IMPROVE
STANDARD OPERATING PROCEDURES

SOP 276
Optical Absorption Analysis

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1.0 PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) describes the analysis of Teflon filters for the coefficient of optical absorption b_{abs} using the Hybrid Integrating Plate/Sphere Analysis method (HIPS).   This method is used to measure the optical absorption of the particles on the fine stage ($PM_{2.5}$) Teflon filters. 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. The coefficient without correction, LRNC, is stored in the internal database. A correction to the measured value, based on the areal density of particles on the filter, is made at the time of data processing. This parameter, call BABS, is used in the FTP database and in all reports.

Prior to spring of 1994 (A94 quarter), a pure integrating plate system, which was 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 coefficient of absorption can be determined from the exposed filter with the simultaneous measurement by two detectors. The main advantage of the new system is that we can maintain better quality control with the ability to do true replicate analyses. Theoretically, the new system is better because it is closer to the integrating sphere method, which accounts for all light in the system. In addition, the new system is more efficient in the work-time required.

2.0 RESPONSIBILITIES

2.1 Spectroscopist

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.

2.2 Laboratory Technician

The lab technician shall:
- run the HIPS system under the supervision of the spectroscopist

3.0 REQUIRED EQUIPMENT AND MATERIALS

The equipment and materials required for HIPS analysis are listed below.

3.1 Hybrid Integrating Plate/Sphere System

- HeNe laser
- diffuser/collimator
- integrating sphere
- reflectance radiometer & detector
- slide changer
- reflectance standards

- opal glass (integrating plate)
- transmittance radiometer & detector

3.2 Calibration Requirements

- 6" research integrating sphere
- reflectance standards
- Standards tray containing 20 Teflon filters representative of the range of mass loadings and composition in the IMPROVE aerosol sampling network.

3.3 Analysis Requirements

- Standards tray (from section 3.2)
- tray of filters analyzed in the previous quarter for reanalysis
- "A" module filters, in quarterly site trays, for HIPS analysis

4.0 METHODS

4.1 Overview of the Hybrid Integrating Plate/Sphere 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 0.7 cm^2 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. (This is approximately 20% of the transmitted light.) The slide-changer arm has 2 positions: a hole, and the sample filter. The hole is used to check the calibration of the two detectors (reflectance off of the opal glass is used to check the response of the integrating sphere).

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Figure 1 UCD Hybrid Laser Integrating Plate/Sphere Method
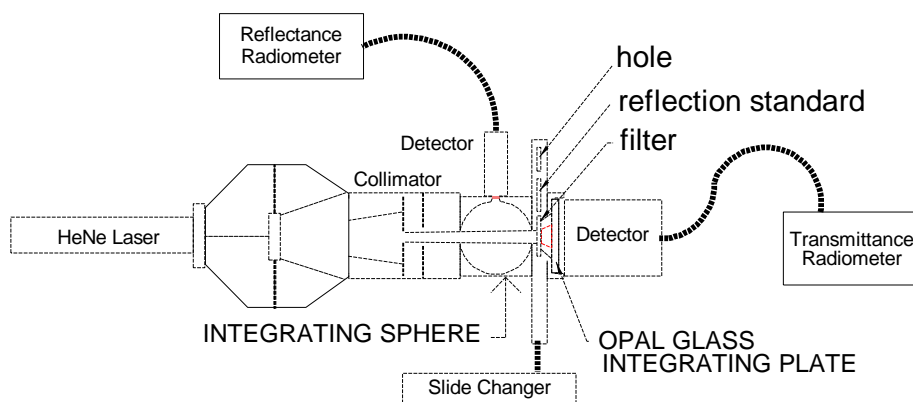
The absorption of the exposed filters measured by either the integrating sphere or the new hybrid integrating plate/sphere system is equivalent to the absorption by the particles alone. Numerous measurements of clean Teflon filters shows that Teflon has zero absorption. This is verified each analytical session by analyzing a series of clean filters.

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

$$\boldsymbol{s} = \ln\left(\frac{1000 - R}{T}\right) \tag{1}$$

where R is the reflected intensity measured by the integrating sphere (normalized to 1000) 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.

To calibrate the system, the LIPM sphere detector is adjusted to give the same value of R for a reference filter as the research sphere in the reflectance mode. The LIPM plate detector is adjusted to give the same value of T as the research sphere in the transmittance mode. This procedure ensures that the new HIPS system is equivalent to the old LIPM system, and to our 6" research integrating sphere system (described in section 4.2) for a wide variation of sample loadings and aerosol types.

4.2 Calibration of the Hybrid Integrating Plate/Sphere System

The HIPS system is calibrated relative to a 6" research model integrating sphere (Labsphere). The research sphere is used to calibrate a set of 20 filters having mass loadings and compositions representative of those found in the IMPROVE aerosol sampling network. These twenty filters are used to calibrate the HIPS system. The procedure for creating the calibration filters follows.
1. Remove the integrating plate and 2" integrating sphere from the HIPS system
2. Install the 6" integrating sphere in place of the integrating plate.
3. Calibrate the 6" research integrating sphere system to give a value for T (transmittance) of 1000 for a hole by adjusting the detector settings.
4. Check the calibration of the 6" research sphere by testing two NIST-traceable reflection standards, 10% and 99%, and verifying they give an R value of 100 and 990 (±5) respectively. If not, the system is malfunctioning and must be repaired.
5. Select twenty exposed Teflon filters, representative of the range of mass loadings and compositions on filters from the network. Number them 1 through 20, mount the filters in slide frames, and install the filters, in order, in a slide tray labeled as the Standards Tray
6. Analyze the filters in the standards tray with the 6" integrating sphere system, recording the values of R (reflectance) and T (transmittance) on the computer. These values of R and T will be used to calibrate the HIPS system.
7. Steps 1 through 6 must be repeated to create new standards if the current Teflon filter lot displays significant variation in reflectance from previous lots.

4.3 Preparation for Routine Analysis

Routine HIPS is performed once per quarter after the Level I validation of the collection parameters, gravimetric mass, and XRF are completed (a single analysis session maximizes quality control). The slides shall be arranged in site-specific 27-position slide trays, with each tray containing the filters for an entire quarter. Three trays from the previous quarter shall be used for reanalysis. The three trays generally used are from Crater Lake, Grand Canyon National Park, and Washington D.C., as these represent lightly loaded, moderately

loaded, and heavily loaded sites in the IMPROVE network. The HIPS system shall be prepared for routine analysis by the Spectroscopist. Only after the standards and reanalysis have been run shall the system be released for normal analysis.

The reanalysis and analysis data will be stored in the LASER database, tied to the LOGS database through the LASER program. The LASER database is organized to include transmission and reflectance measurements, calculated uncorrected absorption values, and filter identifications for each channel 'A' filter. For each filter, this data is recorded in a single record. containing status, site, sample date, start time, channel, elapsed time, flow rate, transmission, reflectance, absorption values uncorrected for sample density, measurement errors, measurement minimum detectable limit, initials of person collecting data, and date and time of measurement.

Prior to analysis, the LASER database will contain only the status, site, sample date, start time, channel, elapsed time, and flow rate for each valid sample in the current analysis quarter. However, for reanalysis filters, the LASER database will already contain a complete data set. Extra fields have been added to each record to allow entry of reanalysis data (and time and date of measurement). The fields identified by a postscript of '1' are the primary data fields. Fields identified with the postscripts '2', '3', or '4' are reanalysis fields.

The following steps are involved in the setup and calibration of the system.

1.   Allow the HIPS system to warm up for at least two hours. This allows the laser and detectors to stabilize.

2.   Verify that each detector system, both the reflectance and transmittance radiometers, has the appropriate start-up settings specified in the calibration logbook.

3.   Start the computer and access the STANDARDS tracking file;
        V:\tests\analysis\B_abs\Isphere\standard\stnd25mm.xlw

4.   Analyze the tray of Standards
        a)   Load the tray of standards.
        b)   Insert the prime reference filter, as indicated on the HIPS calibration log and adjust the settings for the two detectors to give the desired readings.
        c)   Shift to the hole (position 3 in the slide changer arm) and record R and T. These values of T and R are the standard values for the analytical session and will be referred to as T_0 and R_0.
        d)   Return to the filter and check the R and T are still at the standard for this filter.

5.   Run the entire set of standards, recording R and T by hand into the STANDARDS tracking file. Between each analysis shift to the hole and adjust T_0 and R_0.

6. Verify that the values for the Standards analysis run match the historical values in the STANDARDS database to within 5%. If not, identify the reason and rectify before proceeding.

7. Run reanalysis.
   a) Load the first reanalysis tray, a tray that had been run during the previous quarter, into the HIPS system.
   b) Open the LASER database for the quarter in which the reanalysis tray was first analyzed. Enter the site code for the reanalysis tray to jump to the appropriate point in the database. Use the right arrow key $<\rightarrow>$ to move to an empty column to enter the reanalysis data. Verify that the cursor position reflects the first filter identification.
   c) Insert the slide indicated on the screen into the HIPS system for analysis.
   d) Once the values have stabilized, press the enter key to record the values of R and T from the radiometer outputs into the computer for the slide indicated on the computer screen.
   e) The database will increment down to the next valid slide position. Remove the slide analyzed in step b, insert the slide listed on the computer screen, and repeat step d to collect data for the current slide.
   f) Use the arrow keys to move non-sequentially.
   g) After every 5-10 samples, shift to the hole position and adjust to R_0 and T_0.
   h) Repeat steps a through j for the other two reanalysis trayfiles.

4.4 Routine Analysis

Routine analysis shall be performed by laboratory technicians, under the supervision of the Spectroscopist. No routine analysis shall occur until the Spectroscopist has completed all quality control procedures and releases the instrument for use to a trained technician. The procedures for routine analysis are listed below.

1. Run analysis.
   a) Run the Laser program to open the LASER database for the current quarter. The cursor should be in the first position for the first filter (the filters will be listed vertically by site code and sample date)
   b) Load the first analysis tray into the HIPS system. Verify that the filters in the tray match those displayed on the screen.
   c) Insert the slide indicated on the screen into the HIPS system for analysis.
   d) Once the values have stabilized, press the enter key to record the values of R and T from the radiometer outputs into the computer for the slide indicated on the computer screen.

e)   The database will increment down to the next valid slide position. Remove the slide analyzed in step d, insert the slide listed on the computer screen, and repeat step d to collect data for the current slide.

f)   After every 5-10 samples, shift to the hole and adjust to R_0 and T_0.

g)   To move non-sequentially through the database, use the arrow keys.

h)   When all the slides in the tray have been analyzed, remove the tray from the HIPS system and install the next tray (listed in the database). Verify that the filters in the tray match those displayed on the screen.

i)   Repeat steps c through h for all site trays in the current analysis quarter.

2.   If the analysis must be interrupted, do not turn off the HIPS system. Save and exit the database, then notify the Spectroscopist. Prior to resuming analysis, the Spectroscopist shall perform reanalysis to verify the stability of the system.

4.5 Data Reduction

Data reduction shall be performed by the quality assurance specialist. Much of the reduction is performed automatically, but the procedures followed to derive Babs measurements from the collected HIPS data are listed below.

4.5.1 Calculating LRNC

The HIPS system records R (reflectance), and T (transmittance) for each analysis performed.   These data are processed to derive the absorption measured on the filter, labeled LRNC for 'laser not corrected'. For an aerosol deposit area in cm^2 and sampled air volume, V, in m^3, the equation for the uncorrected coefficient of absorption in $10^{-8}\ m^{-1}$ is

$$\mathrm{LRNC} = \left(\frac{\mathrm{area}}{\mathrm{V}}\right) 10^4\ \ln\left(\frac{1000 - \mathrm{R}}{\mathrm{T}}\right) \ . \qquad (2)$$

No measurement of the clean filter is needed because Teflon does not absorb light. However, the layering effects inherent in collecting particles on a filter cause the absorption measured on the filter (LRNC) to be less than the ambient absorption (BABS).

The uncertainty in LRNC is determined by replicate measurements of ambient filters where f_v = fractional volume precision = fractional flow rate precision

$$\left[\sigma(\mathrm{LRNC})\right]^2 = \left(\frac{\mathrm{area}}{\mathrm{V}} * 225.\right)^2 + \left(f_v * \mathrm{LRNC}\right)^2 \qquad (3)$$

The minimum detectable limit is defined as twice the precision in the measurement for a sample with low absorption. The approximate expression for the mdl in $10^{-8}\ m^{-1}$ is then

$$mdl = \frac{area}{V} * 450 \qquad (4)$$

For a typical filter with a collection area of 2.2 cm^2, the mdl is approximately 30 10^{-8} m^{-1} or 0.3 (Mm)$^{-1}$.

4.5.2 Calculating BABS

BABS has an unusual position in the data base. The uncorrected coefficient of absorption, LRNC, is stored in the internal data base, but is not provided for external users. The external users are only provided with the corrected (or ambient) coefficient, BABS.

The first and smallest correction is associated with the integrating plate method. In the integrating plate method any scattering with angles large enough to miss the plate causes an increase in apparent absorption. In order to quantify the effect of the large angle scattering, a series of comparisons were made between the integrating plate system and an integrating sphere system. The integrating sphere system, is somewhat more difficult to use routinely, but eliminates the scattering component. Comparison of the results indicates that approximately 3% of the apparent absorption by LIPM is associated with scattering. The measured coefficient is therefore multiplied by 0.97.

Several tests involving simultaneous measurements of the same atmosphere but with differing mass per unit area (areal density) have shown that it is necessary to correct the values measured on a filter to obtain the proper atmospheric absorption. This is true for both integrating plate and integrating sphere. The correction is small for very lightly loaded samples, but we are constrained to design a sampler primarily for other particle measurements. The hypothesis is that the absorption of particles on a filter is less than the ambient absorption of particles because other particles on the filter can shield a given absorbing particle. A form was chosen that included two exponents of the areal density of particles measured by gravimetric analysis in µg/cm^2. Note that the effect is observed even if the layering mechanism is not correct. The equation used is

$$R = 0.36 \exp\left(-\frac{\rho t}{22}\right) + 0.64 \exp\left(-\frac{\rho t}{415}\right) \qquad (5)$$

where the constants were determined by fitting data from independent studies at Davis and Los Angeles.

The equation for the ambient coefficient of absorption in 10^{-8} m^{-1} is derived from the uncorrected coefficient using:

$$BABS = LRNC * \frac{0.97}{R} . \qquad (6)$$

The uncertainty in R is estimated to be 10% of (1-R), based on the precision of the fit for the test data. The equation for the precision of the corrected coefficient of absorption is:

$$\sigma(BABS) = \left(\sigma(LRNC) * \frac{0.97}{R}\right)^2 + \left(0.10 * \frac{1-R}{R} * b\right)^2 \qquad (7)$$

The minimum detectable limit is defined as twice the precision in the measurement for a sample with low absorption. Although this will vary with the intensity for a clean filter, it is more convenient to use a single intensity of 390 units for a typical clean filter. The expression for the mdl is then approximately

$$mdl(BABS) = mdl(LRNC) * \frac{0.97}{R} \qquad (8)$$