

UCD IMPROVE Standard Operating Procedure #276

Optical Absorption Analysis of PM_{2.5} Samples

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IMPROVE SOP #276: OPTICAL ABSORPTION ANALYSIS OF PM_{2.5} SAMPLES

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1.0 PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) describes the measurement of optical absorption of PM_{2.5} loaded Teflon® filters (collected in the IMPROVE network) using the Hybrid Integrating Plate/Sphere Analysis method (HIPS). The absorption by the particles on the filter is smaller than the absorption by particles in the atmosphere because of the layering of particles on the filter. Readings for transmittance (T value) and reflectance (R value) are stored in the internal database. A calculated light absorption coefficient for the absorption for particles on the filters (LRNC) is reported to the National Park Service database.

2.0 SUMMARY OF THE METHOD

IMPROVE “A” module filters are prepared for HIPS analysis by being transferred into labeled 2”x2” slides. Log files are generated and filters are double-checked before being cleared for analysis. The HIPS system is warmed up and then calibrated with 15 Teflon® standards. A reanalysis tray is run, followed by a sampling months’ worth of IMPROVE “A” module filters. Two or three days are typically required to complete analysis for the month.

3.0 DEFINITIONS

- HIPS: Hybrid Integrating Plate/Sphere Analysis.
- PM_{2.5}: particles less than 2.5 micrometers in diameter; fine particulate matter.
- “A” module: one of four channels routinely run at every site in the IMPROVE network. Collects PM_{2.5} samples on 25mm Teflon® filters.
- He (Ne): Helium-Neon laser operating at a wavelength of 632.8 nm in the red part of the visible spectrum, used in the HIPS system.
- T value: transmittance measurement; measured by the integrating plate in the HIPS system.
- R value: reflectance measurement; measured by the integrating sphere in the HIPS system.
- LRNC: derived, uncorrected, light absorption coefficient for particles on the filters.
- LRNC_{abs}: corrected light absorption coefficient for particles on the filters.

4.0 PERSONNEL DUTIES

The personnel responsible for HIPS analysis include a spectroscopist, a trained laboratory technician, and a trained student assistant, all of whom work under the general supervision of the laboratory manager.

The spectroscopist shall:

- Oversee and maintain records on the Hybrid Integrating Plate/Sphere operation
- Perform maintenance and repair of the HIPS system as necessary
- Supervise and train lab technicians to run HIPS
- Calibrate and run controls on the HIPS system

- Resolve any inconsistencies in calibrations, controls, or individual analyses
- Provide quality assurance

The laboratory technician shall:

- Inventory filters for HIPS analysis
- Generate log files for HIPS analysis
- Calibrate and run controls on the HIPS system under the supervision of the spectroscopist
- Supervise and train student assistants to run HIPS
- Run the HIPS system under the supervision of the spectroscopist

The student assistant shall:

- Prepare filters for HIPS analysis by moving them from petri dishes to slides
- Calibrate and run controls on the HIPS system under the supervision of the laboratory technician
- Run the HIPS system under the supervision of the laboratory technician

The laboratory manager shall:

- Oversee and maintain records on the Hybrid Integrating Plate/Sphere operation
- Provide quality assurance
- Release light absorption data for upload to the SQL server
- Oversee work performed by the spectroscopist and lab technician

5.0 EQUIPMENT AND SUPPLIES

The equipment and materials required for preparing filters for HIPS analysis and for creating log files can be found in technical documents 276A and 276B. The equipment and materials required for HIPS analysis are listed below:

5.1 Hybrid Integrating Plate/Sphere System

- He(Ne) laser (Thorlabs HNL050R)
 - User manual available
U:\IMPROVE_Lab\LASER\HNL050RSupportDocumentation
- Diffuser/collimator (Edmund optics: EO 48-265 and EO 47-876)
- Integrating sphere
- Reflectance photodiode detector and radiometer (Labsphere LM-4000)
- Slide changer
- Neutral density material
- Opal glass (integrating plate)
- Transmittance photodiode detector and radiometer (ORIEL detection system 7072)

5.2 Initial Calibration Requirements

- 6" research integrating sphere
- Reflectance standards (NIST)
- Standards tray, containing 20 Teflon® filters representative of the range of mass loadings and composition in the IMPROVE aerosol sampling network

5.3 HIPS Analysis Requirements

- Standards tray
- Tray of filters previously analyzed for reanalysis
- "A" module filters, in monthly site trays, for HIPS analysis

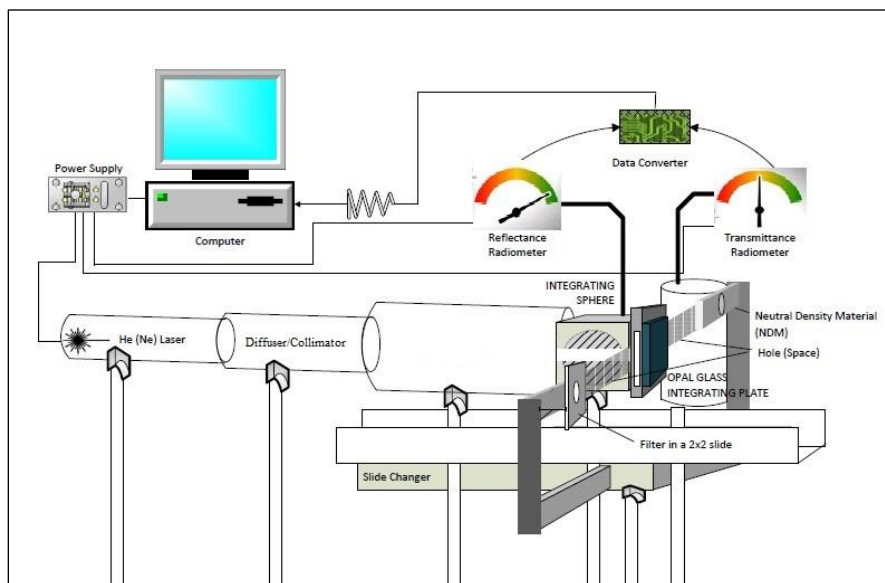
6.0 PROCEDURAL STEPS

6.1 Overview of the Hybrid Integrating Plate/Sphere System

Before spring of 1994 (quarter: A94), a pure integrating plate system called LASER Integrating Plate Method (LIPM) was used for all analyses. The old system required analysis before and after collection. The new system, HIPS, combines an integrating sphere with the same integrating plate used for LIPM analysis. The reflectance measured by the integrating sphere replaces the initial integrating plate measurement. Thus, the absorbance can be determined from the exposed filter with the simultaneous measurement by two detectors. The main advantages of the new system are increased efficiency and better quality control along with the ability to perform true replicate analyses. The new system is also technically closer to the integrating sphere method, which accounts for all light in the system.

A schematic of the current system is given in Figure 1. Light of 633 nm wavelength from a He (Ne) laser is diffused and collimated to provide a uniform beam of light of approximately 0.7cm² in area at the sample. The filters are mounted in standard 2"x2" 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 collected with an Oriel 7022 photodiode detection system. This portion of the new system is identical to the old LIPM system. The reflected light is collected by a 2" sphere (Labsphere) and measured with a photodiode detector. The only light not accounted for is the transmitted light at very large angles (which is approximately 20% of the transmitted light). The slide-changer arm has three positions: (1) the filter, (2) a hole (space), and (3) the neutral density material (NDM).

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



The absorption of the exposed filters measured by either the integrating sphere or the new hybrid integrating plate/sphere system is equivalent to the absorption by the particles alone. Numerous measurements of clean Teflon® filters show close to zero absorption.

The equation for the absorbance for the particles on the filter is given by:

$$b = LRNC = \ln \left(\frac{1025.5 - (1.235 * R)}{T} \right)$$

where 1.235*R is the reflected intensity measured by the integrating sphere (normalized to 1025.5) and T is the transmitted intensity, which is the normalized intensity measured by the integrating plate. It is assumed that the fraction of transmitted light that is captured by the plate does not change as the filter loading increases. This has been demonstrated to be a valid approximation for samples with a wide range of loadings.

6.2 Initial Calibration of the Hybrid Integrating Plate/Sphere System

To initially calibrate the system, the HIPS reflectance sphere detector was adjusted to give the same value of R for a reference filter as the research sphere in the reflectance mode. The HIPS plate detector was adjusted to give the same value of T as the research sphere in the transmittance mode. This procedure ensured that the new HIPS system was equivalent to the old LIPM system and to the 6" research integrating sphere system (described in section 5.2) for a wide variation of sample loadings and aerosol types.

The HIPS system was calibrated relative to a 6" research model integrating sphere (Labsphere). The research sphere was used to calibrate a set of 20 filters having mass loadings and compositions representative of those found in the IMPROVE aerosol sampling network. The procedure used for creating the calibration filters follows:

- 1) Removed the integrating plate and 2" integrating sphere from the HIPS system.
- 2) Installed the 6" integrating sphere in place of the integrating plate.

- 3) Calibrated the 6" research integrating sphere system to give a value for T (transmittance) of 1000 for a hole by adjusting the detector settings.
- 4) Checked the calibration of the 6" research sphere by testing two NIST-traceable reflection standards, 10% and 99%, and verifying that they give an R value of 100 and 990 (± 5) respectively.
- 5) Selected 20 archived exposed Teflon® filters, representative of the range of mass loadings and compositions on filters from the network. Numbered them 1 through 20, mounted the filters in slide frames, and installed the filters, in order, in a slide tray labeled as the standards tray.
- 6) Analyzed the filters in the standards tray with the 6" integrating sphere system and recorded the measurements of R (reflectance) and T (transmittance) on the computer. These measurements of R and T were used to calibrate the HIPS system.

6.3 Preparation of Filters for HIPS Analysis

A lab technician transfers filters from labeled Petri dishes to labeled slides in preparation for HIPS analysis. Slides are organized alphabetically by site name and chronologically by sample date. Slides for four sites (typically ten slides per site) are placed in each slide tray. Slide trays are labeled with a sticker indicating the site codes and the sampling month and year of the filters inside the trays. Detailed instructions for this procedure are located in TI 276A.

6.4 Generating Log Files/Tray Check

Log files are created for use in running HIPS analysis on one sampling months' worth of filters. A lab technician generates these log files through Microsoft Excel or through a macro that pulls data from SQL server. The log files consist of a list of filters that need to be lased, providing the status, site code, sample date, and start time for each filter. The information for terminal status filters is highlighted in red as a reminder to remove those filters from their slide trays before the tray goes through HIPS analysis. Once log files are generated, tray checks are done to ensure that the log files have accurate references. A lab technician confirms that the inventory of filters in the slide trays matches the log file. Slides in each tray are checked against the log file to confirm that each filter is present (or absent, if a filter has a terminal status), in the correct sample-side up orientation, and that the filter information on each slide sticker matches the information in the log file. Detailed instructions for this procedure can be found in TI 276B.

6.5 Preparation for Routine HIPS Analysis

Routine HIPS analysis is performed for all IMPROVE filters in a sampling month after the Level 1 validation of the collection parameters, gravimetric mass, and XRF are completed. A single analysis session is preferable for HIPS as it maximizes quality control. The HIPS system is prepared for routine analysis by the spectroscopist or a lab technician. Only after the standards and reanalysis filters have been run shall the system be released for routine HIPS analysis.

The calibration, reanalysis, and analysis data are stored in the U: drive (U:\IMPROVE_lab\LASER). Files for both reanalysis and analysis data are placed in the appropriate folder, designated by sampling month and year of the analysis filters. The Excel files are organized to include T and R measurements. For analysis filters only, the Excel files also include T and R measurements from the neutral density material (NDM) taken before each sampled filter is

measured. For each filter, data is recorded in a single row, containing information for filter identification (status, site, sample date, start time), T and R measurements, and the date and time that measurements were taken.

Prior to HIPS analysis, the Excel files will contain only status, site, and sample date for each sample in the current analysis month. Excel files for reanalysis data include assigned true values for each sample in the reanalysis set. Columns are color-coded and properly labeled to indicate assigned reference values and the newly-measured reanalysis values.

The HIPS system is turned on the day before it is set to analyze in order to allow the laser and detectors to stabilize. On the day of HIPS analysis, a trained lab technician or the spectroscopist calibrates the system by running a tray of 15 standards. Then, a reanalysis tray (25 filters) of previously-run IMPROVE filters is analyzed. Reanalysis filters are pre-determined based on stability and spread of original analysis so as to best represent the values that is typically measured from IMPROVE filters. T and R data for these filters is recorded using a macro. After the integrity of the data is confirmed for the standards and the reanalysis filters, HIPS analysis of IMPROVE filters can begin. Step-by-step instructions for these procedures are located in TI 276C.

6.6 HIPS Analysis of IMPROVE samples

HIPS analysis of IMPROVE samples are performed by laboratory technicians, under the supervision of the spectroscopist. Routine analysis of IMPROVE samples requires that in addition to the measurements of T and R for the sample filter, the measurements of T and R for the NDM (reference material) must also be taken before each sample. Data for both the reference values and actual values are recorded using a macro. After every five slide trays are analyzed, the laser is readjusted offline using position 3 from the standards 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 TI 276C.

6.7 Data Delivery and Reporting

Once a complete sampling months' worth of data is collected, the Excel files are delivered to the laboratory manager for the final quality check and to the database manager for the upload to the SQL server. The data is then available through SQL. Data reporting is performed after final data validation is performed.

7.0 QUALITY ASSURANCE AND QUALITY CONTROL

Several checks throughout the laser analysis process ensure that the laser data is 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 and that any terminal status filters have been removed. Log files are compared to the contents of the slide trays to confirm that the order of filters is correct before the filters undergo analysis.

A standards tray is run before reanalysis and routine analysis can occur. The values for the standards must be within $\pm 3\%$ of their reference values before the process can continue. After this, a reanalysis tray is run. The coefficient of determination between the assigned reference values of the reanalysis set and the results obtained from running the reanalysis set should be at least

0.90 for each independent variable (T, R and calculated b). For details refer to TI 276D, “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 standards and reanalysis filters have been met, routine HIPS analysis of IMPROVE samples can begin.

After every five trays of routine filters, the HIPS system is readjusted using position 3 of the standards tray in order to maintain accurate results throughout analysis.

Files are carefully reviewed by the spectroscopist and the laboratory manager before being released for upload to the SQL server.

For more information on quality assurance and quality control checks, please see TI 276D.

8.0 DATA AND RECORDS MANAGEMENT

Until the “Q/A” and “Q/C” checks have been performed, HIPS analysis data is kept in Excel worksheets. The calibration data taken before routine analysis is recorded in a designated Excel file that can be found in U:\IMPROVE_Lab\LASER. Files for both reanalysis data and routine analysis data are both prepared and stored on the U: drive as well.

Calibration data is recorded manually into the Excel file by a trained lab technician or the spectroscopist. The reanalysis and routine analysis data are recorded using automated macros in order to prevent user error and typing mistakes.

All files needed to run the automated versions of the macro, which is called M401xVB41.xlsm, can be found in U:\IMPROVE_Lab\LASER\M401_Automatic. There are two different versions of the automated macro. The macro used for reanalysis takes one data point (R and T values) for the sample and then moves down to the next row in Excel. The macro used for routine analysis takes two data points per HIPS system cycle; R and T measurements from NDM (the reference values) are acquired first, followed by the R and T measurements of the sampled filter.

Once a data set for a sampling month is complete, the data is reviewed by the spectroscopist and lab manager. Once approved, the data is ingested via a .csv file into the IMPROVE webapp. Following ingestion the data is accessible via the IMPROVE webapp and the SQL server (Refer to TI 276E for details). Please add the paragraph about how. Original Excel sheets containing measurements of T and R values are archived in the U: drive.

During the validation of the data, the LRNC values are calculated and reported (see SOP 351 for details).

9.0 REFERENCES

TI 276A: Preparation for HIPS

TI 276B: HIPS Logs and Tray Check

TI 276C: Performing HIPS Analysis

TI 276D: Quality Assurance and Quality Check of Analysis of PM_{2.5} Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption

TI 276 E: Ingesting Results

Related SOPs:

SOP 251: Sample Handling Laboratory

SOP 301: XRF Analysis of Aerosol Deposits on Teflon Filters

SOP 351: Data Processing and Validation