UCD IMPROVE SOP #276 Technical Instruction

TI 276A: Preparation of Filters for HIPS Analysis

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TI 276E: Ingesting HIPS Results to IMPROVE Database

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TI 276A: Preparation of Filters for HIPS Analysis

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1.0 PURPOSE AND APPLICABILITY

This SOP describes the procedure used for preparing filters for HIPS analysis. All routine, valid IMPROVE "A" module filters are prepared for HIPS analysis using the described method.

2.0 SUMMARY OF METHOD

All valid, routine IMPROVE "A" module filters are transferred from Petri dishes or similar containers to 2"x2" slide frames. Slides are stored in trays that house 40 filters (typically ten filters from four sites each tray). Slides are organized alphabetically by site and chronologically by sampling month and year.

3.0 CAUTIONS

Many site codes are similar. Ensure that the identifying information on the container matches the information on the slide before transferring the filter to the slide.

Make sure that the filter is placed in the slide so that the sampled side of the filter is facing away from the labeled slide piece.

Note any mishaps that occur while transferring the filters (such as dropping a filter) on a status adjustment sheet.

Be sure the slide is secured tightly after the filter is transferred.

Make sure that the filters being prepared for HIPS analysis have already been weighed and have undergone XRF analysis.

4.0 EQUIPMENT AND SUPPLIES

- Slide trays containing labeled slides organized by month and site
- Forceps with ceramic tips
- Slide block
- Slide press
- Slide labels
- 2x2 Slides

5.0 PROCEDURE

Filters that are ready for HIPS analysis are in labeled Petri trays that are typically stored in the XRF Lab (Room 116).

The station for transferring filters from Petri dishes to their slide trays is located in Mezz 208. All pertinent equipment and supplies (pre-labeled slide trays, slide blocks, etc.) for transferring filters from Petri dishes to slides are at the station.

Print labels for the sampling month using the templates for "filter slide by month" and "slide tray by month" – found here: U:\IMPROVE_Lab\LASER\Templates\stickers. Also use Reporting Services "Sample Analysis Laser Stickers" to generate the list of sites, FB dates, and sample dates for a given month. (http://cl-sql/Reports/Pages/Folder.aspx?ItemPath=%2fImprove_2.1+Reports%2fXRF+Analysis+Lab&ViewMode=Detail). For further details refer to 5.1 and 5.2.

5.1   Print Filter Slide Labels

1) Follow the link to Reporting Services and select "Sample Analysis Laser Stickers."

2) In the box for "Year" type the four digit number eg. 2017 and for "Month" type the two digit number for the month eg for April is 04. Then click "View Report."

3) Export the file in Microsoft Excel by clicking ⬇️ ▾, from the drop down menu select "Excel".

4) Copy/Paste the sites only to the template "macro_Sticker_updated_20160512".

5) Delete the dates from the FB from column, then type in the dates for the FBs into the correct site. Double/triple check the stickers list.

6) Delete the worksheet "Diez"

7) Open "Stickers Macro"- go to "view," select "Macros" icon open "view Macros"

8) highlight "Stickers_Slide"

9) Click "Run" to run macros

10) Review the stickers and verify all stickers are formatted correctly

11) If stickers are not formatted correctly then manually fix the formatting

12) For the following sites BYIS1, MEVE1, PMRF1, SAMA1, YOSE1, change the "A" to a "5" on the upper left corner only for the second set of slide stickers.

Figure 1. BYIS1 slide stickers fixed for second set.
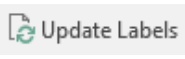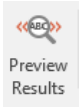
13) Before printing the slide stickers, verify the row high is consistent with the rest of the stickers.

14) After printing the labels, cross off or remove labels for terminal status samples. For filter status review HIPS log file, instructions located in TI276B

15) Individually label the slide, do not label terminal status slides. Place slides into the correct Trays, use an unlabeled slide for terminal status filters. For more information about trays review printing instruction in 5.2.

5.2   Printing Tray Stickers

1) Open the Microsoft Excel workbook "source," located on the U:\IMPROVE_Lab\LASER\Templates\stickers\slide tray by month

2) Open the sheet "START," follow the instructions described in the document.

3) Save and close the workbook after the data has been updated.

4) Open the Microsoft Word document "printout," located in the same folders as the "source" workbook.

5) The message window below will appear, click "Yes" to continue.

Figure 2 Message window to run SQL command.
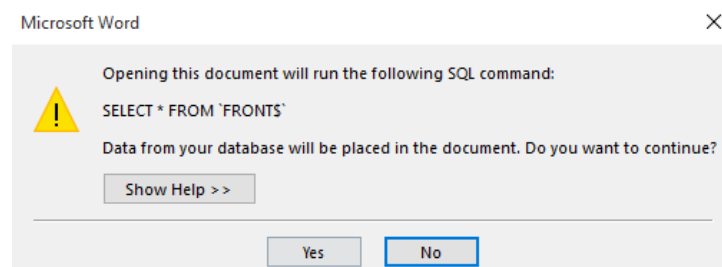
6) From the Mailing menu, select Update Labels, then click Preview Results.

7) Select "Edit Individual Documents" from Finish & Merge submenu. A window box will appear select "All."

8) Review the labels, manually generated Field Blank labels for each months once or twice per year.

9) Place the labels in the printer and select print. The document has custom margins expect a warning for each page.

10) Label the trays in preparation for the labeling of the Filter slides.

5.3   Transfer samples to slides

Prepare the workstation; ensure the correct Slide Trays are on the racks. A technician will bring and stack the petri Trays to be transferred on the desk. Note the Petri trays may have samples from multiple months, only transfer samples from one month, then go back and transfer samples from another month. Place the Petri trays on the counter. Next, remove the Filter Inventory sticker and place on a blank AQRC-IMPROVE (HIPS Analysis) Form, located on the U:\IMPROVE_Lab\LASER\Templates\template status adjustment form (Laser). Inventory the samples in the tray against the Filter Inventory Sticker. If any issues notify the Laboratory manager and/or the laboratory technician.

Transfer samples from the lowest set number, with the lowest tray number. Select the first Petri dish from the number one position (IDX#1 on the Filter Inventory). Note the enclosed sample's

site and sampling date (sampleIdentity on the Filter Inventory). The information is printed on the label on top of the Petri dish. Ensure the information on the label matches the information on the Filter Inventory.

Locate the corresponding slide in the proper slide tray. Each slide tray is organized by sampling month, then by site in alphabetical order. There are slides for four sites in each tray. Typically, each site will have ten slides in the tray; for shorter months with fewer sampling dates there may be nine slides per site and for longer months with more sampling dates there may be eleven slides per site. Note for sampling months with eleven sample dates, the samples from the eleventh sampling date are placed in a separate tray and are organized alphabetically.

Be cautious when locating the proper slide. Many IMPROVE site codes are similar site names eg. BADL1 and BALD1 or SAGA1, SAGO1, and SAGU1, so it is important to make sure that the filter is transferred to the correct slide. Note; for terminal status filters an unlabeled slides serves as placeholders. Do not place any filters in these slides.

Mount the slide on the slide press, label-side down. Open the Petri dish and pick up the filter using ceramic-tipped forceps. Center the Teflon® filter, sample-side faced up, on the slide. Now, place an unlabeled slide frame on top to sandwich the filter and snap it into place with the slide press.

Rotate the arm to lower the press. Press the slides so they secure tightly, but use as little force as possible to do so. Slide the sample sandwich through the slot at the bottom of the press, if the slides fits through without issues then continue. If the slide does not pass through the slot then remove the unlabeled slide and select a different slide.

Handling the slides by the edges, remove the slide from the press and place it back into its original position in the slide tray. The empty Petri dish should be placed back in the tray in the order it was removed from.

Repeat these steps for each filter in the tray. Handle only one filter, Petri dish, and slide at a time. If selecting a different slide tray, close the previous slide tray and return it to its original location.

When the tray is complete, visually check that all petris are empty. Store empty Petri trays in a box for later cleaning and reuse.

5.4   Field Blanks

About 40 samples of each month will have field blanks assigned. Field blanks can be identified by a Petri label with a designation of "FB-A" along with site and sample date. These field blanks are placed in a separate pre-labeled tray grouped by the month and year of the sample. Match field blanks to their corresponding slides and mount them as described previously. Place them in their correct positions in the slide tray.

TI 276B: HIPS Logs and Tray Check

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1.0 PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the procedures used to create log files for running HIPS and for performing tray checks of the filters before going through HIPS analysis.

2.0 SUMMARY OF THE METHOD

Log files for running HIPS analysis consist of an excel file for IMPROVE filters and field blanks for a given sampling month. These files are primarily generated through Reporting Services using "HIPS Analysis By Month", but they may also be generated manually through Microsoft Excel. Filters are then double-checked to confirm that they are in the proper order and that terminal filters have been removed.

3.0 CAUTIONS

Pay close attention when entering information into any macro. The information has to be in the exact format as the example shown in the input box. If an incorrect format is entered, the macro will not work correctly and an error will occur. If an error does occur, close the files and start over.

4.0 PROCEDURE

4.1 Creating Log Files Using Reporting Services

1) Go to Reporting Services and select "HIPS Analysis By Month" (http://cl-sql/Reports/Pages/Folder.aspx?ItemPath=%2fImprove_2.1+Reports%2fXRF+Analysis+Lab&ViewMode=Detail). Enter the desired month and year and generate the report.

2) Export the file as excel and save in the respective folder under U:\IMPROVE_Lab\LASER\000-WorkingSpreadsheet-000.

3) Sort and arrange the order position for sites with 1 and 5 positions so that the 5th positions appear after the 1st position and in chronological order. Before sorting, cut the field blank rows and paste to a new sheet. Then Sort the "SITE" column in alphabetical order from A to Z. Then cut and paste the Field blanks to the bottom of the list. Delete the extra sheet.

4) Make a copy of the 'template_laser analysis" in U:\IMPROVE_Lab\LASER\Templates. Place in the respective folder and rename it for the given month and year with "copy" at the end.

5) Copy the status, site names, and dates columns from the file generated by Reporting Services and paste into the template file. Then add a HOLE row to the first row and every 200 samples. Manually change the status for field blanks to FB.

6) The template file will be used to capture data from HIPS with M40x tool.

4.2 HIPS Log File Check

Once the set of files for the sampling month are generated, the checks below are done to ensure that the HIPS logs have accurate references:

a) Make sure terminal statuses are in red font.

b) Make sure sites are in alphabetical order.

c) Make sure dates are in numerical order.

d) Make sure all the Field Blanks are alphabetically arranged at the end of the list.

4.3 Tray Check Prior to HIPS Analysis

Using the log files as a guide, do a quick check of the filters that will be going through laser analysis. Confirm the slides in each tray match up to the log file. After verification that all slides are in their correct positions, the filters are ready for HIPS analysis.

Some discrepancies that one may encounter in tray check are listed below:

a) <u>Sample Swaps:</u> In any case a swap is suspected, reweighing(s) is/are performed to check sample identity. Follow-up reweighing(s) may also be performed (samples from the same sampling month, samples from the same XRF tray file, etc.) to aid in identifying the anomalous sample.

b) <u>Missing Sample:</u> In the event a sample is missing in the slide tray, an inventory check is performed by checking the database. If the sample does not have a terminal status in the database, weights are checked to see if the sample was placed into special tray due to unacceptable status before or after the filter sets were prepared for HIPS analysis (i.e. usually damaged filter).

TI 276C: Performing HIPS Analysis

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1.0 PURPOSE AND APPLICABILITY

The purpose of this standard operating procedure is to describe the process of performing light absorption analysis on routine IMPROVE samples and field blanks with the Hybrid Integrating Plate/Sphere System.

2.0 SUMMARY OF THE METHOD

The HIPS system is warmed up overnight before being used. A calibration verification is performed using a set of 15 selected IMPROVE samples serving as standards. In addition, reanalysis of a selected set of previously analyzed IMPROVE filters is done to monitor system stability. After the standards and reanalysis set has been measured and it has been ensured that the results meet designated criteria, one sampling month's-worth of IMPROVE filters are then

analyzed. This task can take approximately 2-3 days. An automation macro is used to record the data for reanalysis and routine IMPROVE filters.

3.0 PERSONNEL QUALIFICATIONS

A trained laboratory technician, under the supervision of the spectroscopist and/or the laboratory manager, performs all analyses utilizing the HIPS system, including calibration verifications, adjustments (if necessary), reanalysis and analysis of routine IMPROVE samples.

4.0 CAUTIONS

Make sure that the correct slide tray is being loaded for analysis. Loading the wrong tray will cause the recorded data to be incorrect.

Confirm that the correct macro is being used and that the switch is in the proper orientation for reanalysis and for routine IMPROVE samples.

5.0 EQUIPMENT AND SUPPLIES

The following equipment and supplies are used for HIPS analysis:

- Hybrid Integrating Plate/Sphere System (HIPS)
- Prepared HIPS log files for the sampling month to be analyzed
- Standards set
- Reanalysis set
- Slides with IMPROVE filters
- Computer connected to HIPS

6.0 PROCEDURE

6.1 Preparation

1) Turn on the HIPS system at least 12-24 hours prior to intended use.
2) Before starting analysis, make sure that the air compressor system is functional. In the current set-up (at the time this SOP was written), the air compressor system is located in the Chemistry Laboratory in Mezzanine 203 of Jungerman Hall.

6.2. Logging into the HIPS Server

1) The current server for HIPS is the newer CNL server. All programs and applications on this server are current versions. Specifically, the server used for HIPS has Microsoft Excel 2010, so HIPS log files are saved as ".xlsm."

a. The username for the HIPS server is: <u>ou\cl-hips</u>. This is not case sensitive.

b. The password is <u>Laserh1pster</u>. This *is* case sensitive.

6.3 Calibration Verification and Adjustments

1) Go to U:\IMPROVE_Lab\LASER\Standards and open the document called "laser_standards_date.xlsx." Place the current date in the next available cell in column A of the spreadsheet. Record all reflectance (R) and transmittance (T) data taken during standards for the day in this row.

2) Set the Control Box Mode switch to Manual.

3) Retrieve the standards slide tray and place it in the instrument. The current tray (at the time this SOP was written) is labeled "Laser Standards, December 2011."

4) Using the current tray, calibrate with position 3. Set the Reflectance to 332 (read from Labsphere radiometer) and Transmittance to 437 (read from Oriel Detection System). In the current standards tray (at the time this SOP was written) the sample in position 3 is ACAD1 07/07/10.

5) Go back to position 1 and record the values of positions 1 and 2 in the spreadsheet. If by the time position 3 is analyzed again and the R and T values are *not* within ±1% of 332 and 437 respectively, return to step 4 and repeat until the values are correct for position 3.

6) Continue with all positions until finished with the tray.

7) Once finished, record the measurement for R and T from the Neutral Density Material (NDM) in the Rref and Tref columns. These Rref and Tref values are what the reflectance and transmittance values are when no tray is loaded in the arm and the NDM is exposed to the laser beam.

8) Check the integrity of the data by looking at the absorbance spreadsheet "b" and the graphs on the subsequent spreadsheets that will automatically be generated. Make sure all the values are within the set criterion. For details about the criterion for the standards set, refer to TI 276D, "Quality Assurance/Quality Check of PM$_{2.5}$ Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption."

9) When finished, save and close the spreadsheet. This same spreadsheet will be used for every calibration, with new values appended each time, until a new set of standards is implemented.

6.4 Reanalysis

1) In U:\IMPROVE_Lab\LASER\Templates, open the document named "template_ReAnalysis_20160818.xlsm." Enable macros by pressing "Enable content" if prompted. The column labels "Day 1," "Day 2," and "Day 3" refer to the calendar dates on which the reanalysis data is collected before running routine IMPROVE samples.

2) After opening, rename the file to represent the data set that is later going to be analyzed. The format to follow is "Month Year Reanalysis.xlsm." For example, if the filters that are going to be analyzed were sampled during January 2012, the file name would be "January 2012 Reanalysis.xlsm." Save it in a folder named by the month and the year. The folder format is "NumberofMonth Month Year." For instance, the above example would have a folder named, "01 January 2012." These folders should also contain the prepared HIPS log files.

3) To prepare this spreadsheet for the "Log Once" macro, go to U:\IMPROVE_Lab\LASER\M401_Automatic and open the file Log_Once_Template.xlsm. Make sure to enable macros by pressing "Enable content" if prompted.

4) Press ALT+F11. A Visual Basic Application will open and a window with lines of code will appear. Copy all of this code and then close the file.

5) Go back to the reanalysis spreadsheet and press ALT+F11.

6) On the left-hand side, in the "Project-VBA Project" box, double-click on the option labeled "This Workbook," which should be in the drop-down menu for the folder entitled "Microsoft Excel Objects." When "This Workbook" is double-clicked, an empty window should appear.

7) Paste the lines of code into the empty window. Save the application. Then, close the application by going to the "File" menu and choosing "Close and return to Microsoft Excel."

8) In U:\IMPROVE_Lab\LASER\M401_Automatic, open the file M40xVB41_Log_Once.xlsm. Enable macros by pressing the "Enable content" button if prompted.

9) In the top menu bar on the far right, click on M40x Tools, then Connect.

10) Wait until "Ready" is registered on the bottom left of the Excel file.

11) Return to the Reanalysis workbook and make sure that the correct day has the proper date filled in. Then, double-click on the cell data should be placed in first. Also confirm the mouse pointer is in the cell area of the Excel file, but not on column F. It is safest to move it to the right-hand side of the screen.

12) With the control box switch set to Manual mode, load the reanalysis tray into the system and set it for position 1. Make sure to use the tray forward button to align the sample. Note that the tray advance button must be used while the mode switch is set to manual mode, otherwise the slide arm will run into the tray. The current tray (as of the time of this SOP) is labeled "Laser Reanalysis, December 2011."

Figure 1. Control box layout.
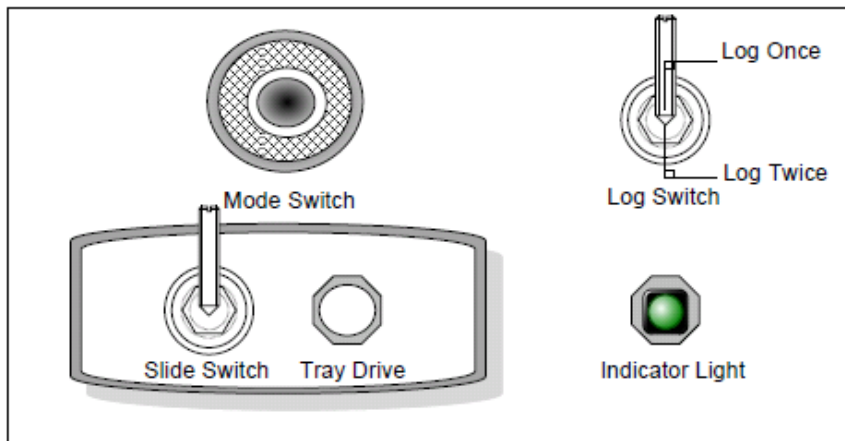
13) Next, make sure the Log switch is set to Log Once and change the mode from Manual to Auto.

14) Press the big green button to start analyzing.

15) As the tray is analyzing, make sure that the data is filled in each cell in the proper order and that the values make sense for the current filter being analyzed.

16) Switch the mode switch to single cycle once the last data point has been collected to stop the Auto cycle.

17) When the reanalysis tray is complete, check the integrity of the data by looking at the automatically generated graphs in the subsequent spreadsheets. For details about the criterion for the reanalysis set, refer to TI 276D.

18) When finished, go back to the M40x file and disconnect from the macro using the M40x Tools drop-down menu. Then, close the M40x file.

19) In the Reanalysis workbook, press ALT+F11 to get back to the Visual Basic Application. Delete the lines of code that were pasted in the window earlier. Then, save and close both the application and the worksheet.

6.5 IMPROVE Samples

1) IMPROVE samples are run in much the same way as reanalysis filters except with a few key differences:

    a) Use the prepared HIPS log files that were created for the IMPROVE samples and field blanks. If there is no prepared worksheet, there are instructions for creating those files in U:\IMPROVE_Lab\LASER\IMPROVE Laser SOPs.

    b) Instead of copying code from the file Log_Once_Template.xlsm into the Log workbook, copy and use the code from the file Log_Twice_Template.xlsm.

    c) Instead of using the macro from M40xVB41_Log_Once.xlsm, use the macro from M40xVB41_Log_Twice.xlsm. When acquiring data with this template, always make sure that the "active cell" is the cell where the sample's T value should be written to. The sample's R value will be written to the right of the T measurement.

    d) The Log switch should be set to Log Twice. This enables HIPS to take a reading of the NDM between each filter in order to confirm the stability of the system.

    e) Before analyzing a tray, make sure the contents have been tray-checked and that the slides in the tray match the order of the log file list.

    f) When a tray is finished, simply load the next tray and press the green button to continue. Keep an eye on the R and T measurements taken from the NDM. Note that the R value from the NDM can drift about 20 points, so the transmittance value is a more accurate measure of the system's stability.

    g) If the system jams, just give the slide arm a gentle push or pull. The system should continue on as if nothing happened. Measurements from the NDM may fluctuate, but do not do anything about this unless both the R and T has changed significantly and are not within + 5% of average from the first 200 measurements of the NDM. For details, refer to TI 276D.

    h) Every five trays, readjust the HIPS system using the standard in position 3 from the standards tray by setting the R and T values to 332 and 437 respectively. After, take T and R measurements from the instruments without a slide. A user can do this by turning the Mode Switch from Auto to Single Cycle. Then, press the big green button to take a reading.

Remember to turn the mode switch back to Auto and continue analyzing samples.

i) Follow the same procedure for field blanks, making sure to use the prepared Excel file for field blanks.

j) At the end of all analyses for the month, turn off the HIPS system.

k) If new tabs were created in the log workbook for routine IMPROVE filters or for 11th sample dates, make sure to recombine those data with the data in the first tab so that everything is in the same place. Make sure to sort by date and site.

7.0 REFERENCES

TI 276D, "Quality Assurance/Quality Check of $PM_{2.5}$ Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption."

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

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1.0 PURPOSE AND APPLICABILITY

The purpose of this technical document is to describe the process of measuring transmittance (T) and reflectance (R) values of $PM_{2.5}$ loaded samples using the Hybrid Integrating Plate/Sphere (HIPS) system. From the acquired T and R values, a calculated value for light absorption (b) is provided. This document provides:

   • The necessary steps to assure quality measurements of transmittance (T) and reflectance (R) values and calculated absorption (b) value.

   • Instructions on monitoring of the instrumental drift.

2.0 DEFINITIONS

   • Reference Values of Standards: pre-determined T, R and calculated b values based off previous laser analysis of the current standards set.

   • Assigned True Values of Reanalysis (RA) Set: pre-determined T, R and calculated b values based off previous laser analysis of the current reanalysis set.

   • Current Values: Any new T, R and calculated b values acquired from the instrument.

3.0 EQUIPMENT AND SUPPLIES

   • HIPS: Hybrid Integrating Plate/Sphere Method for Measuring Light Absorption

   • Standards set: 15 samples from the IMPROVE July 2010 sampling month that is currently used to calibrate the instrument.

   • Reanalysis (RA) set: Set of 25 samples from the IMPROVE June 2010 sampling month that is currently used to establish instrumental stability.

   • Sample set: Set of IMPROVE samples from a given sampling month that is to be analyzed through HIPS.

   • Reserve standards set: Set of 25 samples from the IMPROVE November 2011 sampling month that is kept on reserve in case samples in the standards set require replacement.

   • Reserve reanalysis set: Set of 25 samples from the IMPROVE December 2011 sampling month that is kept on reserve in case samples in the reanalysis set require replacement.

4.0 PROCEDURE

4.1 Initial Instrumental Calibration

An initial calibration of the system was performed during its assembly using a 6" research model integrating sphere (Labsphere). The initial T and R values were obtained using NIST standards. For specific instructions on how the system was calibrated, refer to SOP 276, "Optical Absorbance Analysis."

4.2 Selected Standards Set

Fifteen IMPROVE $PM_{2.5}$ samples collected in the IMPROVE network during July 2010, listed in Table 1 below, are currently utilized in instrument calibration verifications and instrument adjustments. The standards were selected ensuring that T, R and calculated b values represent the range of T, R and calculated b values for all IMPROVE samples. Standards are analyzed on the system regularly, prior to the analysis of network samples. The position 3 standard (reference sample, ACAD1 7/7/2010*) is currently used to adjust the system every 200 filters thereafter, or when the acceptance criterion is not met.

Table 1. Standards set.

List of Standards (updated 2/13/2013)			
POS 01	ACAD1	7/1/2010	
POS 02	ACAD1	7/4/2010	
POS 03	**ACAD1**	**7/7/2010**	*
POS 04	ACAD1	7/10/2010	
POS 05	ACAD1	7/13/2010	
POS 06	CRLA1	7/4/2010	
POS 07	CRLA1	7/7/2010	
POS 08	CRLA1	7/10/2010	
POS 09	CRLA1	7/13/2010	
POS 10	CRLA1	7/16/2010	
POS 11	SHEN1	7/1/2010	
POS 12	SHEN1	7/4/2010	
POS 13	SHEN1	7/7/2010	
POS 14	SHEN1	7/10/2010	
POS 15	SHEN1	7/13/2010	

4.3 Calibration Verification for Standards Set

1) The standards set are analyzed at the beginning of each day that laser analysis is performed. For specific instructions on how to run the standards set, refer to TI276C, "Performing HIPS Analysis." Worksheets related to the routine acceptance of the standard set are located in U:\IMPROVE_Lab\Laser\ Standards\laser_standards.xlsx. Values recorded for the run in the standards set are added to the worksheet tab labeled "DataSheet". Graphs pertaining to the primary and secondary checks should update automatically once a new data set for a new calibration date is added.

2) One day before laser analysis is set to occur, the laser system is turned on in order to warm up the system. After ensuring that the sample set of filters that needs to be analyzed has been visually checked and is in their correct location in the slide trays, the radiometer and the detection system are set to specific reference values based on the position 3 standard (reference sample, ACAD1 07/07/10). Transmittance (T) is set to 437 and reflectance (R) is set to 332. After the designated transmittance and reflectance values have been set, the standards set is analyzed in consecutive order. If T and R values for the position 3 standard

are not within ±1% of 437 and 332 respectively, the meters are re-adjusted and the set of standards is reanalyzed.

3) Primary Checks:

- The graphs of "T Graph", "R Graph" and "b graph" are visually checked to ensure that they do not show any sudden and/or significant fluctuations.

- Obtained values should be within ± 3% of independent T and R values and within ± 3% of calculated b values. The upper and lower limits of calculated b were assigned using the limits ± 3% T and R values. As previously mentioned, position 3 values use ± 1% acceptance limits. These limits can be checked by looking at the worksheet tabs named "transmittance (3%check)", "reflectance (3%check)" and "calculated_b (3%check)".

4) Secondary Checks:

- Two methods are used to check the integrity of the values for the standards. The coefficient of determination between the reference and current values should be at least 0.95 for each independent variable (T, R and calculated b). In addition, the differences between reference and current values should be within their expanded uncertainties (coverage factor 2), estimated through the ISO Guide to the Expression of Uncertainty in Measurement (GUM) Method (2008). By ensuring this, the reference values and current values are determined to be statistically the same.

5) If one of the standards in the set fails to meet the primary and secondary criteria, the said standard(s) is reanalyzed. After eight failed attempts to meet the criteria, the said standard is replaced with a sample that has similar T, R and calculated b values from the reserve standards set. The eight attempts should be performed over at least two different days in order to account for instrumental stability and possible environmental interferences.

4.4 Selected Reanalysis Set

The reanalysis set is comprised of 25 IMPROVE samples from the June 2010 sampling month (inventory below) to ensure that T, R and calculated b values represent the array of T, R and calculated b values for IMPROVE samples.

Table 2. Reanalysis set list.

Reanalysis Set List		
RA 01	PASA1	6/4/2010
RA 02	PASA1	6/7/2010
RA 03	PASA1	6/10/2010
RA 04	PASA1	6/13/2010
RA 05	PASA1	6/16/2010
RA 06	PASA1	6/19/2010
RA 07	PASA1	6/22/2010
RA 08	PEFO1	6/1/2010
RA 09	PEFO1	6/4/2010

RA 10	PEFO1	6/10/2010
RA 11	PEFO1	6/13/2010
RA 12	PEFO1	6/16/2010
RA 13	PENO1	6/1/2010
RA 14	PENO1	6/4/2010
RA 15	PENO1	6/7/2010
RA 16	PENO1	6/10/2010
RA 17	PENO1	6/13/2010
RA 18	PENO1	6/16/2010
RA 19	PENO1	6/19/2010
RA 20	PHOE1	6/1/2010
RA 21	PHOE1	6/4/2010
RA 22	PHOE1	6/7/2010
RA 23	PHOE1	6/10/2010
RA 24	PHOE1	6/16/2010
RA 25	PHOE1	6/19/2010

4.5 Instrumental Stability Check with Reanalysis Set

1) The reanalysis set is run after the standards set on days that laser analysis occurs. Spreadsheets for the reanalysis set are located in every folder, organized monthly. Previous years are compiled in one folder under U:\IMPROVE_Lab \Laser\LaserData, while the current analysis year is located in U:\IMPROVE_Lab\Laser.

2) Values are taken for each sample in the reanalysis set using an automated macro named M401X_Automatic, which is located in U:\IMPROVE_Lab\Laser. The reanalysis set results are added to the worksheet, "Data for MMM YYY," with "MMM" and "YYY" pertaining to the month and year of the sample set that is currently being analyzed. For specific instructions on how to run the reanalysis set, refer to TI276C, "Performing HIPS Analysis."

3) Primary Checks:

   - The coefficient of determination between the assigned true 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).

   - Upper and lower acceptance limits of the regression lines between the assigned reference values for each sample in the reanalysis set and current values obtained are calculated by adding and subtracting the "critical value", which is twice the maximum standard deviation of previous results (n=8) of each reanalysis sample.

4) Secondary Checks:

   - Two methods are used to check the integrity of the values of the reanalysis sets. Orthogonal regression between the assigned reference values with the average of the current reanalysis values for each variable (T, R and calculated b) was established to ensure that the slope is statistically significant, as it is

higher than twice its accompanying standard deviation. In addition, slope should be within 0.95 and 1.05. The intercept should be statistically insignificant as it is less than twice its accompanying standard deviation, which can be accepted as zero. In addition, the differences between assigned reference and current values should be within their expanded uncertainties (coverage factor 2), estimated thru the GUM Method. By ensuring this, the assigned true values and current values can be accepted to be statistically the same.

5) If at any point the reanalysis samples do not meet the current acceptance limits, possibly due to damage, the sample(s) in question is excluded from the current reanalysis set. Once the number of samples in the current reanalysis set falls below twenty (threshold for ~1% of IMPROVE samples in one sampling month), the sample(s) is replaced with one from the reserve reanalysis set (samples from the December 2011 sampling month). New assigned reference values shall be implemented reflecting the change.

4.6 Additional Quality Control Checks

1) For regular laser analysis of sample sets, a neutral density material (NDM) is exposed to the laser beam right before the sample is analyzed and the T and R values are registered. The average of the first 200 measurements of this NDM (the meters are recalibrated using the position 3 filter after 200 filters have been analyzed) is used as a reference value. Each of the NDM measurements should fall within ± 5% of the assigned reference value. For specific instructions on how to analyze sample sets, refer to TI276C, "Performing HIPS Analysis."

2) If one of the individual T and R values of the said NDM exceeds the acceptance limits, the system is recalibrated using position 3 of the standards tray and the current active tray in the sample set is re-run.

3) T and R values for both the NDM and sample set are reported in the spreadsheets. Regular sample sets (samples with status as NM, QD, or any other statuses) and field blank (FB) sample sets are stored in separate workbooks, both of which are located in the same folder pertaining to the sampling month of the filters. After all samples have been analyzed and data has been checked to meet the designated criteria, the lab manager is informed and the data is exported to the IMPROVE SQL Database for further checks and validation.

4.7 Generating Quality Control Graphs for Standards Set Using R

1) Update the "Standards Master Results" CSV file located in the "Standards" folder U:\IMPROVE_Lab \Laser\LaserData by adding the latest raw data from the "laser_standards" excel file. Save the file.

2) Open the R script titled "HIPS Standards" located in the "Standards" folder U:\IMPROVE_Lab \Laser\LaserData. Run all the lines by selecting all and pressing CTRL+ENTER. This should generate all the graphs for the Standards

set. Review all the graphs and check that they meet the criteria stated in section 4.3.

4.8 Generating Quality Control Graphs for Reanalysis Set Using R

1) Update the "Reanalysis" CSV file located in U:\IMPROVE_Lab\LASER\Templates\Reanalysis data by copying the latest raw data from the last month's reanalysis excel file found in its respective folder in U:\IMPROVE_Lab\LASER\LaserData. Save the file.

2) Open the R script titled "HIPS Reanalysis" located U:\IMPROVE_Lab\LASER\Templates\Reanalysis data. Review the script and change the export file name for each analysis day where prompted by the comments. File name format is "Reanalysis_yyyymmdd.csv". The date is respective to each date the reanalysis is run. Run all the lines by selecting all and pressing CTRL+ENTER. The script will export a file with the statistics analysis for each day into the "Reanalysis data" folder and generate the QC graphs. Move the files to the appropriate folder in U:\IMPROVE_Lab\LASER\LaserData.

3) Review the data tables in the exported files and review all the graphs. They must meet the criteria stated in section 4.5.

5.0 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. SOP 276, "Optical Absorbance Analysis."

3. TI 276C, "Performing HIPS Analysis."

Figure 3. Flow diagram of quality control processes and actions taken.
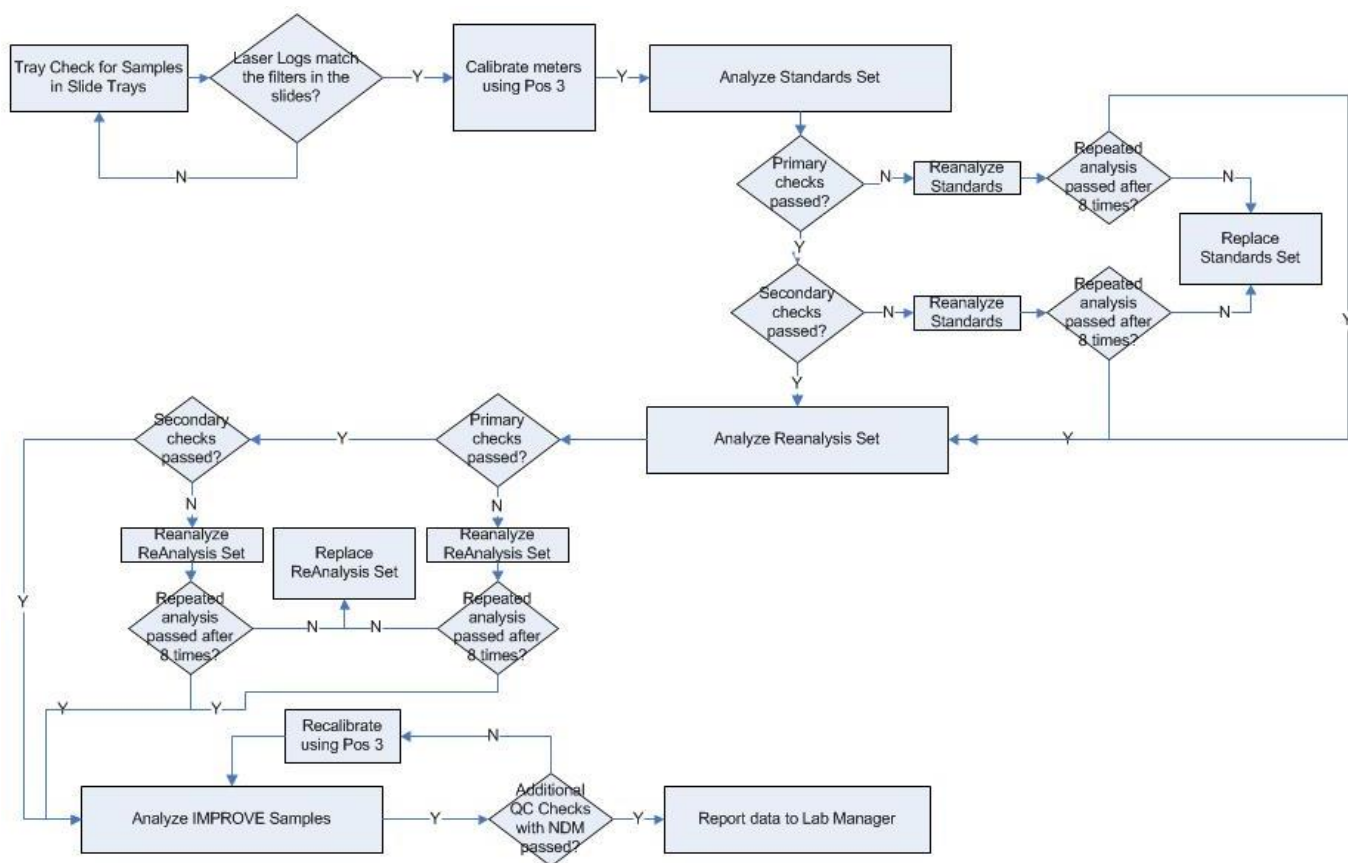
TI 276E: Ingesting HIPS Results to IMPROVE Database

TABLE OF CONTENTS

1.0 PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the procedures used for ingesting HIPS results into the IMPROVE database.

2.0 SUMMARY OF METHOD

Completion of HIPS analysis results in a macro excel file for IMPROVE filters and field blanks for a given sampling month. Relevant data is then transferred from this excel file to the original file generated through Reporting Services. The file is reviewed to verify only data collected from valid samples is included. Once this verification is complete the excel file is saved as a .csv file for ingestion.

3.0 CAUTIONS

Pay close attention when copying data from macro excel file to file generated through the Reporting Services website to ensure only relevant data is included.

4.0 PROCEDURE

1) In the excel file used to record HIPS data called "month year A copy", filter and remove the HOLE results.

2) Copy the columns for T1, R1, INNAME, INDATE, INTIME1, T REFERENCE, R REFERENCE, INNAME2, INDATE2, and INTIME2 into the "month year A" excel file generated by Reporting Services.

3) Filter the Status to only show terminal status filters and delete the results – those are not needed for the database. Clear the filters and save as a .csv file.

4) On the webapp (http://webapp.improve.crocker.ucdavis.edu/) go to "Analysis Data" then "HIPS".

5) Click on the button "Upload Data" and select the .csv file and "Continue".

6) Click "Submit" and then the file is ingested.