UCD IMPROVE Technical Information #276C

QA/QC of Analysis of Loaded Filters Using HIPS

Interagency Monitoring of Protected Visual Environments
Air Quality Research Center
University of California, Davis

April 19, 2023
Version 5.6

Prepared By: DocuSigned by: 95E2EA1AFEE441A... Date: 4/19/2023

Reviewed By: DocuSigned by: Jason Giacomo B62B01F81613421... Date: 4/19/2023

Approved By: DocuSigned by: Marcus Langston 0A10CFCF79B0452... Date: 4/19/2023

UCDAVIS
AIR QUALITY RESEARCH CENTER

DOCUMENT HISTORY

Revision	Release Date	Initials	Section/s Modified	Brief Description of Modifications
	05/20/21	SRS	All	Previous anthologized document version separated into individual TIs.
	7/26/2022	LMK	5.1	Added HIPS QC application
	8/18/2022	JG	5.5	Updated laser power parameter and alignment procedure after new fiber optic cable install.
5.6	04/19/2023	JRS, LMK, ML	2, 3, 5	Updated number of verification filters from 15 to 14. Added Sample Replicate definition and description of procedure. Added QC table.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. PURPOSE AND APPLICABILITY

The purpose of this technical information (TI) is to describe the process of performing quality control checks of the transmittance (T) and reflectance (R) values of $PM_{2.5}$ loaded samples using the Hybrid Integrating Plate/Sphere (HIPS) system. This document provides:

- The steps to ensure proper setting of the optical detectors
- Quality control checks of the reanalysis set results
- Review of sample results

2. SUMMARY OF THE METHOD

No standards for light absorption of particulate matter on filter media exist. Therefore, all quality control checks for the HIPS instrument are performed on sampled filters. Reference values for these filters are set based on multiple measurements performed over multiple days. Consistency is paramount when no standards exist to check accuracy. To maintain this consistency the raw detector response to a set of 14 filters is checked to be within ± 3% of the reference values. Then a reanalysis set of filters is measured and calibrated results are checked against reference values. Only after these checks pass all acceptance criteria are samples analyzed on the system. A final review of the sample results is performed to check for instrument drift or individual filter issues prior to finalizing the results.

3. DEFINITIONS

- Field blanks: PTFE filters which 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, $r = -a_1 R/a_0$, 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 are reported.
- Verification filters: a set of 14 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 22 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.
- Sample Replicates: replicate measures of approximately 2%-%55% or more of network samples are made.
- Acceptance limits:
  - Verification filters: analyzed daily during HIPS operation, are determined as ± 3% of the reference values for T and R, except for filter #3, the registration filter, which is ± 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 ≥ 0.90.
  - Reanalysis accuracy: τ must be within ± 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 τ > 0.1 (approximately 5*MDL) must be ≤ 3%.
  - Replicate Analysis: Currently replicate data is being collected to help determine appropriate acceptance criteria. There are no laboratory level acceptance tests for the replicate measurements yet.

4. EQUIPMENT AND SUPPLIES

- HIPS: Hybrid Integrating Plate/Sphere Method for Measuring reflectance and transmittance
- Verification filters
- Reanalysis (RA) filters

- Sample filters; set of IMPROVE samples from a given sampling month to be analyzed through HIPS

5. PROCEDURAL STEPS

Figure 1 below shows the overall HIPS process from start to finish including routine troubleshooting steps. Table 1 contains the routine QC activities to check if HIPS is in a good and stable condition to take measurements and record data.

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

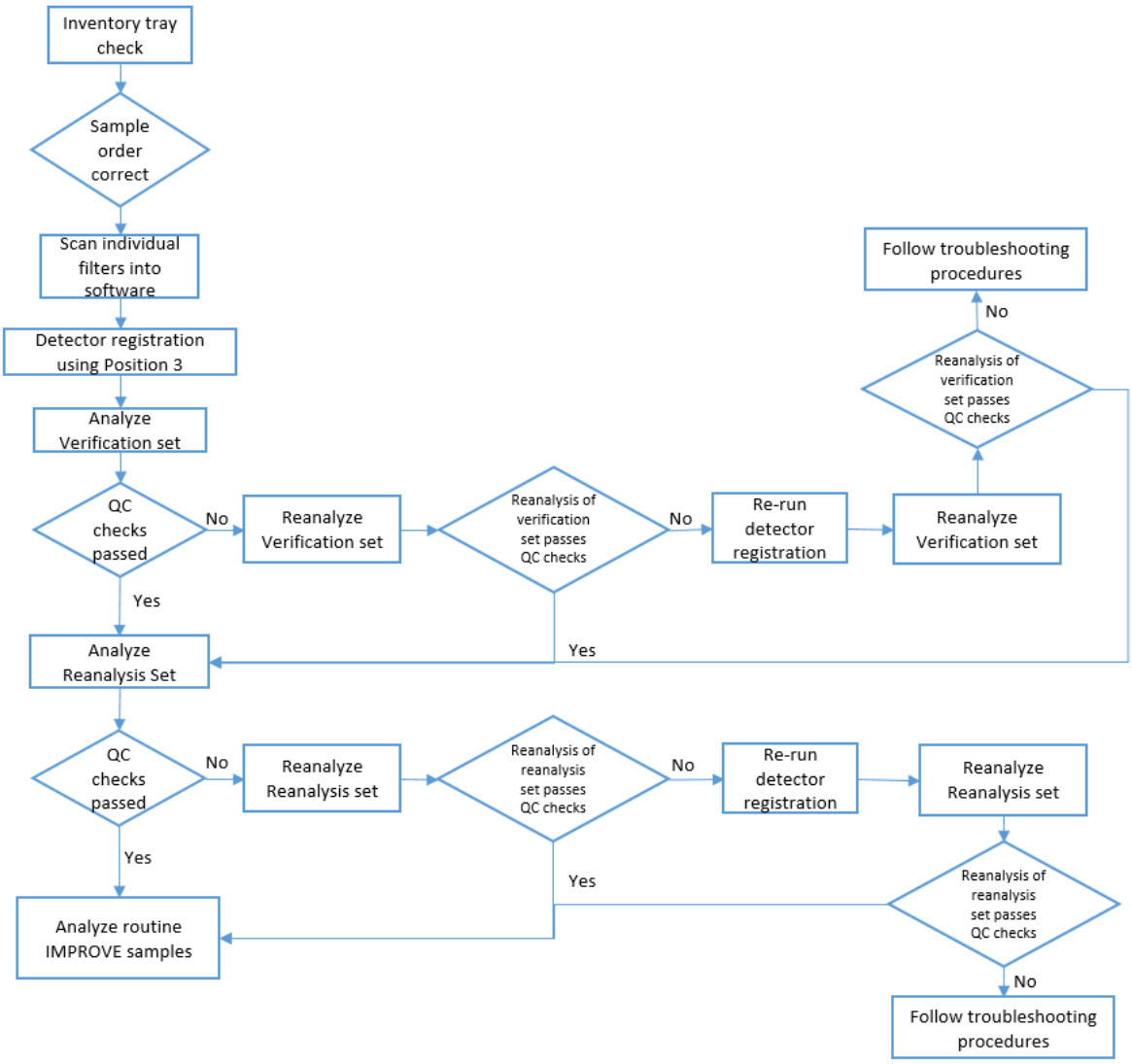

Table 1The routine QC activities, criteria, and corrective actions.

Analysis	**Frequency**	**Criterion**	**Corrective Action**
Verification Set	Daily	Within ± 3 % of their reference values	• Visually inspect filter for damage or contamination. • If no damage is found, rotate filter. • Ensure sample was loaded correctly • Re-register detectors • Reanalysis required
Reanalysis Set	Once at the beginning of analysis and once at the end of total analysis for the day.	Linearity coefficient of determination must be greater than 0.95 and the slope must be within 0.95 and 1.0. Long-term reanalysis acceptable mean z-scores are ≤ 1	• Visually inspect filter for damage or contamination. • If no damage is found, rotate filter. • Ensure sample was loaded correctly • Re-register detectors • Reanalysis required
Registration filter	Once at the beginning of the day, and once every 200 samples, or 5 full trays.	Within ± 1 % of the accepted values	Reanalysis required
Routine Replicates	Once a sample month	TBD	TBD

5.1 Detector Registration Verification

1. To ensure consistency in measurements from day to day, 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. The transmittance and reflectance detectors are set to values of 437 and 332 respectively for this filter.
2. Refer to *UCD IMPROVE TI 276B* 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 reviewed using the HIPS QC shiny app, https://shiny.aqrc.ucdavis.edu/HipsQC/.
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 ± 3%, except position 3 (the registration filter) which must be within ± 1%, of the accepted values..

4. Accepted values for the verification filters were determined as the mean of sixteen measures 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 ± 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 276B. If the registration values are acceptable then continue to the next step.
    ii. Re-measure the verification filter set. If the new values are acceptable then mark the original results in the database as invalid and continue to reanalysis. If the re-measurement fails again, see the troubleshooting section and notify the spectroscopist and/or laboratory manager before proceeding.

5.2 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 276B for specific instructions to measure the reanalysis filters. Results are written to the database following analysis. Results for T and R of the reanalysis filters are reviewed via the HIPS Lab QC shiny app.
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 *UCD IMPROVE SOP #276: Optical Absorption Analysis*.
4. Accuracy check: The τ_{abs} results are then compared to the reference values determined from ten measures 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.

$$U(\tau_{abs}) = k\sqrt{\left(\frac{\partial \tau_{abs}}{\partial r}u(r)\right)^2 + \left(\frac{\partial \tau_{abs}}{\partial t}u(t)\right)^2}$$

$$= k\sqrt{\left(\frac{u(r)}{1-r}\right)^2 + \left(\frac{u(t)}{t}\right)^2} \quad \text{Eq. 1}$$

where,

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

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

$u(r)$ 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 of the intercept and slope in 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 which, in this work, is set to 2, which is approximately 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 an on-going plot. The mean z-score must be ≤ 1 to be acceptable and any sudden jumps in the plotted mean z-score value compared to previous values should 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 the reanalysis set should be reanalyzed. If it continues to fail the check, see the troubleshooting section and notify the spectroscopist 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 or laboratory manager.
    c. If the end-of-day reanalysis QC check fails any test and can't be resolved by reanalyzing the set a second time, then the results for all samples analyzed that day are suspect and should be invalidated. Notify the spectroscopist or laboratory manager. Samples will need to be reanalyzed once the problem is corrected and QC tests pass.

5.3 Sample Check

1. Routine analysis of sample filters is monitored by checking the NDM reference filter values recorded with every sample measurement. The reference T and R values from the NDM filter are exported from the database and plotted along with acceptance limits. The acceptance limits will be automatically calculated as ± 5% of the mean result for the first 200 measures 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 or laboratory manager before proceeding.
2. The registration filter is analyzed after 200 sample filters have run through HIPS analysis. This is done to ensure that the detector registration has not changed. See TI 276B for details. If the registration values are found to be outside of ± 1% of their set values (T = 437, R = 332) then follow the directions in TI 276B and notify the spectroscopist or laboratory manager.

5.4 Replicate Analysis

1) Replicate samples analyses are performed per sampling month. Two full slide trays worth of network samples totaling 80 filters are selected from the sampling month for replicate analysis. Slide trays selected for replicate analysis will exclude monthly field blanks. Replicate analyses are performed following the completion of routine analysis for a sampling month. Once replicate trays have been analyzed, the database QC Code is updated via the IMPROVE webapp from "Valid" to "Routine Replicate".

5.5 Final Check

1. After all analysis for the sampling month is complete and the QC checks have passed, notify the spectroscopist or laboratory manager that the data are ready for review.
2. The spectroscopist or laboratory manager will review all the HIPS data and QC checks and ensure the integrity of the data.

5.6 Troubleshooting

1. Failure of a single verification or reanalysis filter
    a. This section assumes you have checked the registration filter is still within 1% of the set values for T and R.
    b. For any filters which fail acceptance, begin troubleshooting by visually inspecting the filter for any holes, tears, or other defects. If any are found, notify the spectroscopist or lab manager. Analysis can continue as the issue is with the filter and not the instrument. The damaged filter will have to be removed from service.
    c. If no damage or defects are discovered during visual inspection, try rotating the filter slide in the slide tray and measure again.
    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 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 or laboratory manager. Then, proceed to the “Instrument troubleshooting” section below.
    c. In the event that some 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 hold. In this case, the reanalysis field blanks should be re-measured 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. If the NDM reference value drifts outside of the acceptance limits, you should stop analysis of samples.
    b. Take a measure of the registration filter and verify it is within 1% of its set values. Then, take a measure of the NDM (slide arm out) and check if it is within 5% of the mean value calculated for the day. If it is acceptable, then proceed by re-measuring the affected sample filters. Monitor the NDM reference values during re-measurement 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 then.
    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 for that day. Notify the spectroscopist or laboratory manager so they can 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 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 11.8 µ W ± 10%.
        iv. If the power reading from the detector is outside of this range then something in the system has changed. The possibilities are that the laser output power has changed, perhaps due to age or impending failure, an optical element of the integrating plate has changed or has become dirty, or the laser is misaligned. 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 or lab manager.

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.

   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. The HIPS system was upgraded to use a fiber optic cable to connect the laser to the integrating sphere through a laser collimator. These components are mechanically robust against misalignment due to their direct connection to each other. However, it is possible that the integrating sphere or integrating plates have moved slightly in relation to each other. To check this, carefully remove the integrating plate from the sample holder area. With a filter in the measurement position, check that the laser spot is centered on the filter membrane. If not, the integrating sphere mount will need to be adjusted to center it. If it is centered, then reinstall the integrating plate assembly making sure that the lens tube is seated correctly and flush against the sample changer.

   iv. Perform a laser power check and detector registration and verification to ensure the alignment is good.

   v. 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 re-measured, then sample filter field blanks will also have to be re-measured 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 or laboratory manager.

6. REFERENCES

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.

UCD SOP #276: Optical Absorbance Analysis

UCD SOP #276 Technical Instruction – TI 276B: Performing HIPS Analysis