set of sampled filters used to register and verify the registration of the HIPS detectors for long-term consistency of results.
- Reanalysis filters: a set of sampled filters used to monitor performance of the HIPS system.
- Neutral density material (NDM): a material which reduces the intensity of all wavelengths of light equally. The NDM in HIPS acts as a reference absorber, providing reference reflectance and transmittance values during HIPS analysis.

4. PERSONNEL DUTIES

The personnel responsible for HIPS analysis include a spectroscopist and trained laboratory technicians, who work under the general supervision of the laboratory manager.

The spectroscopist will:

- Oversee and maintain records on HIPS operation
- Perform maintenance and repair of the HIPS system as necessary
- Supervise and train lab technicians to run the HIPS system
- Calibrate and run controls on the HIPS system
- Resolve any inconsistencies in calibrations, controls, or individual analyses
- Provide quality assurance

The laboratory technician III will:

- Inventory filters for HIPS analysis
- Prepare filters for HIPS analysis by moving them from Petri dishes to slides
- Run quality control samples on the HIPS system under the supervision of the spectroscopist
- Perform HIPS analysis of sample filters under the supervision of the spectroscopist
- Supervise and train laboratory technician I to run the HIPS system

The laboratory technician I will:

- Prepare filters for HIPS analysis by moving them from Petri dishes to slides
- Run the HIPS system under the supervision of the laboratory technician III or spectroscopist

The laboratory manager will:

- Oversee and maintain records on HIPS operation
- Provide quality assurance
- Oversee work performed by the spectroscopist and lab technician

5. EQUIPMENT AND SUPPLIES

The equipment and materials required for preparing filters for HIPS analysis and for building trays can be found in the technical document UCD SOP TI #277A. The equipment and materials required for HIPS analysis are listed below:

5.1 HIPS System

- HeNe laser (Thorlabs HNL050R)
  - User manual available in the shared folder U:\IMPROVE_Lab\LASER\HNL050RSupportDocumentation\
- Diffuser/collimator (Edmund optics: EO 48-265 and EO 47-876)
- Integrating sphere (Labsphere: 4P-GPS-040-SF, 4-inch sphere with Spectralon coating)
- Reflectance photodiode detector (Newport 918D-SL-OD3R)
- Slide changer (UC Davis: custom construction, pneumatic operation)

- Neutral density material
- Opal glass (integrating plate)
- Transmittance photodiode detector (Newport 918D-SL-OD2R)
- Optics bench and mounts
- Laser mounting cage
- PC (Microsoft Windows based with LabVIEW installed)

5.2 HIPS Analysis Requirements

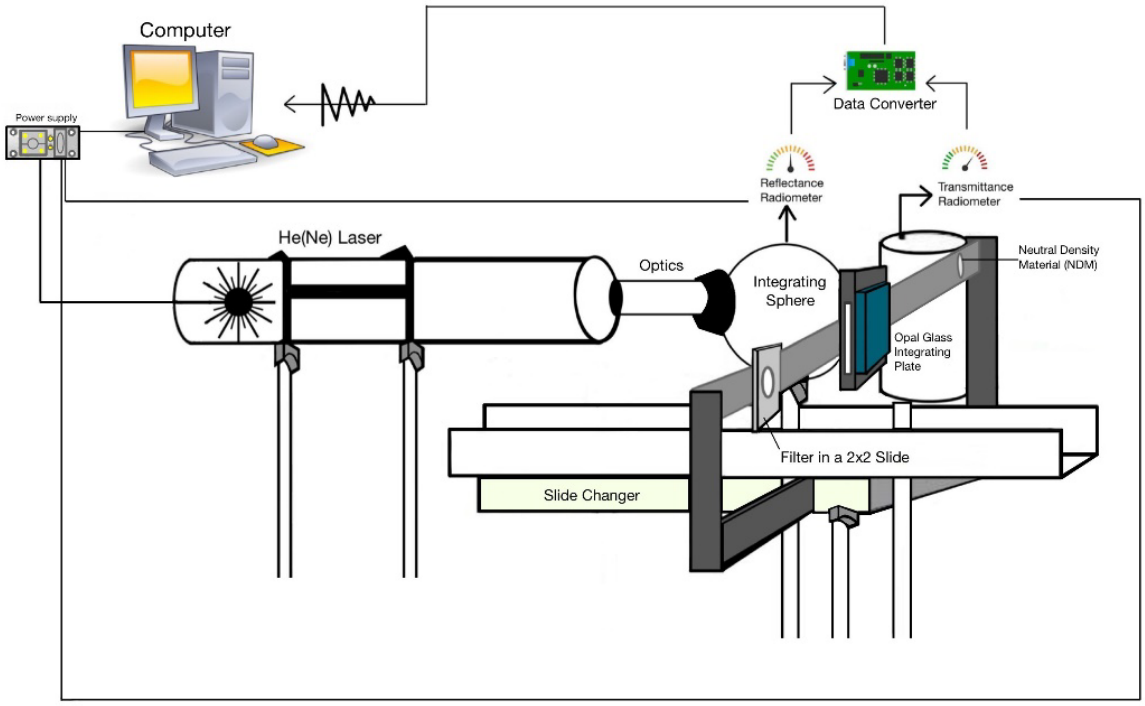
- Tray of verification filters
- Tray of reanalysis filters
- Field blank filters, in monthly site trays, for HIPS analysis

6. PROCEDURAL STEPS

6.1 Overview of the HIPS System

A schematic of the HIPS system is shown in Figure 1. Light of 633 nm wavelength from a HeNe laser is diffused and collimated to provide a uniform beam of light of approximately 0.8 cm^2 in area at the sample. The filters are mounted in standard 2" x 2" slide frames with the particles on the side of the filter away from the incident light. The light transmitted through the sample into a forward cone is diffused by an optical diffusing plate and collected with a photodiode detection system. The reflected light is made uniform by an integrating sphere and measured with a photodiode detector. The slide-changer arm has two positions: (1) the filter, and (2) the neutral density material (NDM).

Figure 1. UC Davis Hybrid Laser Integrating Plate/Sphere (HIPS).



The absorptivity of PTFE is known to be negligible in the visible spectrum (Weidner et al. 1985; Li et al. 2008). This property of PTFE allows blank filters to be used to calculate the transformation of the raw measured reflectivity and transmittance so the blanks fall on the line of zero absorption, $t + r = 1$. A linear regression is performed on the field blanks and the intercept, a_0, and slope, a_1, are used to transform the raw R and T values to the field blank corrected values by starting with the linear equation:

$$T = a_0 + a_1 R.$$

Then, moving the measured terms to one side and dividing by the intercept:

$$\frac{T}{a_0} - \frac{a_1 R}{a_0} = 1.$$

Comparing this with the zero-absorption line, $t + r = 1$, we find the following relationships:

$$t = \frac{T}{a_0}, \quad r = \frac{-a_1 R}{a_0}.$$

The equation for the absorption optical depth is then given by:

$$\tau_{abs} = ln\left(\frac{1-r}{t}\right) = ln\left(\frac{a_0 + a_1 R}{T}\right).$$

The intercept and slope values, a_0 and a_1, in the equations above are dependent on the filter membrane as thinner filters will transmit more and reflect less light than thicker filters, as well as the characteristics of the HIPS components, laser, lenses, and detectors. By measuring field blanks of similar filter type to the sample filters and under the same instrument conditions, the equation above removes these dependencies making the absorption coefficient measurement consistent for all samples and independent of the instrumental characteristics.

6.2 Preparation of Filters for HIPS Analysis

A lab technician transfers filters from labeled Petri dishes to numbered slides in preparation for HIPS analysis. Detailed instructions for this procedure are located in UCD TI #277A.

6.3 Tray Generation in LabVIEW

As filters are transferred into slides, files are generated concurrently for analyzing filters via LabVIEW. A lab technician generates files using the Build a Tray software within LabVIEW. The files consist of a list of filters that need to be analyzed. Barcode ID and manufacturer serial numbers are verified for each filter prior to scanning into the software. Once the information is verified the Barcode ID is scanned into the Build a Tray software. The filter is transferred into a slide and then placed in the slide tray. Filters are placed into the slide tray in the same order they are scanned into the software. The first and last filter in a slide tray will be verified again before the slide tray is analyzed. Detailed instructions for this procedure can be found in UCD TI #277A.

6.4 Preparation for Routine HIPS Analysis

Routine HIPS analysis is performed for all sample filters in a sampling month. A single analysis session is preferable for HIPS as it optimizes quality control. The HIPS system is prepared for routine analysis by the spectroscopist or a lab technician III. Only after the verification and reanalysis filters have been run and quality control criteria met will the system be released for routine HIPS analysis.

The verification, reanalysis and routine analysis data are ingested into the database immediately following analysis of a tray. The verification and reanalysis data are exported from the database for QC verification steps. T and R measurements are recorded by LabVIEW for filters analyzed. Additionally, T and R measurements are recorded from the neutral density material (NDM) taken before each sampled filter is measured.

Prior to HIPS analysis files generated using the Build a Tray software will only contain FilterID information and slide tray position.

The HIPS system is turned on at least four hours before it is scheduled for analysis in order to allow the laser and detectors to stabilize. On the day of HIPS analysis, a trained lab technician III or the spectroscopist registers the detectors in the system by running the registration filter and ensuring the transmittance and reflectance values are in the accepted range. The registration is then verified using a tray of 15 verification filters. Then, a reanalysis tray (currently 22 filters) is analyzed. T and R data for these filters are ingested into the database. After acceptance criteria for the verification and the reanalysis

filters have been met, HIPS analysis of CSN filters can begin. Following the completion of sample analysis each day the reanalysis tray is reanalyzed to verify end of day QC. Step-by-step instructions for these procedures are located in UCD TI #277B.

6.5 HIPS Analysis of CSN samples

HIPS analysis of CSN samples is performed by laboratory technicians, under the supervision of the spectroscopist. In addition to the measurements of T and R for CSN samples, routine analysis requires measurements of T and R for the NDM must also be taken before each sample. Results for both the NDM and samples are recorded using LabVIEW. After analysis of five slide trays, the registration of the HIPS detectors must be re-verified offline using position 3 from the verification tray. At the end of the analytical session for the month of samples, which can take up to 3 days, the HIPS system is turned off. Detailed instructions for this procedure can be found in UCD TI #277B.

6.6 Data Delivery and Reporting

Once a slide tray has finished analyzing, data is verified and written to the database. The data are then available through the SQL server database. Data reporting is performed after final data validation is performed.

7. QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Several checks throughout the analysis ensure that the data are as accurate as possible. Before the filters are analyzed by the HIPS system, they are checked to ensure that the integrity of the filters remains acceptable. The Barcode ID and manufacturer serial number are verified with the chain of custody for each sample prior to scanning or transferring. Once this information has been verified filters are scanned one at a time and transferred into slides. Handling filters one at a time helps ensure the order integrity prior to analysis. Additionally, filter information for the first and last filter in each slide tray are verified before proceeding with analysis.

A verification tray is run before reanalysis and routine analysis can occur. The values for the verification filters must be within ± 3 % of their reference values before the process can continue. This ensures the detectors of the system report values that are comparable with historical measurements. After this, a reanalysis tray is run. τ_{abs} is calculated using the linear regression of a selection of field blanks collected in 2010 to correct for non-absorption. The results of the measured τ_{abs} must meet certain acceptance criteria. For details, refer to UCD TI #277C "Quality Assurance and Quality Check of Analysis of $PM_{2.5}$ Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption." Once the criteria for both verification and reanalysis filters have been met, routine HIPS analysis of CSN samples can begin.

For more information on QA/QC, please see UCD TI #277C.

8. FIELD BLANK CORRECTION COEFFICIENTS

To properly scale the raw T and R values so the field blanks have zero absorption, a linear regression must be performed on the field blanks and the coefficients, a_0 (y-intercept) and a_1 (slope), must be determined. This is performed by measuring at least 80 field blanks from the same PTFE filter lot as the samples which are being analyzed. Next, a linear regression of T to R is performed and the coefficients are calculated. These are then reported to the QA and validation team so they can be entered into the database for proper field blank correction of measured samples.

There are many factors which can change the field blank correction coefficients. These include changes to the HIPS system (e.g. replacement of a detector, laser, or optical component, adjusting the alignment of the optics) or changes in the PTFE filter lot or manufacturer. Anytime a change occurs, a set of field blanks of matching PTFE filter material must be analyzed on HIPS and new regression coefficients determined and uploaded to the database. The spectroscopist is responsible for ensuring this is properly done.

9. REFERENCES

UCD SOP #277: Technical Instruction –

- TI #277A: Preparation for HIPS
- TI #277B: Performing HIPS Analysis
- TI #277C: Quality Assurance/Quality Check of Analysis of $PM_{2.5}$ Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption