

UCD CSN Technical Instruction #277C

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

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

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Prepared By: _____ Date: _____

Reviewed By: _____ Date: _____

Approved By: _____ Date: _____

DOCUMENT HISTORY

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4/28/2020	LMK	All	Changed procedures to reflect new software for slide tray generation and analyzing samples, update figures.
4/29/2020	LMK		Update wording on flow diagram
5/7/2021	NJS	2	Changed Fabs to fAbs for consistency

TABLE OF CONTENTS

1. PURPOSE AND APPLICABILITY 4

2. DEFINITIONS..... 4

3. EQUIPMENT AND SUPPLIES 5

4. PROCEDURE..... 5

 4.1 Detector Registration Verification 5

 4.2 Reanalysis Check 6

 4.3 Sample Check..... 8

 4.4 Final Check 8

 4.5 Troubleshooting 9

5. REFERENCES 11

LIST OF FIGURES

Figure 1. Flow diagram of quality control processes and actions taken. 12

1. PURPOSE AND APPLICABILITY

The purpose of this technical instruction (TI) document is to describe the methods for assessing measurement quality for the Hybrid Integrating Plate/Sphere (HIPS) system. This document provides:

- The necessary steps to assure quality of transmittance (T) and reflectance (R) measurements and the calculated absorption optical depth (τ_{abs}) value.
- Instructions on monitoring of instrumental drift.

2. DEFINITIONS

- **Field blanks:** PTFE filters that travel to field sampling sites with sample filters but are not sampled.
- **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 back-scattered 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, $r = -a_1R/a_0$, 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 that is reported by the HIPS system.
- **Verification filters:** a set of sampled filters encompassing a range of mass loadings and composition used to verify the registration of the HIPS detectors for long-term consistency of measurements.
- **Reanalysis filters:** a set of sampled filters encompassing a range of mass loadings and composition 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.
- **Acceptance limits:**

- **Verification filters:** analyzed daily during HIPS operation, are determined as $\pm 3\%$ of the reference values for T and R, except for filter #3, the registration filter, which is $\pm 1\%$ of its reference values for T and R. Reference values are determined as the mean of 15 measurements after registration of the detectors.
- **Reanalysis linearity:** The coefficient of determination of the measured and calculated τ values plotted against the reference τ values must be ≥ 0.95 .
- **Reanalysis accuracy:** τ must be within $\pm 3\%$ of the reference values. Reference values are calculated as the mean of 15 measurements of the reanalysis set.
- **Reanalysis precision:** Current reanalysis measurement of τ will be added to the previous 7 measurements (for a total of 8) and the relative standard deviation (RSD) will be calculated. The RSD for $\tau > 0.1$ (approximately $5 \times \text{MDL}$) must be $\leq 3\%$.
- **PPE:** Personal Protection Equipment.

3. EQUIPMENT AND SUPPLIES

- HIPS: Hybrid Integrating Plate/Sphere Method for Measuring reflectance and transmittance
- Verification filters.
- Reanalysis (RA) filters.
- Sample filters: Set of CSN samples from a given sampling month that is to be analyzed through HIPS.

4. PROCEDURE

4.1 Detector Registration Verification

- 1) To ensure consistency in measurements during measurement runs, the transmittance and reflectance detectors are registered to set values at the beginning of every day of analysis. This ensures consistent detector readings between the days the field blanks (used for correcting the absorption) are run and the days the sampled filters are run. Registration of the detectors is verified by running the verification filters. Position 3 in the verification filter set is the registration filter.
- 2) Refer to TI 277B for specific instructions to perform the detector registration and run the verification filters. Results are written to the database following analysis. Results for T and R of the verification filters are then exported from the database and recorded in the Excel workbook "U:\IMPROVE_Lab\Laser\Detector Verification\laser_detector_verification.xlsx".
- 3) Once the results of the verification filters are complete, they are checked against the acceptance criteria. All T and R values must be within $\pm 3\%$, except position 3 (the registration filter) which must be within $\pm 1\%$ of the accepted values listed

at the top of the “laser_detector_verification” Excel sheet. Any measurement result outside of these acceptable criteria will be colored red in the Excel worksheet.

- 4) Accepted values for the verification filters were determined as the mean of sixteen measurements of each filter over the course of three days. These were performed 11/6/2018 – 11/8/2018 after the HIPS system underwent an upgrade including a new laser, new four inch integrating sphere, new reflectance detector, new integrating plate, and new transmittance detector.
- 5) If any value fails to meet the acceptance criteria, then the following steps must be completed:
 - i. Check that the detectors have not drifted by re-measuring the registration filter. The T and R values must be within $\pm 1\%$ of the registration values (T=437, R=332). If they are outside of this range, perform a new detector registration and verification according to TI 277B. If the registration values are acceptable then continue to the next step.
 - ii. Re-measure the verification filter which failed acceptance. If the new values are acceptable then replace the original result in the “laser_detector_verification” sheet with the new values and continue reanalysis. If the new measurement fails again, see the troubleshooting section and notify the spectroscopist and/or laboratory manager before proceeding.

4.2 Reanalysis Check

- 1) To ensure final results are consistent with historical results, a set of reanalysis filters is analyzed at the beginning and end of every day of analysis. The main difference between the reanalysis filters and the verification filters is that the reanalysis filters will undergo calculation of the field blank corrected optical absorption coefficient, τ_{abs} , for monitoring the long-term performance of the final HIPS result.
- 2) Refer to TI 277B for specific instructions to measure the reanalysis filters. Results are written to the database following analysis. Results are then exported from the database and recorded in the excel workbook, “U:\IMPROVE_Lab\Laser\Reanalysis\HIPS_Reanalysis_QC.xlsx”.
- 3) The linear regression coefficients, a_0 and a_1 , have been determined from a selection of IMPROVE field blanks from July, August, and September 2010 to match the reanalysis filters. These field blanks were measured five times over three days with the current HIPS system. The linear regression coefficients from the non-absorbing field blanks are used to calculate the field blank corrected absorption coefficient, τ_{abs} , for the reanalysis filters. For details of these calculations see SOP 277.
- 4) Accuracy check: The τ_{abs} results are then compared to the reference values determined from ten measurements of the reanalysis filters collected over two days. For each reanalysis filter, the τ_{abs} must be within the expanded uncertainty

of the reference value. The expanded uncertainty, $U(\tau_{abs})$, considers the uncertainties from each part of the analysis and is shown in Equation 1.

$$\begin{aligned}
 U(\tau_{abs}) &= k \sqrt{\left(\frac{\partial \tau_{abs}}{\partial r} u(r)\right)^2 + \left(\frac{\partial \tau_{abs}}{\partial t} u(t)\right)^2} \\
 &= k \sqrt{\left(\frac{u(r)}{1-r}\right)^2 + \left(\frac{u(t)}{t}\right)^2}
 \end{aligned}
 \tag{Eq. 1}$$

where,

$$u(r) = \sqrt{\left(\frac{R}{a_0} u(a_1)\right)^2 + \left(\frac{a_1 R}{a_0^2} u(a_0)\right)^2 + \left(\frac{a_1}{a_0} u(R)\right)^2}
 \tag{Eq. 2}$$

$$u(t) = \sqrt{\left(\frac{1}{T} u(a_0)\right)^2 + \left(\frac{a_0}{T^2} u(T)\right)^2}
 \tag{Eq. 3}$$

$u(r)$ and $u(t)$ are the uncertainties of the blank corrected reflectance and transmittance and are given by Equations 2 and 3. $u(a_0)$ and $u(a_1)$ are the standard errors in the intercept and slope of the linear regression of field blank filters. $u(R)$ and $u(T)$ are the uncertainties of the raw reflectance and transmittance which are estimated as the median standard deviation from seven measures of the reanalysis filters in November and December 2018. k is the coverage factor. In this work the coverage factor is 2, which approximates the 95% confidence interval.

- 5) Linearity check: The τ_{abs} results for the reanalysis run are plotted against the reference values and a linear regression is applied. The coefficient of determination must be greater than 0.95 and the slope must be within 0.95 and 1.0.
- 6) Long-term reanalysis: To monitor the long-term trend of the reanalysis results a z-score is calculated for each reanalysis sample, i , according to Equation 4. The z-scores for all n reanalysis samples in a day are then averaged to determine the mean z-score, Equation 5, which is then added to a time-series plot. Acceptable mean z-scores are ≤ 1 and any sudden shifts in the plotted mean z-score value compared to previous values must be investigated.

$$z\text{-score} = \frac{\tau_{abs,i} - \tau_{abs,accepted}}{\sqrt{U_{rel}(\tau_{abs,i})^2 + U_{rel}(\tau_{abs,accepted})^2}} \quad \text{Eq. 4}$$

$$mean\ z\text{-score} = \frac{1}{n} \sum_i z\text{-score}_i$$

Eq. 5

7) Failure of QC checks:

- a. If any sample fails the accuracy check or is the cause of failure of the linearity or long-term checks then reanalysis is required. If measurements continue to fail QC checks, see the troubleshooting section and notify the spectroscopist and/or laboratory manager.
- b. If the linearity or long-term checks fail and no single filter is obviously at fault, then see the troubleshooting section and notify the spectroscopist and/or laboratory manager.
- c. If the end-of-day reanalysis QC check fails any test, then the results for all samples analyzed that day are suspect and should be invalidated. Samples will need to be reanalyzed once the problem is corrected and QC tests pass.

4.3 Sample Check

- 1) Routine analysis of sample filters is monitored by checking the NDM reference filter values recorded with every sample measurement. In the HIPS log file where the results are being recorded (refer to TI 277B), move to the “Reference – Integrity Check” worksheet. Here the reference T and R values from the NDM filter will be plotted along with acceptance limits. The acceptance limits will be automatically calculated as +/- 5% of the mean result for the first 200 measurements of the NDM. Ensure that the reference T and R values stay within the limits and there are no sudden large jumps in the values. If a failure is observed, see the troubleshooting section and notify the spectroscopist and/or laboratory manager before proceeding.
- 2) The registration filter is analyzed after 200 sample filters have undergone HIPS analysis. This ensures that the detector registration has not changed. See TI #277B for details. If the registration values are outside of ± 1 % of their set values (T = 437, R = 332) then follow the directions in TI #277B and notify the spectroscopist and/or laboratory manager.

4.4 Final Check

- 1) After all analyses for the sampling month are complete and the QC checks have passed, notify the spectroscopist and/or laboratory manager that the data are ready for review.
- 2) The spectroscopist will review all the HIPS data and QC checks to assess the integrity of the data.

- 3) Once complete, the data will be released for ingestion into the database.

4.5 Troubleshooting

- 1) Failure of a single verification or reanalysis filter
 - a. This section assumes the registration filter has been verified to be within 1 % of the set values for T and R.
 - b. For the filter that failed acceptance, begin troubleshooting by visually inspecting the filter for any holes, tears, or other defects. If any are found, notify the spectroscopist and/or lab manager. Analysis can continue as the issue was filter-specific and not related to the instrument. The damaged filter will be invalidated and archived.
 - c. If no damage or defects are discovered during visual inspection, next rotate the filter slide in the slide tray and measure again. The filter may have been loaded upside down.
 - d. If rotating the slide does not resolve the problem, perform a new detector registration and verification regardless of whether the registration filter is still within 1 % of its set values. If this does not resolve the issue, continue to the steps below.
- 2) Detector registration verification failure
 - a. If step 1 above did not resolve the issue or more than one filter is failing, then perform a new detector registration and verification.
 - b. If the verification continues to fail, stop analysis and notify the spectroscopist and/or laboratory manager. Then, proceed to the “Instrument troubleshooting” section below.
- 3) Reanalysis check failure
 - a. If step 1 above did not resolve the issue or more than one filter is failing, then perform a new detector registration and verification.
 - b. If the registration verification check passes and the reanalysis check continues to fail, stop analysis and notify the spectroscopist and/or laboratory manager. Then, proceed to the “Instrument troubleshooting” section below.
 - c. In the event that maintenance has been performed on the HIPS instrument or some part has been replaced (especially an optical component), then the values measured for the field blanks, which correct the transmittance and reflectance of the reanalysis filters, may no longer be relevant. In this case, the reanalysis field blanks should be reanalyzed and new field blank linear regression coefficients (a_0 and a_1) will need to be determined to properly correct τ_{abs} .
- 4) NDM reference value failure

- a. Assuming the troubleshooting procedures in TI 277B have been followed and the NDM reference is still unacceptable, then analysis of samples must be halted.
- b. Take a measurement of the registration filter and verify it is within 1 % of its set values. Then, take a measurement of the NDM (slide arm out) and check if it is within 5 % of the mean value in the worksheet. If it is acceptable, then proceed by reanalyzing the affected sample filters. Monitor the NDM reference values during reanalysis and ensure the NDM is acceptable. If it is, continue with sample analysis.
- c. If the registration filter is still within 1 % of its set values and the NDM fails acceptance then review the results from a previous week of analysis and determine if the NDM reference is more than 5 % different from the mean value obtained in the previous week.
- d. If the unacceptable NDM value is within 5 % of the previous week's mean NDM value then it is likely that there was a problem with the first 200 NDM measurements which determine the mean. Notify the spectroscopist and/or laboratory manager. They will review the data and decide whether the day's analyses must be repeated.
- e. If the unacceptable NDM value is different from the previous week's, then it is likely the alignment of the laser has changed. Notify the spectroscopist and/or lab manager and proceed to the "Instrument troubleshooting" section below.

5) Instrument troubleshooting

- a. Check laser power.
 - i. With the laser and detectors on and warmed up, remove any slide tray and slides from the HIPS instrument.
 - ii. Move the slide changer arm in, but with no slide inserted. This will open the optical path from the laser directly to the integrating plate.
 - iii. With the laser illuminating the integrating plate directly, the transmittance detector should read $16.5 \mu\text{W} \pm 10 \%$.
 - iv. If the power reading from the detector is outside of this range then something in the system has changed. The possibilities are: 1) that the laser output power has changed, perhaps due to age or impending failure, 2) an optical element of the integrating plate has changed or has become dirty, or 3) the laser is mis-aligned. Proceed to the laser alignment step below. Align the laser and re-check the power. If the power reading is still outside of the acceptable range stop analysis and notify the spectroscopist and/or lab manager so that replacement parts can be ordered.
- b. Check laser alignment.

- i. The filters have a larger area than the spot size of the laser beam. However, the alignment of the laser can affect the reflectance and transmittance measurements even when the beam is still on the sampled area of the filters. To properly align the laser, it is best to use the NDM filter which is installed in the sample changer arm.
- ii. Safety and PPE. Before removing any components or making any changes to the HIPS system ensure that you have checked the laser and are sure of the class of laser in use. Currently, the HIPS HeNe laser is a class 3b unit, but this could change if the laser is changed. Make sure you have the proper PPE for the type of laser in use. Eye protection is required when working with the laser in any capacity other than routine HIPS measurement (when the system is closed and no light escapes).
- iii. To align the laser, remove the transmittance detector and plate optics assembly from behind the slide holder. This allows you to see the backside of the NDM filter when the slide changer arm is in the “out” position. Observe the laser light on the NDM filter and adjust the laser mount to center the laser spot on the NDM filter. The laser spot is nearly as large as the NDM filter so centering is fairly easy to determine visually.
- iv. Once aligned, reinstall the plate optics and transmittance detector.
- v. Perform a laser power check and detector registration and verification to ensure the alignment is good.
- vi. A final check of the reanalysis filters will determine, based on passing acceptance, if the alignment change will require a new field blank correction for the reanalysis set. If the reanalysis set requires the field blanks be reanalyzed, then the sample filter field blanks will also have to be reanalyzed to determine new linear regression coefficients, which will then need to be entered into the database. If the reanalysis check does not pass acceptance after laser alignment, notify the spectroscopist and/or laboratory manager.

5. REFERENCES

1. Evaluation of measurement data-Guide to the expression of uncertainty in measurement, 2008. Joint Committee for Guides in Metrology, JCGM 100:2008. www.bipm.org.
2. *UCD SOP #277: Optical Absorbance Analysis*
3. *UCD TI #277B: Performing HIPS Analysis*

Figure 1. Flow diagram of quality control processes and actions taken.

