UCD IMPROVE SOP #301 Technical Instruction

TI 301A: LN2 Fills and Detector Calibration
TI 301B: Tray File Web Creation
TI 301C: Sample Changes for 8-Position Trays
TI 301D: QA/QC of XRF Performance
TI 301E: Level 1 Validation of Monthly XRF Data

Interagency Monitoring of Protected Visual Environments
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University of California, Davis

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Updated By: Sinan Yatkin Date: 11/1/2017

Approved By: Krystyna Trzepla Date: 12/14/2017

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AIR QUALITY RESEARCH CENTER

TI 301A: LN2 Fills and Detector Calibrations

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1.0 PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the procedure used for the liquid nitrogen (LN2) fill, liquid nitrogen calibration, and detector calibration for the Epsilon 5 instruments.

2.0 SUMMARY OF THE METHOD

The Epsilon 5 instruments use liquid nitrogen to cool the PAN-32 Ge X-Ray Detector. Liquid nitrogen fills for each Epsilon are performed on a weekly basis. The liquid nitrogen level is calibrated automatically. Several hours after the LN2 fill is completed, detector calibration is performed for each instrument.

3.0 SAFETY

Liquid nitrogen must be handled with care in ventilated rooms. Wear a face shield or safety glasses, safety gloves, and a laboratory coat when performing liquid nitrogen fills. For more information, see section 3.3.3, “Liquid Nitrogen Handling,” in the Epsilon 5 EDXRF

Spectrometer System User's Guide, in addition to SOP 301, Attachment 1 on liquid nitrogen safety.

4.0 PERSONNEL QUALIFICATIONS

Only trained lab personnel designated by the laboratory manager may perform liquid nitrogen fills. A course offered on the UC Davis campus, "Safe Use of Cryogenic Liquids," is recommended (http://safetyservices.ucdavis.edu/tr/cd/suoclcd).

5.0 EQUIPMENT AND SUPPLIES

- Liquid nitrogen tank
- Liquid nitrogen tubing
- Adapter
- Timer
- Safety glasses/face shield
- Cryogenic Safety gloves
- Laboratory coat

6.0 PROCEDURE

6.1 Epsilon 5 LN2 Fill

The detector in the Epsilon 5 should be filled on a weekly basis by staff that has been fully trained in the safety hazards of working with liquid nitrogen.

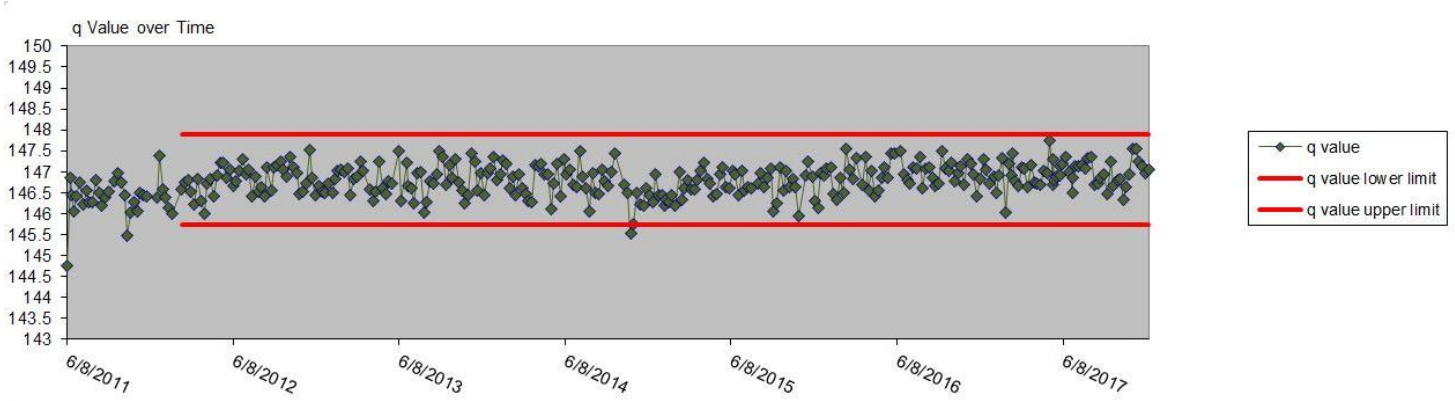
1. The Epsilon 5 has several potential "detector states" that are displayed on the Maintenance screen (circled in blue in Figure 1). These detector states include Pre-Operational, Operational, Long Grace, Short Grace, Filling Allowed, Cooling, and Forced Heat-Up. Ensure that the detector state is not in Forced Heat-Up prior to filling the detector with liquid nitrogen. Check this by clicking on the picture of the liquid nitrogen dewar (circled in red in Figure 1).
2. Open the LN2 fill access door on the right-hand side of the Epsilon 5.
3. Connect the liquid nitrogen tubing to the adapter.
4. Connect the tubing to the LN tank then carefully insert the adapter into the Epsilon 5 dewar.
5. Slowly open the valve on the LN tank while ensuring that the line from the LN tank into the detector fill tube does not come apart. In addition, start the timer at the same time the valve to the LN tank is open.
6. Note the time required to fill the detector and the temperature of the cabinet in the corresponding log book. Also create a new entry with the same information in the Microsoft Access log on the desktop.

6.2 Epsilon 5 Detector Calibration

Before starting the detector calibration, abort analysis. No sample can be running during detector calibration, as the Tungsten (W) underside of the vacuum seal is utilized to perform the measurements.

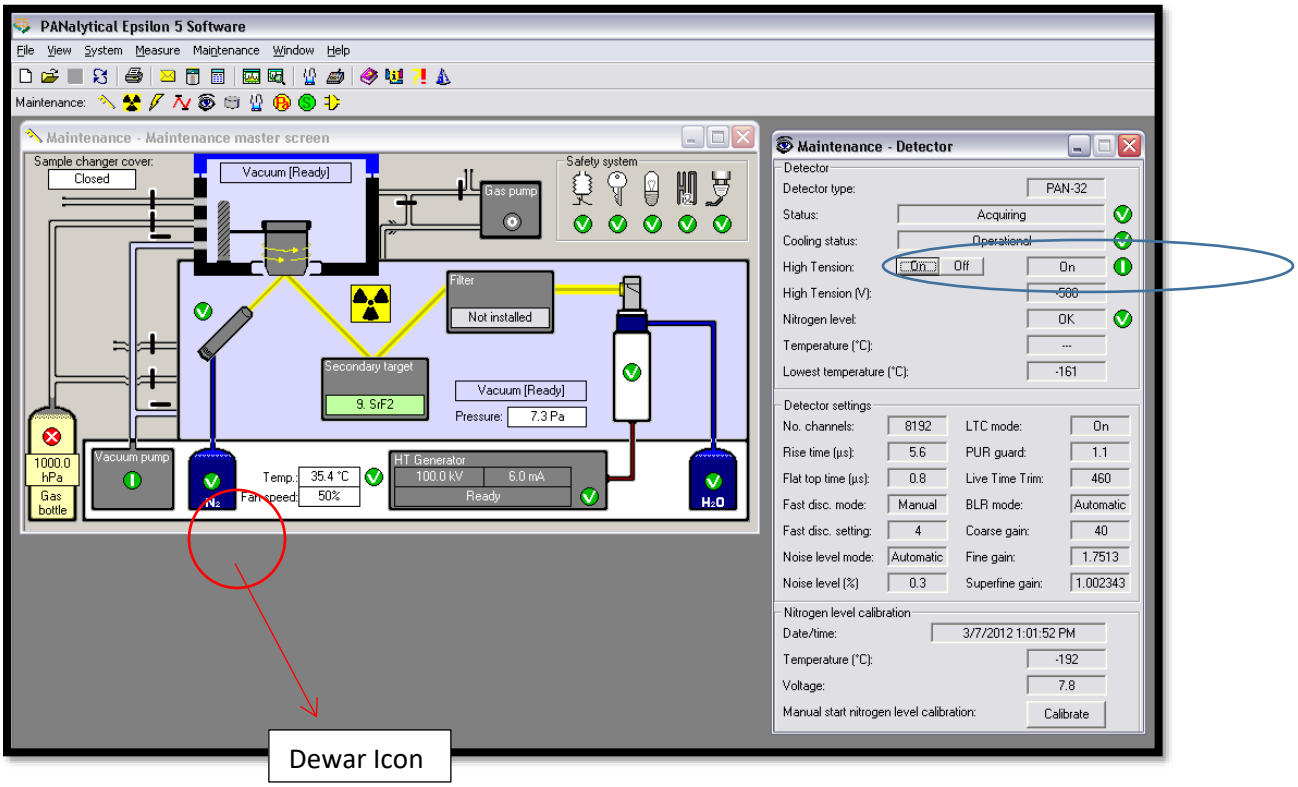
1. Click on the "System" drop-down menu, then "Detector Calibration."
2. Select, "Calibrate All."
3. When both the detector calibration and the liquid nitrogen calibration are complete. Click the "Detector Calibration window" to activate window. Then using the keyboard "Ctrl +P", verify the data is set to "copy to the clipboard" in a "delimited" format, click on "OK". Open the desktop folder named "Detector and LN Calibrations." Then open the excel sheet called EpsilonName_ Detector and LN Calibrations. Paste the corresponding numbers at the bottom of the data set based on their respective setting.
4. Review the graphs and verify all the values are within the acceptable limits, see Figure 1 Detector Calibration below as an example. If the values exceed the acceptable limits, repeat detector calibrations (Step 2 above) and notify the Laboratory Manager.

Figure 1: Detector Calibrations Graph, q value over Time



5. In the Epsilon 5 software, copy the screen using the "Snipping Tool," then open the folder "Detector and LN Calibrations." Type the date and press "CNTRL+V" to paste the screen shot. Save and close the file.
6. In the Epsilon Software, close the sub-windows for the detector and the detector calibrations.

Figure 2. Maintenance master screen.



6.3 Epsilon 5 Detector States

The different detector states which may be encountered by the user of Epsilon 5 during operation, will be briefly described. The user software displays the state in the detector status screen.

Filling allowed

The detector is ‘warm’. Both the LN2 level sensor as well as the detector temperature are at room temperature for at least one hour. It is allowed to start filling with liquid nitrogen.

Cooling

After the N2 level sensor has detected more than 20 degrees temperature decrease due to filling the dewar, one has to wait for 6 hours before switching on the detector high tension in order to allow the crystal and the FET to cool down to -178ºC.

Pre-operational

The system is available for normal use. As the liquid nitrogen consumption is not yet constant it can warm up a little quicker than expected.

Operational

The system is available for normal use.

Short grace period

The system is available for normal use. Please refill as soon as possible. There are 75 hours (3 days) left to refill the dewar.

Long grace

The system is available for normal use. Please refill as soon as possible. There are 100 hours (4 days) left to refill the dewar.

Forced heat-up

The detector crystal has to be brought to room temperature. This can be done just waiting for the state ‘filling allowed’, which can be rather time consuming. Acceleration of this procedure can be achieved by blowing with dry air into the liquid nitrogen fill opening.

TI 301B: Tray file Web Creation

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1.0 PURPOSE AND APPLICABILITY

The purpose of this standard operating procedure is to describe the process of generating tray files usingthe IMPROVE webapp. Tray files are a set of procedures that are used to queue samples to the Epsilon 5 software.

2.0 SUMMARY OF THE METHOD

Trayfiles are generated by utilizing the Trayfile Generator on the IMPROVE webapp. After trayfiles are generated, the files are saved on the U:\ drive where they can be accessed when they are ready for use. The trayfiles will be transferred to the respective XRF instrument for use.

3.0 PRIVILEGES

The lab manager, spectroscopist, and designated lab technicians can generate tray files. Permissions to access and work with the IMPROVE webapp are granted by the IMPROVE Database Manager, or any member of the IMPROVE Software Development Team.

4.0 CAUTIONS

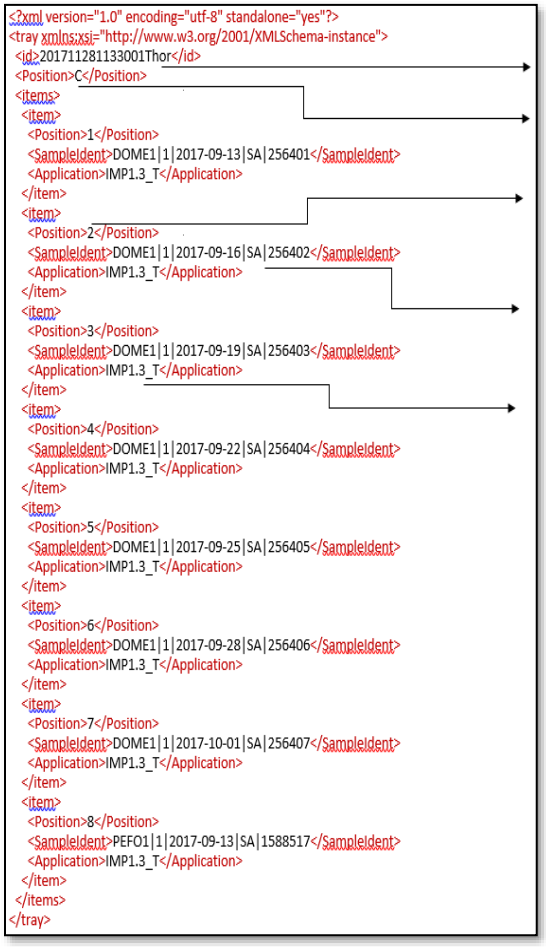
Pay close attention when making modifications to the tray files. The information in a tray file has to follow the format above precisely in order for the LIMS program to translate the file properly.

5.0 PROCEDURE

5.1 Trayfiles

Written in .XML format, tray files are used to queue samples to the Epsilon software. A diagram depicting the composition of a typical 8-position tray file is shown in Figure 1.

Figure 1. 8-Position tray file.



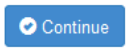
Trayfile ID: in format YYYYMMDDfilenumber

Tray Position: indicates which Epsilon tray the particular tray file will populate
Position Number: indicates what position in the Epsilon tray the particular sample will populate
Sample Identity: identifies the filter, in format Site|Sampler Ord. Pos.|Sample Date|Filter Purpose|ID #
Application: identifies which application the filter will run

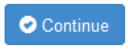
5.2 Preparation before Generating Tray files

5.2.1 Creating TrayFiles

1) Go to the IMPROVE webapp - http://webapp.improve.crocker.ucdavis.edu/
2) Under the XRF Menu, click on Trayfiles sub-menu.
3) On the first form, specify position cup format, # of tray file sets, sample year and Analyzer.
   - **Tray File Format:** select whether the Tray File are for an 8-pos or 21-pos format
   - **# of Files to generate:** indicate how many .xml files to make (input in integer)
   - **Sample Year:** indicate what Sample Year to analyze (input in YYYY format)
   - **Analyzer:** select which analyzer for the trayfiles (Odin, Froya, Thor)

     1. Click on 

.
4) On the follow-up form, specify starting position of first file in set.
   - **Starting Position:** refers to the next empty tray to fill up (input in alpha-numeric format: A, B, C, D, E, or F)

     2. Click on 

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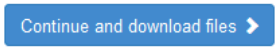
5) To download the .xml files and save, click on 

. The files are saved in the analyzer specific folder located in U:\IMPROVE_Lab\Trayfiles.

5.2.2 Generating Tray Labels

1) On the IMPROVE webapp (http://webapp.improve.crocker.ucdavis.edu/) go to "Reports" and select "Reporting Services".
2) Open "XRF Analysis Lab" and click "Sample Analysis Tray File List".
3) From the U:\ drive, open the last trayfile label created - U:\IMPROVE_Lab\XRF_Epsilon5\Cruz\trayfilestickers_working\archived
4) Use the .xml file to look up the first sample in the trayfile and enter the information in Reporting Services to generate the relevant tray file list. Enter the Filter ID number and Sample Year.

5) Export the file and open as excel. Then copy the Sample Ident, Application, and Analyzer columns into the label file on the “paste” tab. The “print” tab will automatically update with the new sample list.
6) Save the file with today’s date and print the labels.

5.2.3 Data Preservation

The current version of this software, does not allow Tray Files to be re-generated. It is recommended that operators save a back-up copy of the .xml files for future use.

Filter Identities are also preserved. Filter identities that already have a corresponding trayfile will not be re-generated. If a sample needs to be reanalyzed, a copy of the original trayfile could be retrieved &/or manual entry may be performed. In both cases, it is highly recommended to consult with trained personnel to implement the change.

5.2.4 File Assignment

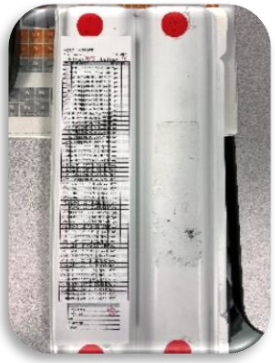
Tray Files are analyzer-specific. The current version of the web application automatically assigns the most recent analyzer specific application to the Tray File Batch. The analyzer specific application is based on the current calibration. For more details review IMPROVE SOP 301 XRF 2017 section 9.1 Calibration. In special cases, a user may contact the IMPROVE Software Development Team e-mail (*cnldevteam@ad3.ucdavis.edu*) for possible work-around.

5.2.5 Tray Checks

Sample Identities are generated based on a valid filter list from cl-SQL. After generating trayfiles and labels, a physical tray check is performed to ensure the correct filters are assigned and prepared.

1) Printed trayfile inventory labels are taken to the XRF lab (room 116) to perform a physical tray check.
2) Trays that were just assigned to an analyzer will be located in Lab 116 on the shelves labeled “unassigned”. Locate the tray that corresponds to the first generated trayfile inventory label, remove this tray from the shelf.
3) Starting with the petri dish in position 1 of the tray (top, left) physically check the petri dishes are in the same order as the inventory sticker. Using a red pen make a small dash mark on the inventory label indicating the petri dish is in the correct location.
4) Once all the petri dishes in a tray have been verified, then initial the bottom of the inventory label next to traycheck.
5) Place the trayfile inventory label on the front-left side of the white petri tray. See figure below.

Figure 3. Petri Tray and inventory label.



6) Place the white petri tray in the designated cabinet for the relevant analyzer.

TI 301C: Sample Changes for 8-Position Trays

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1. PURPOSE AND APPLICABILITY

The purpose of this SOP is to describe the process of loading and unloading samples using standard cups in 8-position trays in the Epsilon 5 EDXRF instruments.

2. SUMMARY OF THE METHOD

Tray files are transferred to the PANalytical sample changer software using a program called LIMS. Filters are transferred from Petri dishes into cups in the order designated by the corresponding tray file. The cups are placed into one of six 8-position trays (as designated by the tray file). The trays are placed into the Epsilon 5 sample changer compartment then the samples are queued in the software. After analysis is complete, trays are removed and filters are transferred back into labeled Petri dishes.

3. SAFETY

The Epsilon 5 produces X-rays which can be dangerous if appropriate precautions are not taken.

4. PERSONNEL QUALIFICATIONS

The lab manager, spectroscopist, and designated lab technicians perform sample changes on the Epsilon 5 instruments.

5. CAUTIONS

Once filters are placed into cups, they are completely unidentifiable beyond their positions in the tray. Be very attentive when transferring filters into cups, and be sure to place every filter in the correct tray as well as the proper position in the tray as designated by the tray file.

Similar caution must be taken when unloading filters from the cups. Ensure that the filters return to the proper labeled Petri dish.

Check the green "Free to Open" light on the control panel of the Epsilon 5 before opening the sample changer cover. Only open the cover if the button is illuminated.

Report any mishaps or unusual occurrences that happen during a sample change. If the Epsilon 5 generates an error message or has a software malfunction, note it in both the physical log book at the station as well as the Microsoft Access logbook on the desktop at the station. If a filter is dropped or appears unusual (hole, particles, uneven sampling, etc.), fill out a status adjustment form explaining the issue. No notes in electronic or physical log records are required.

6. EQUIPMENT AND SUPPLIES

- Filter mount cups
- Sample retaining cups

- 8-position sample trays (labeled A-F)
- 4-position sample tray (labeled S)
- Forceps
- Tray files
- Log books (physical and electronic)
- Petri dish holder

7. PROCEDURE

Because the Epsilon 5 instruments run 24 hours a day, seven days a week, trays must be unloaded before tray files can be uploaded and new filters can be loaded in trays. In order to stay consistent with how the procedure occurs in practice, the procedure section will begin with the unloading of filters.

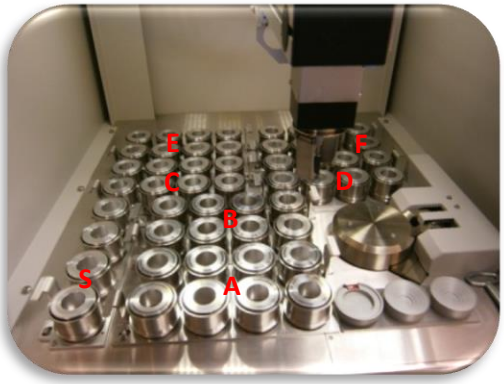
Overview and General Definitions

The following picture outlines the terms given to each element that houses the samples:

Figure 4. 8-position tray contents.

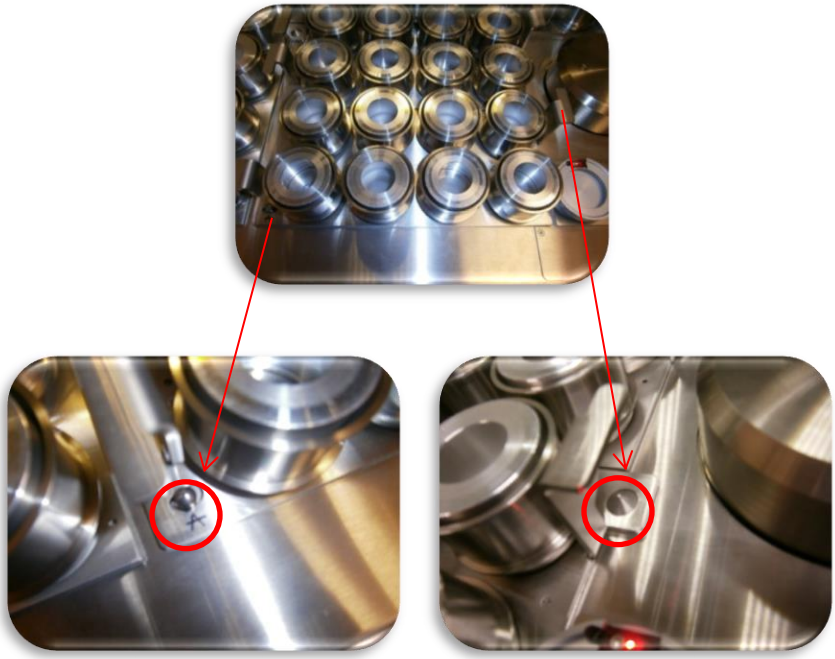
The Epsilon 5 sample changer compartment holds six 8-position sample trays labeled A-F. Positions in the tray are numbered #1-8. There is also one 4-position tray labeled S. The "S" tray houses the Teflon® blank and a multi-elemental reference filter. Each Epsilon 5 (Odin, Froya, and Thor) have an assigned "S" tray that is analyzed daily for monitoring sampling performance.

Figure 5. Sample changer compartment with trays.



The letter on each sample tray matches an etched letter on the surface of the sample changer. The trays are keyed to prevent them from being loaded backwards in the sample changer; this ensures samples #1-8 are in the proper order.

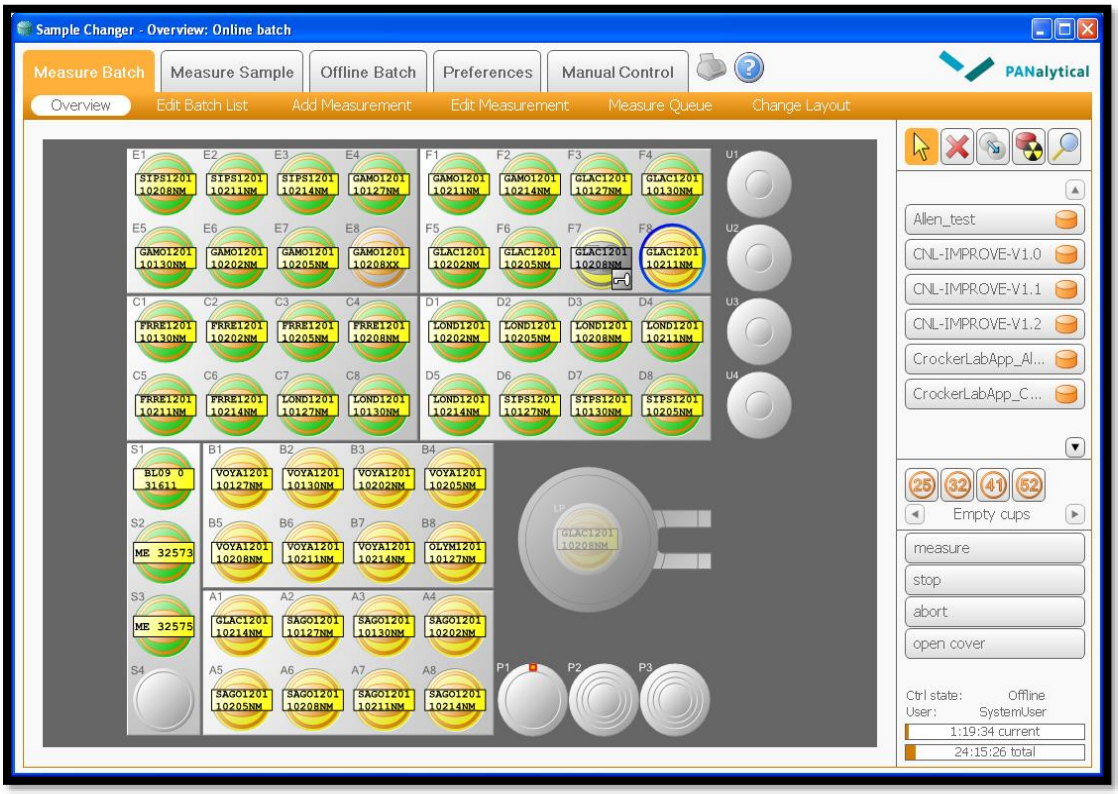
Figure 6. Tray keys.



The Epsilon software displays the configuration of the trays in the compartment. The individual samples are color-coded. Examples are shown in the figure below:

- Orange/Gray: Not queued to be measured (Ex. E8)
- Yellow/Orange: Queued to be measured (Ex. F8, Tray A, Tray B)
- Green/Orange: Measured and okay (Ex. Trays S, C & D, E1-E7, F1-F6)
- Gray/Yellow: Currently analyzing (F7)

Figure 7. Color-coded samples.



The samples that are loaded in the sample changer compartment correspond with the empty Petri dishes located in the Petri dish holder. Each Petri dish holder is labeled with the instrument it is used with (Odin, Froya, or Thor). Each compartment is labeled with a letter that matches one of the trays (A-F, S). The top Petri dish in the stack in each compartment corresponds to the filter in Position 1 for that tray.

Figure 8. Petri dish holder.

Procedure for Unloading Analyzed Samples

Sample changes can be made while the instrument is analyzing as long as the "Free to Open" light is illuminated.

Figure 9. "Free to Open" light.

1) Note which trays have completed analysis. They will be unloaded in alphabetical order, starting with the earliest letter.
2) After making sure that all 8 samples in the tray have been analyzed, open the sample changer cover and remove the first tray of filters. As a precautionary measure, perform sample changes for one instrument at a time.
3) Set the tray on the desk or sample handling table and close the sample changer cover.
4) Remove the Petri dishes in the corresponding compartment of the Petri dish holder. Typically, the top Petri dish will be flagged with a sticky tab to indicate that it is the first tray that needs to be unloaded. Begin with the Petri dish on the top of the stack.

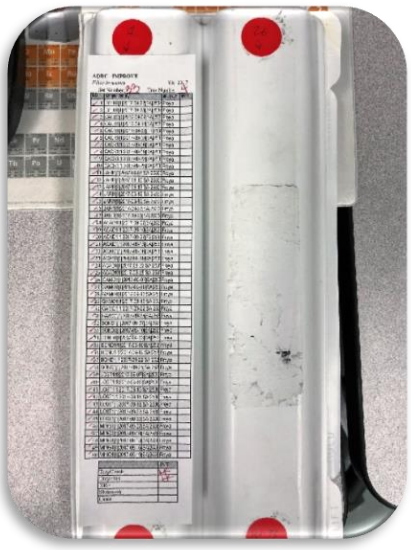
Figure 10. Layout of petri dishes.

5) Pick up the sample retaining cup from position A1. Place one finger on the inner filter mounting cup for support, then turn the sampling cup upside down and place it on the desk or sample handling table. Take the first petri dish from the stack and line it up with the sample retaining cup.

Figure 11. Sample retaining cup handling and positioning.

6) Now, remove the sample retaining cup by lifting it up and off of the filter mounting cup. Pick up the filter by its outer support ring using forceps and place it in the Petri dish. Make sure the sample side remains face-up.
7) Place the Petri dish in its white Petri tray (located next to the Petri dish holder). Confirm that it is the correct tray by examining the filter inventory list sticker on top of the tray.

Figure 12. Petri tray and inventory list.



8) Place the filter mount cup back into the retaining cup.
9) Repeat steps 5-8 for positions 2-8, and then for the rest of the completed trays except for the “S” tray. The “S” tray should not be unloaded during routine sample changes. See Section 7.8 below for instructions regarding analysis of the “S” tray. Empty trays may be placed back into the sample changer compartment if necessary to keep them out of the way until loading occurs.

10) NOTE: Remember that for now, the Teflon® filters have no functional identifier of any kind. Therefore, it is extremely important to keep everything in the proper order while the filters are separated from their corresponding Petri dishes.

Removing the Analyzed Filters from the Queue

After removing the analyzed filters, they need to be deleted from the Epsilon queue. Towards the right side of the sample changer window, there is a  symbol. Click on the symbol to activate the "Delete" function. Then, move the mouse over the middle of the picture of the completed tray and click once. This should delete the entire tray. It is also possible to delete one sample at a time by clicking on each position. Do not delete the S tray.

Weekly Check of the Designated Blank

On a weekly basis, the blank filter is checked before adding new samples to make sure that the filter is properly designated. Please see TI 301E QA_QC of XRF Analysis for more information.

Adding New Samples to the Queue with a Pre-Made Batch File

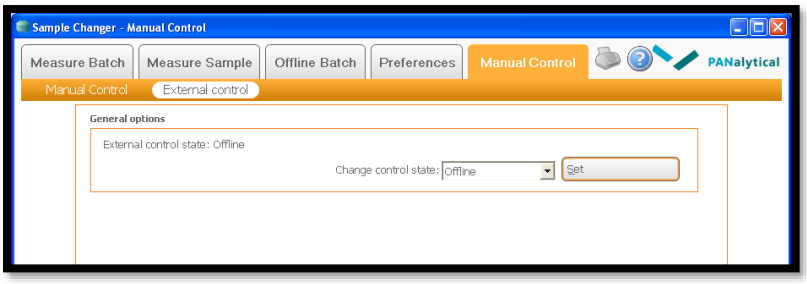
1) On the desktop of the Epsilon computer, there is a folder named "Tray files." This folder contains pre-made batch files and a subfolder named "Queued." If there are no batch files in "Tray files," transfer them from the U:\ drive. For instructions on how to access pre-made tray files, refer to Section 8.1 in the Additional Checks/Procedures section.
2) There is one tray file for each tray. The naming format is YYYYMMDDHHMM### Instrument, where YYYYMMDD is the date the file was created, HHMM is the time the file was generated, ### is the sequence number, and "Instrument" is the Epsilon the files are being created for. For example, 201711281133001Thor was created on 11/28/2017 at 11:33 AM for Thor. The "001" in the sequence number means it is the first of the series created. This number is intended to be used so that if the files are sorted in ascending order, they will be in the correct loading order.
3) When the different tray files are sorted by name, the first file on the list will be the first file that needs to be loaded. Check the file by clicking on it. See figure 10 for an example.
4) Copy the necessary files to the folder called "Shortcut to LIMS." Once the files have been copied over, move them from their current location in the "Trayfiles" folder to the "Queued" subfolder, so that the next user performing sample changes can easily find the files that they need.

Figure 13. Sample tray file.

```
<?xml version="1.0" encoding="utf-8" standalone="yes"?>
<tray xmlns:xsi="http://www.w3.org/2001/XMLSchema-instance">
 <id>2017112811330O1Thor</id>
 <Position>C</Position>
 <items>
  <item>
   <Position>1</Position>
   <SampleIdent>DOME1|1|2017-09-13|SA|256401</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>2</Position>
   <SampleIdent>DOME1|1|2017-09-16|SA|256402</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>3</Position>
   <SampleIdent>DOME1|1|2017-09-19|SA|256403</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>4</Position>
   <SampleIdent>DOME1|1|2017-09-22|SA|256404</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>5</Position>
   <SampleIdent>DOME1|1|2017-09-25|SA|256405</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>6</Position>
   <SampleIdent>DOME1|1|2017-09-28|SA|256406</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>7</Position>
   <SampleIdent>DOME1|1|2017-10-01|SA|256407</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
  <item>
   <Position>8</Position>
   <SampleIdent>PEFO1|1|2017-09-13|SA|1588517</SampleIdent>
   <Application>IMP1.3_T</Application>
  </item>
 </items>
</tray>
```

5) Find the LIMS2UAI.exe icon on the desktop, and then check the analysis status for the sample in the chamber. If more than 300 seconds are remaining in the analysis, then double-click the LIMS icon if not then wait until the sample completes analysis and new sample is loaded. Note the Epsilon software will automatically abort analysis if the LIMS software is operating at the same time as the sample changer is unloading/loading a sample.
6) The LIMS window will appear. There will be red highlighted text saying “Offline” that will change to a green highlighted “remote.” Then, in the “Overview Screen” in the “Measure Batch” tab of the sample changer window, filters will begin to populate the trays. When all the trays are complete, close the LIMS window by clicking the “X” in the window. The files in the LIMS folder will now be gone.
7) Now, go to the “Manual Control” tab. Then click on “External Control.” Check to make sure that the External Control State is “Offline.” If not (and it will usually not be), change it to “Offline” and click “Set.” If the status does not change after clicking the button, try setting it to “Local” and then “Offline.”

Figure 14. "Manual Control" tab.



Saving the New Queue

1) When all of the samples have been queued to be measured, save the queue (batch) by first clicking on the "Measure Batch" tab, then "Edit Batch List."
2) A list of what was just loaded will appear. Sometimes, this takes a few seconds to display.
3) On the right hand side, click "Save As."
4) When the "Save Batch" screen appears, the correct folder should already be displayed. The folder is on the desktop and is called "Batch Files."
5) The format for saving batch files is "current_mmddyyyy.batch" (ex. current_09172011.batch).
6) After entering the name, click "Save."

Loading New Samples into the Sample Chamber

1) Find the next white Petri tray with filters to be analyzed.
2) Remove the next eight filters to be analyzed according to the populated tray file. The first petri dish removed from the white petri tray should correspond to the filter populated in position 1 of the current Epsilon tray being loaded. When removing petri dishes from the petri tray remember to keep them in the proper order for loading (position 1 on top of the stack with position 8 on the bottom of the stack of petri dishes).
3) Remove the designated 8-position tray from the Epsilon and place it on the sample handling table.
4) Remove the mounting cups from the tray and place them on the desk or sample handling counter.
5) Open the first Petri dish and use the forceps to lift the filter by the outer support ring and place it on the mount. The sample side should be facing up. Set the now empty petri dish upside down (starting a new stack, the next empty petri dish will be added to this stack in the same manner until the 8 empty petri dishes have been added).

6) Next, place the sample retaining cup over the top of the mounting cup. Tip the cup slightly and support the filter mount cup by applying gentle pressure on the bottom of the cup. Then, turn the assembly upside down and place it in the first position of the tray.
7) Continue with the rest of the samples, moving to position 2, then 3, etc., until all eight have been loaded.
8) Invert the stack of empty petri dishes, position 1 should now be the top of the stack. Double check the order of the empty petri dishes matches the physically loaded filters on the "overview" screen. Place the Petri dishes in the appropriate compartment (A-F) of the Petri dish holder.
9) Look at the front panel display of the Epsilon. Make sure the green "Free to Open" light is lit. Then, open the sample changer cover.
10) Load the filled sample tray into the sample changer compartment with the letter written on the sample tray matching the etched letter in the sample changer.
11) Close the sample changer cover and repeat steps 2-10 for the remaining empty trays.
12) Add the newly populated filters to the analysis queue by clicking the  symbol (in the "Overview" screen of the "Measure Batch" tab. Then, click on the newly-loaded trays. The samples will change from gray to yellow.

Analyzing the "S" Tray

The "S" tray is analyzed once every day. The current method is to add the "S" tray to run directly after the current tray being analyzed, and then continue with the A-F cycle. If the queue needs to be re-ordered for the "S" Tray to be analyzed, refer to Section 8.3 of Additional Checks/Procedures.

Recording Sample Changes

1) Each instrument has its own physical log book as well as an electronic log in Microsoft Access. The physical log book is labeled with the instrument name and is located on the shelf above the respective computer, while the Access log is located on the computer desktop.
2) Open the physical log book to the first available row. Write the date, time, first and last samples loaded, and the letters of the trays loaded. Sign the entry. Make sure to follow the same format as previous entries.
3) Open the Access log by clicking on the icon entitled "Enter_LogBooks .accdb." Click on "Add New Record." The date and time will automatically fill in. The default Code Action is LD, for "Loading." Fill in the first and last filter information and the "Initials" box. Then click, "Save This New Record." Close the log.
4) Additional Checks/Procedures

Transferring Pre-Made Batch Files from the U:\ drive

1) Pre-Made files for each analyzer can be found here - U:\IMPROVE_Lab\Trayfiles
2) Move the files to the analyzer's computer. On the desktop there is a folder called "Trayfiles". Select all the relevant trayfiles from the analyzer specific Trayfile folder found on the U drive and copy them to the Trayfile folder on the analyzers desktop.

Adding the New Samples to the Queue without a Pre-Made Batch File

1) To add filters to the queue, click on the first position that will be loaded in the sample changing software, this position will now have a blue ring. Next click on "Add Measurement" towards the top of the sample changer screen, opening the "Add Measurement" screen.
2) The "location" should already be the correct position.
3) The "Type" should already be set to routine.
4) For "Application," select the current version of the application being run on the particular Epsilon.
5) Place the cursor in the "Sample Identification" box. Type in the filter ID.
6) Check repeat is set on "1" and priority is set on "normal".
7) Click on "Add" located on the right hand side of the screen.
8) Repeat steps 1-7 for any additional filters.
9) Once finished, click on "Overview" at the top of the sample changer software to go back to the main sample changer screen.

Changing the Order of the Queue (Usually for "S" Tray)

1) In the "Measure Batch" tab, click on "Measure Queue."
2) Highlight the samples of the "S" tray (or whatever samples need to be moved).
3) Use the "Move Up" or "Move Down" buttons on the right as many times as needed to change the order.

Aborting Sample Analysis

1) To abort a sample while in mid-analysis, go to the "Measure Batch" tab, then "Overview."
2) Click the "Abort" button towards the bottom right.
3) The instrument will first come to air; then, the sample will be removed and put back to its original tray position. No new analysis will begin until the "Measure" button is clicked or the  button is used to re-queue.

Special Circumstances When Using "Stop" to Suspend Analysis

1) When activated, the "Stop" button will let the current sample finish analyzing, then stop all actions without emptying the queue. The only issue with this button is that it does not change the current sample to green when completed, even though the data is in the "Results" file.
2) To be sure that the filter was successfully analyzed, click on "File," then "Open."
3) On the left of the window that pops up, click on "Results."
4) Then, click on the current version of the application being run on the particular Epsilon. Click "Open."
5) Check the boxes for "Routine," "Measured," "Standard," and "Blank." Then type the name of the sample, standard, or blank. Click "Apply."
6) If the filter was analyzed, it will appear on the list. Otherwise, use the  symbol to queue it for analysis.

Creating Tray Files

Detailed instructions on how to create tray files are located in TI 301B Tray file web creation.

Weekly Check of Blank Identities

1) On a weekly basis, the blank filter is checked to make sure it is properly designated before new samples are loaded during the sample change. To do this, look up the blank used for the last sample analyzed by first clicking on "File," then "Open." On the left of the window that pops up, click on "Results."
2) Selected the current application. In the window that pops up, type a "*" in the Sample ID box. Make sure "Routine" and "Measured" are checked. Then, click "Apply."
3) The list generated should be in descending order so that the top filter is the last filter that was analyzed. Click on the top sample to highlight it and the analysis data will appear.
4) Check that the Blank ID is correct for the Epsilon in use. Refer to the laboratory manager or spectroscopist for the current Blank IDs for each Epsilon. If the blank is not correct, make a note of it and inform the lab manager and spectroscopist immediately. If the blank is correct, close the "Results" window and continue.

Changing Inserts in Filter Mount Cups

The plastic inserts in the filter mount cups are changed on average once a month. Inserts are removed from the filter mount cups and placed in a bin, which is located in a cabinet drawer in the XRF Lab. These used inserts will later be cleaned with ethanol™. Clean inserts can be found in a labeled bin in a drawer. Exchange used inserts for clean inserts, place the new inserts in the filter mount cups, and continue with the sample change.

TI 301D: Quality Assurance/Quality Checks (QA/QC) of XRF Performance

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1.0 PURPOSE AND APPLICABILITY

The subject of this technical instruction (TI) is the quality assurance/control (QA/QC) steps applied in the elemental mass loadings measurements of $PM_{2.5}$ loaded filters collected in IMPROVE network using EDXRF systems, namely Panalytical Epsilon5. The scope is to ensure good laboratory practice of measurements of elements on $PM_{2.5}$ loaded filters including calibration, verification of calibration and routine quality control checks (daily, weekly and monthly), which are analysis of blanks, multi-elemental reference materials and selected IMPROVE samples, later referred to as "Re-analysis set".

2.0 DEFINITIONS

Lab Blanks: These are PTFE (TB) filters placed in the S trays of each Epsilon 5 (E5) to be analyzed daily. TBs are selected from previously accepted batch of filters (currently Teflon from Pall with 3 µm pore size) for regular $PM_{2.5}$ sampling at IMPROVE sites. The monitoring is performed on elemental loadings ($\mu g/cm^2$) basis.

Al&Si Reference Materials from Micromatter (MM-Al&Si): These samples contain Al and Si deposited on Nuclepore filters to be analyzed weekly on 3 E5s.

Multi-Elemental Reference Materials at UCD (UCD-ME): These samples were generated from certified multi-elemental solutions containing all IMPROVE reported elements. E5-specific UCD-MEs are analyzed daily while another ME is analyzed weekly on all E5s to check the analyzer stability as well as between analyzer comparison.

Reanalysis Set: This is a selected set of sixteen IMPROVE samples and a NIST SRM2783 (#1720). The Reanalysis set is analyzed on all E5s every month to provide long-term reproducibility and inter-analyzer compatibility records. The mass loadings for each sample obtained each month are compared to pre-determined reference loadings. The first instrument specific reference loadings of IMPROVE samples have been assigned as the mean results of multiple measurements by each E5; the second ones have been calculated as the average of all analyzers' reference loadings. These reference loadings are fixed, which they are not updated every calibration. The reference loadings of NIST SRM2783 are the certified/reference mass loadings provided by NIST. The average absolute z-score of the reanalysis set must be ≤1 for selected elements.

Relative Expanded Uncertainty (Urel): The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%). Urel of calibration function is estimated following an international method[1].

$$c_{std,ij} = \frac{I_{cor}}{b_j} \rightarrow U_{rel}(c_{\mathrm{std,ij}}) = k\frac{u(c_{std,ij})}{c_{std,i}} = k\frac{\sqrt{\sum\left(\frac{\partial c_{std,ij}}{\partial x}\right)^2 u_x^2}}{c_{std,i}}$$
$$= k\frac{\sqrt{\frac{u^2\left(I_{cor,ij}\right)}{{b_j}^2} + \left(\frac{I_{cor}}{{b_j}^2}\right)^2 u^2\left(b_j\right) + u^2(c_{std,i})}}{c_{std,i}}$$

Where, $c_{std,ij}$ is the re-constructed loading (μg/cm^2) of calibration standard i of element j using the calibration factor (b_j, in [(cps/mA)/(μg/cm^2)]), $c_{std,i}$ is the certified loading standard i and I_{cor} is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA). Although uncertainty of $c_{std,i}$, $u(c_{std,i})$, is not a part of $c_{std,ij}$ calculation, it is added to uncertainty equation for a conservative approach. The coverage factor, k, takes into account the distribution of uncertainties possible for a given measurement and in this work, a coverage factor of 2 is used to give approximately the 95% confidence interval on the uncertainty value (k=1.96 at 95% confidence level for a normal distribution).

Absolute bias: The ratio of difference between measured and certified/reference loading of NIST SRM2783 to certified/reference loading (%).

$$Absolute\ bias = 100 * \frac{|c_{E5} - c_{cer}|}{c_{cer}}$$

Where, c_{E5} and c_{cer} is loadings by E5 and certified/reference loadings of NIST SRM2783, respectively.

z-score: The ratio of absolute difference between each result from Re-analysis set analyzed monthly and reference value to accompanying uncertainty.

$$z = \frac{|c_{E5} - c_{ref}|}{\sqrt{U_{c_{E5}}^{\ 2} + U_{c_{ref}}^{\ 2}}}$$

Where c_{E5} is the mass loading measured (μg/cm^2), c_{ref} is the reference mass loading; U_{cE5} and U_{cref} are the expanded uncertainties of measured (c_{E5}) and reference (c_{ref}) mass loadings. The expanded uncertainties are estimated following an international method[3]. The reference loadings of IMPROVE samples were assigned as the mean of multiple analyses, and are fixed, which means they don't change by calibration. The certified/reference loadings of SRM2783 are used for z-score calculation.

Acceptance limits:

- **Lab blanks:** analyzed daily, are determined as three times Method Detection Limits (MDLs, calculated as three times standard deviations of a set of lab blanks);
- **UCD-MEs:** analyzed daily and weekly, are determined as ±10% of the reference loadings (calculated as the mean of 5 measurements after calibration);
- **MM-Al&Si:** analyzed weekly, are determined as ±10% of the reference loadings (calculated as the mean of 5 measurements after calibration);
- **SRM2783:** analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations from 44 measurements between Jan 2013 and July 2016.

$$RMSREs = \sqrt{\frac{1}{m}\sum_{m=1}^{m}\left(\frac{c_{E5,m} - c_{ref}}{c_{ref}}\right)^2}$$

where, m refers to measurement month.

3.0 GENERAL GUIDELINES

This document is intended to guide users for verifying the calibration to ensure starting of analyzing samples as well as checking the performance of EDXRF analyzers routinely, including analysis of blanks and samples, checks of the results and the action required in case of detected malfunction. The intended audience must have fundamental knowledge of XRF operations and data. A user is required to have access to UC Davis Central Authentication Service (CAS).

4.0 PROCEDURES

4.1 Calibration Verification

The procedure of the calibration verification is shown in Fig.1, and is summarized in Table 1.

The calibration is performed following instructions. The absolute bias of SRM 2783 must be equal to or less than acceptance limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb. The relative expanded uncertainty (Urel) of each element's calibration function is estimated using the designated excel sheet (see ..\Uncertainty_GUM\uncertainty-Calibration2017_OrhReg.xlsx for 2017 calculations). The Urel is checked to be equal to or less than 10% for stoichiometric standards of IMPROVE reported elements. In case Urel is higher than 10%, calibration lines and spectra are examined to determine the reason. Further testing and checks, i.e., checking the calibration lines of corresponding elements at other E5s, are performed to figure out the reason of exceedance. In case similar deviations are observed on the other E5s, the orientation of the standard needs to be examined. If the orientation is correct, one can suspect the quality of corresponding standards and exclude them from calibration. If the problem cannot be solved with excluding standard(s), calibration with the current standards shall be redone. If recalibration does not show changes from previous one, the Laboratory Manager shall be notified for further instructions (e.g. stop analysis, order new standards, etc.)

The finalized calibration lines are verified by analyzing blanks, multi-elemental reference materials and Re-analysis set. Meeting the criteria assures the analysis of IMPROVE samples. Failure in meeting criteria requires further checks/testing to resolve it.

Figure 15. The flowchart of calibration verification.

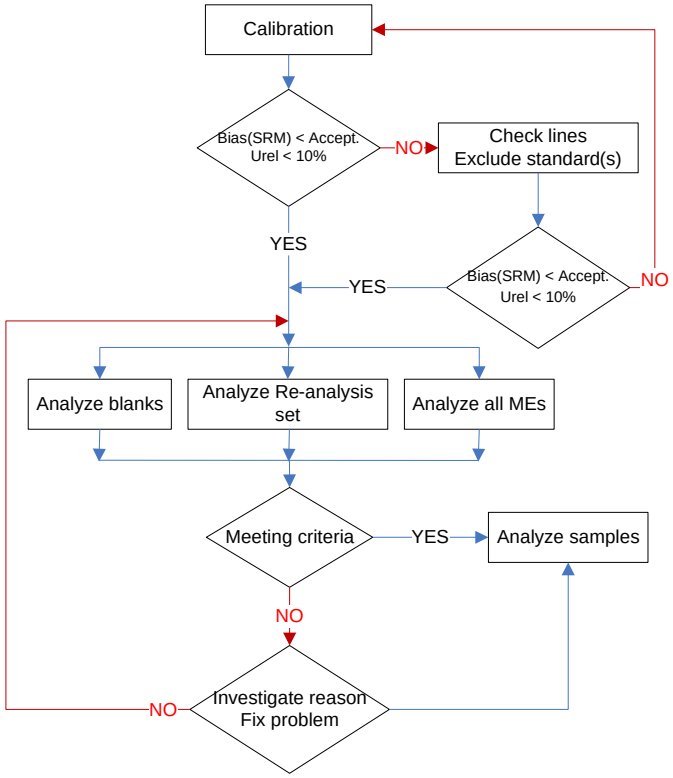


Table 1. The calibration verification activities, criteria and corrective actions.

Analysis	Criterion	Corrective Action
Uncertainty of calibration	Urel≤10% for stoichiometric standards	• Check calibration line and spectra • Check standard(s) for damage/contamination • Exclude standard(s) from calibration line • Further cross-instrumental testing • Recalibration with current or new standards
NIST SRM2783	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	• Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards
PTFE Blank	≤acceptance limits with exceedance of two elements at least in two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
MM-Al&Si	within acceptance limits	• Check sample(s) for damage/contamination • Further cross-instrumental testing • Replace sample(s) as necessary
UCD-ME	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Reanalysis set	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	

4.2 Routine QC of EDXRF Analyzers

The procedures of the routine QC of the EDXRF analyzers' performance are shown in Fig.2, and is summarized in Table 2.

Figure 16. The flowchart of routine QC of EDXRF instruments' performance.

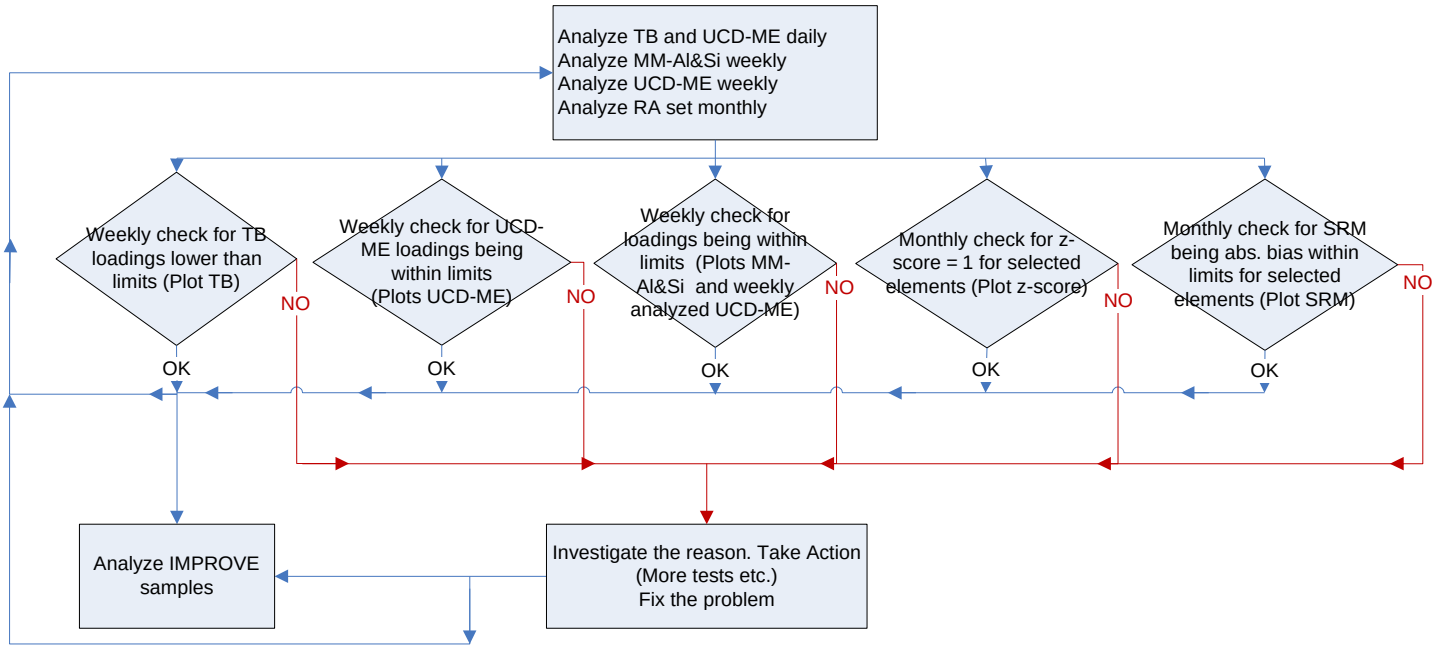


Table 2. The routine QC activities, criteria and corrective actions.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	• XRF software automatically adjust the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of two elements at least in two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD-made ME-RMs	Daily	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	• Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
Micromatter Al&Si RMs	Weekly	within acceptance limits	
UCD-made ME-RMs	Weekly	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Re-analysis set	Monthly	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

4.2.1 Daily Analysis

The S trays containing analyzer specific TB and UCD-ME is analyzed daily using the same application of IMPROVE samples. The samples analyzed must be clean and undamaged.

The TB and UCD-ME results are migrated to the database. The plots can be examined at http://169.237.146.119:3838/xrfControlCharts/

The QC of daily analyzed samples is performed weekly applying the following steps:

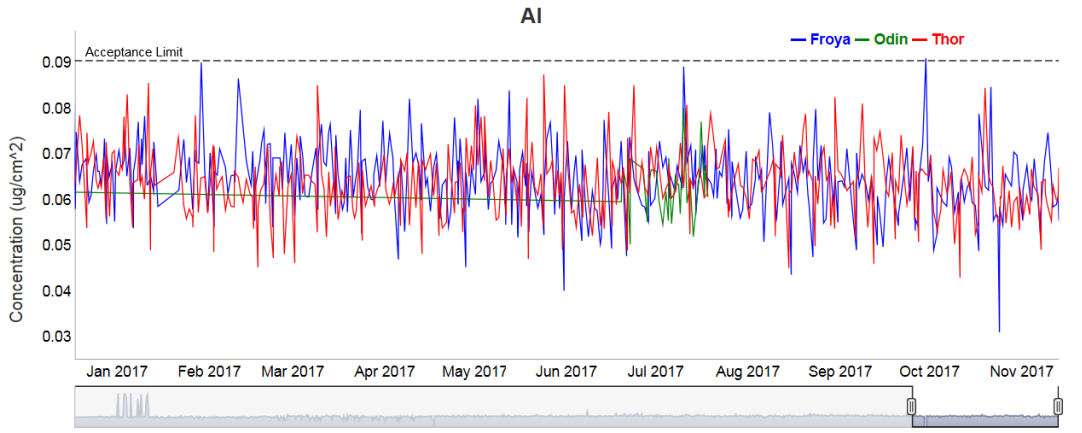
4.2.1.1 QC of TBs

The plot at http://169.237.146.119:3838/xrfControlCharts/ (Fig.3) must be checked for exceedance the limits for at least two elements for failure. The gradually small increase for few elements, e.g., Ca, S and Cl, most likely means atmospheric contamination of TB while increase in Cu and Zn is likely to mean an instrument originate, i.e. abrasion in analytical chamber. The first action is to air-brush TB. If loadings of elements exceeding the limits decrease, no further action is necessary and the analysis may continue. If not, TB is replaced with new one. Repeated failure would suggest the analyzer related contamination. In that case, cleaning the analytical chamber and/or diaphragm should solve the issue. Reanalyzing TB should follow for confirmation. If, however, the problem is not solved, the analysis needs to be stopped and the additional testing needs to be performed to address the issue. For example, in case of sudden huge increase in loadings for few elements, the following are the possible causes:

- Change in geometry (most likely tube or detector distance/angle)
- Filter (or other material) presents in the chamber in addition to analyzed sample
- Sample filter of center during analysis (Zn spikes in the spectra due to the beam interaction with the ring of the filter)

The analysis must be stopped until problem is solved and all samples analyzed in the period in question must be reanalyzed.

Figure 17. The QC plot of TB.



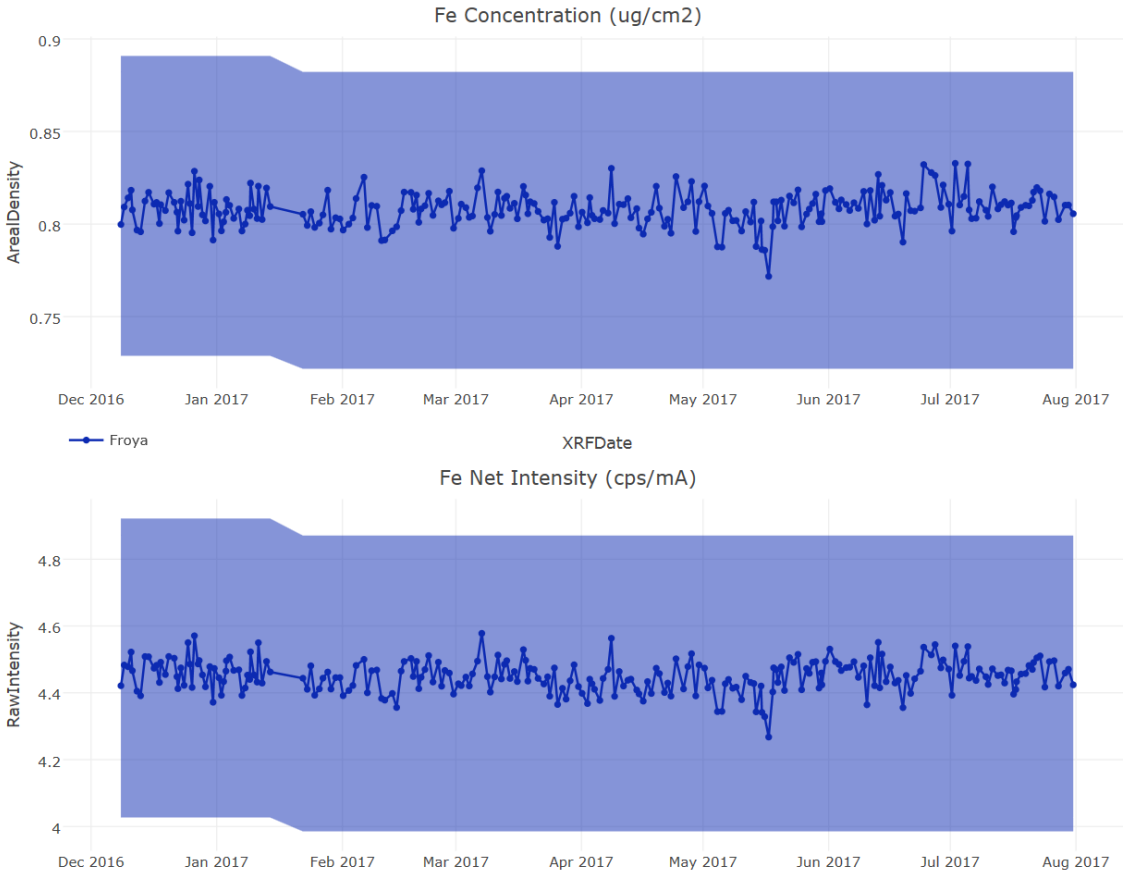
4.2.1.2 QC of UCD-ME

The QC plot includes the intensity and mass loadings in real time for each instrument, see Fig.4. The acceptance limits may slightly change every calibration and in case any changes to the instruments were performed (i.e. new X-ray tube, new detector, etc.).

If the limits are exceeded for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb at least two consecutive days, the investigation is started. The cross-analyzers check, analysis of other ME samples and analysis of single element standards and some of the additional tests listed in Table 2 are performed to address the problem, which can be damage of ME, contamination (particularly Zn, Cu and Ca) etc.

It should be noted that UCD-MEs are torn after ~250 analyses. Therefore, multiple MEs at certain levels must be generated to assure availability in case of damages.

Figure 18. The QC plots of UCD-ME.



4.2.2 Weekly Analysis

These analyses include instrument specific MM-Al&Si and a UCD-ME to be analyzed on three E5s. The analyzed samples must be contamination free and undamaged. The MM-Al&Si plot (Fig.5) and UCD-ME plot (Fig.6) for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb are checked for compliance with the acceptance limits (warning limits also marked on MM-Al&Si plot). UCD-ME plot can also be examined for inter-analyzers comparison, since that sample is analyzed on 3 E5s. In case of exceedance of limits for

above-listed elements at least two consecutive measurements, further testing listed in Table 2 requires to determine the problem.

Since the weekly analyzed samples are loaded manually every time, special attention must be paid to analyze with the active IMPROVE application as well as correct sample identity. In case of mistake in any of those, the plots will be messy, containing many points and acceptance lines. In such cases, results must be invalidated.

Figure 19. The QC plot of MM-Al&Si.

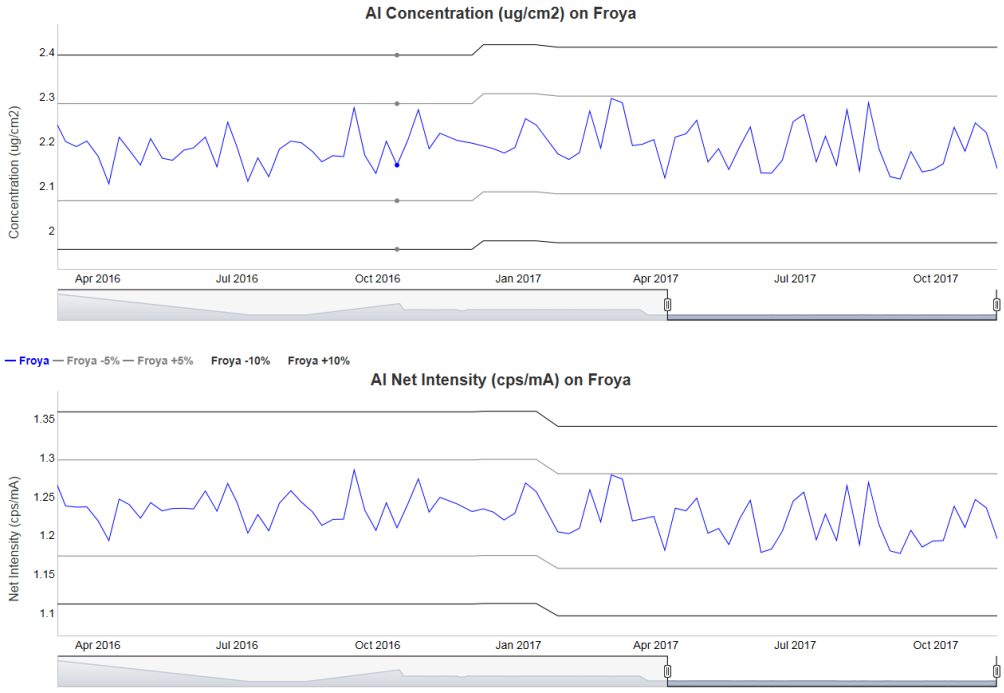


Figure 20. The QC plots of weekly analyzed UCD-ME.

4.2.3 Monthly Analysis

The Re-analysis set is analyzed monthly on three analyzer using active IMPROVE application. A dedicated blank is analyzed along the IMPROVE samples to be utilized for blank subtraction. Since the blank of SRM 2783 was showed to have very repeatable results over years, that blank is analyzed only once in every calibration. When SRM2783 is analyzed every month, corresponding blank used for subtraction is changed with the SRM-blank on each analyzer, and loadings are re-calculated then re-transmitted. The SRM2783 results with wrong blank must be invalidated.

The z-score plot (currently at U:\IMPROVE_Lab\XRF_Epsilon5\QA\Reanalysis\Inter_Instruments\Reanalysis_NewSet_GUM.xlsm, web-plots in progress) shows mean z-score values of 17 samples based on any reference values, see Fig.7. The satisfactory level ($z \leq 1$) is checked for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr . In case of exceedance of the limit, additional tests need to be implemented to address the problem. Year-basis folders at ..\QA\Reanalysis\Inter_Instruments have analyzer-specific workbooks provide calculations and graphs of the regression slopes, intercepts and R^2 between monthly results and two reference values (see Fig.8a). In addition, the relative expanded uncertainties based on the error propagation are calculated and plotted in element specific worksheet (see Fig.8b). The unusual slopes than different from long-term ones and R^2 as well as uncertainty must be further investigated. The *Sheet1* contains summary and plots of annual variation of slopes.

Figure 21. The plot of z-score for Re-analysis set.

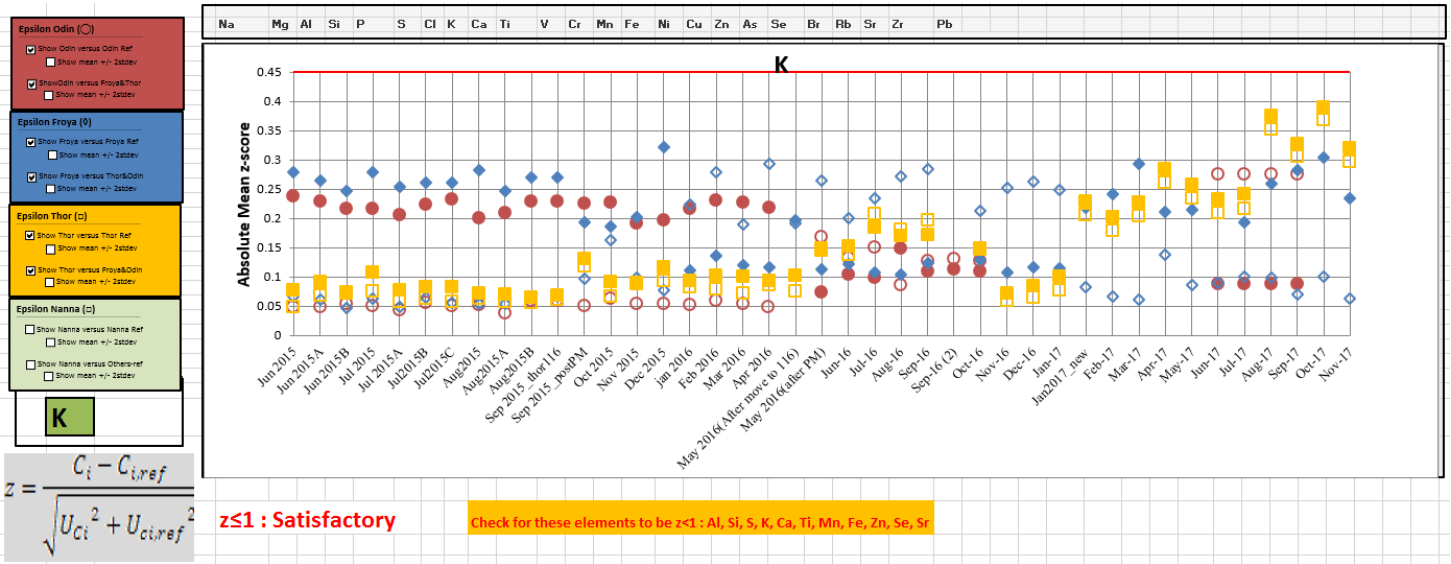
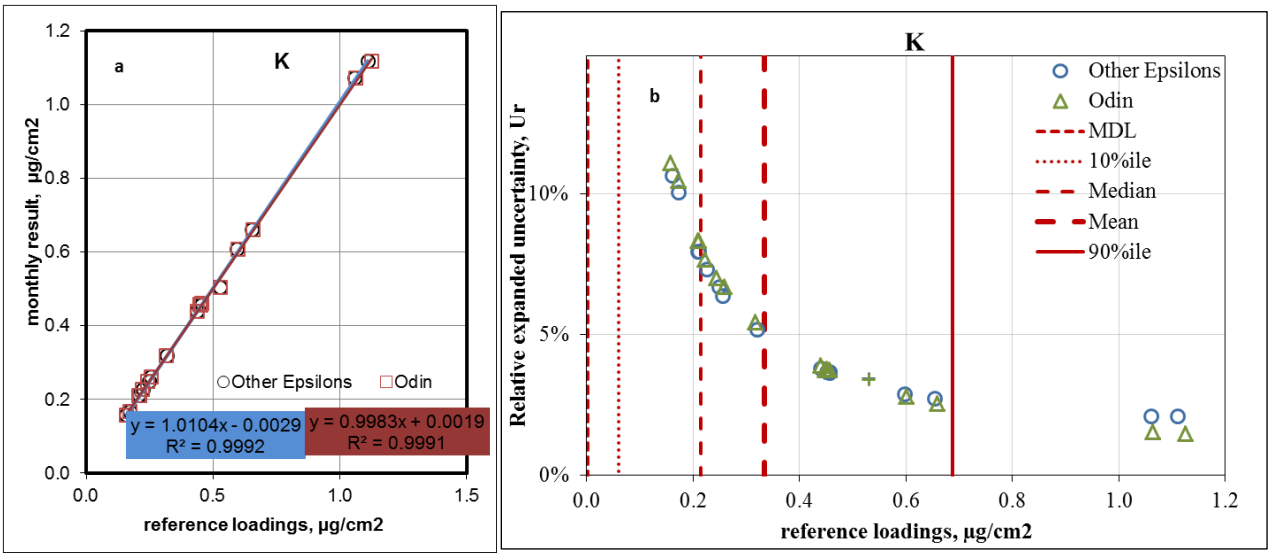
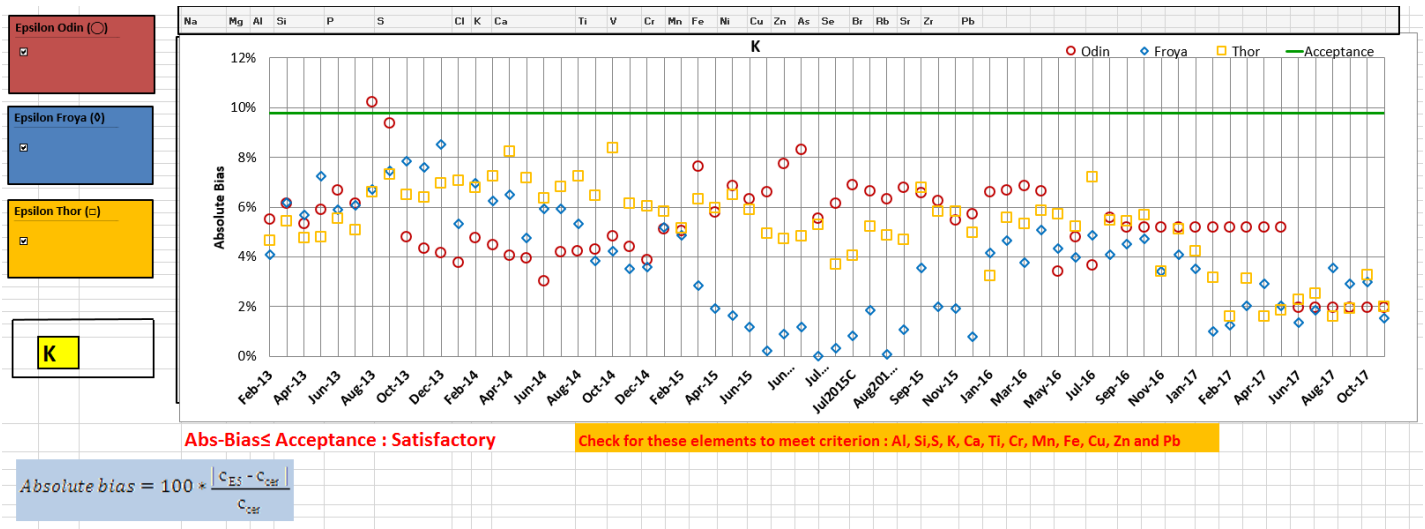


Figure 22.a) The comparison of monthly results of Reanalysis samples with the reference loadings, Odin is reference loadings of Odin; Other Epsilons is the mean reference loadings of Thor and Froya; **b)** Relative expanded uncertainty at the reference loadings.



The absolute bias plots of SRM2783 (Fig.9) is located at U:\IMPROVE_Lab\XRF_Epsilon5\QA\Reanalysis\Inter_Instruments\SRM2783_AbsBias.xlsm. Absolute biases of Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb are checked to be equal to or less than the acceptance limits. In case of exceedance, the actions in Table 2 must be taken to address the issue. Over 4 years of data showed that SRM results are very repetitive, but sample specific, meaning that in case #1720 is changed, the acceptance limits must be re-determined. The most probable reasons of failure in meeting of the criteria are up-side-down analysis and improper placing on insert of sample cup. Special care must be taken for those.

Figure 23. The plot of absolute bias for SRM2783 (#1720).



4.2.4 Reporting

The weekly QC reports about the analyzer performance including the results of daily and weekly monitoring are prepared for the check by the Laboratory Manager. These reports are placed in U:\\IMPROVE_Lab\XRF_Epsilon5\QA\QC_Reports. An example is given in Fig.10. The results of RA samples are reported to the Laboratory Manager in case of a need for further analysis.

Figure 24. An example of weekly QC report for daily and weekly monitoring of analyzers' performance.

07/07/2015
Sinan Yatkin

Observations

Lab Blanks in S tray

TB-Cl on Froya has a small increasing trend just over the limit. Cu-NB-Thor spiked on 4/7/15 and came back to original level.

MM-ME

After PM, all the elements are within their acceptance limits. However, Odin Si, S, K and Fe intensities decreased ~2% after PM in June, 2nd.

MM-Al&Si and CNL-ME

Al&Si ME are normal. ME-38 Odin concentrations of K and S decreased ~2% while Fe and Si are variable. Nevertheless 2% decrease in all elements is more likely.

Conclusion

None.

TI 301E: Level I Validation of Monthly XRF data

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1.0 PURPOSE AND APPLICABILITY

The subject of this technical instruction (TI) is to describe the Level I validation procedures for monthly XRF data set of the IMPROVE network. This Level I validation includes procedures for creating data sets and reporting final validated XRF results. This TI aims to ensure good and consistent output for multiple users.

In order to apply this TI, all the IMPROVE samples for any given month must be analyzed, and the data to be validated must be migrated to the database. In addition, the quality checks of the analyzers' performance during analysis of the given month of samples (described in detail in TI-301E) must yield positive results (good stability, no contamination detected, etc.)

2.0 DEFINITIONS

Level I Validation of XRF data: Contains the validation of only XRF results of any given month performing a set of procedures given in this document

XRF Data Management Pages: *(http://webapp.improve.crocker.ucdavis.edu/Xrf/Home)* : The XRF Data Management Pages are webpages related to the administration and processing of XRF data.

cl-SQL Reporting Pages: The Reporting Pages are user-interface webpages that are used to query and view the datasets. Results could then be exported in a workable office-friendly format e.g. .xls, .csv, .doc

Set ID: The monthly XRF data created using XRF Data Management Pages, e.g. set ID 109.

Template xlsm file: This excel workbook contains the following sheets to check for anomaly in XRF data, possible samples swaps and assigning/changing the validity of samples and field blanks (FBs):

QA_Change - lists samples for which validity needs to be changed;

All - includes all the NM (normal data), QD (questionable data) and FBs (field blank) of the monthly data set;

NMQD - lists the samples with NM and QD status and calculates the elemental loadings higher than 3 times of reported detection limits (MDLs) for further calculation/plotting.

FB - lists the field blanks;

Correlations - contains the correlation matrix of monthly data and long-term data, scatterplots of Al vs Si,, Al vs Fe, Si vs Fe, Al vs Ti, Fe vs Ti, PM vs S and PM vs K, and network metrics table (percentage of detection, MDLs, 10^{th}, 50^{th} and 90^{th} percentiles);

MassRatio - calculates and plots the ratio of sum of elements (by XRF) to PM mass (by gravimetric), and highlights the outliers;

Al vs Si - calculates the reconstructed Si loadings based on the Al measurements and Al/Si ratios of:

a) long-term (all 2011-2016 data), and b) long-term studied month. This sheet plots the measured vs constructed Si scatters, and lists the outliers;

Si vs Fe is the same as *Al vs Si,* but calculates and plots for Fe;

Al vs Fe is the same as *Al vs Si,* but calculates and plots for Fe;

Al vs Ti is the same as *Al vsSi,* but calculates and plots for Ti;

Fe vsTi is the same as *Al vs Si,* but calculates and plots for Ti;

PM vs S is the same as *Al vs Si,* but calculates and plots for S;

PM vs K is the same as *Al vs Si,* but calculates and plots for K;

Basic_Checks - lists the samples with Fe<0, S≤0 and unusually high trace elements (e.g. Pb, Cu, Zn, Cr, Ni and As);

Outliers - lists all the outliers linked to all worksheets described above.

Checks&changes – lists samples to be re-weighed/checked by the weighing lab

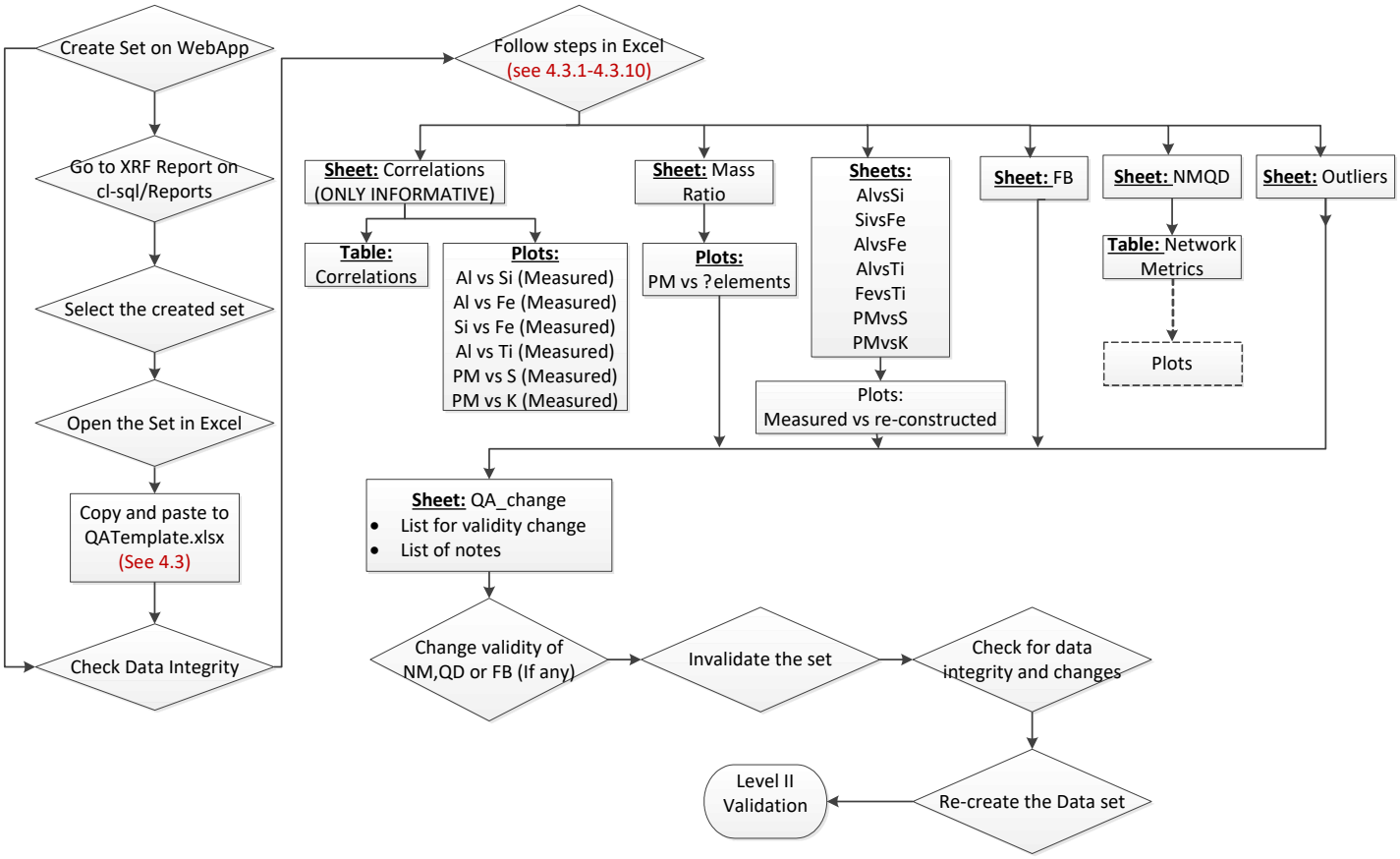
3.0 GENERAL GUIDELINES

This document is intended to guide users for checking the validity of monthly XRF data, including invalidation of samples with questionable XRF results, evaluation of contamination levels on FBs (If repeated contamination for any given site the maintenance crew is notified) and detecting the anomalies of the data looking for possible sample swap(s) (i.e. FB-sample swaps or PM_{10}-sample swap). The intended audience must have fundamental knowledge of XRF operations and data. A user is required to have access to U drive, XRF Data Management pages and cl-SQL reporting pages.

4.0 PROCEDURES

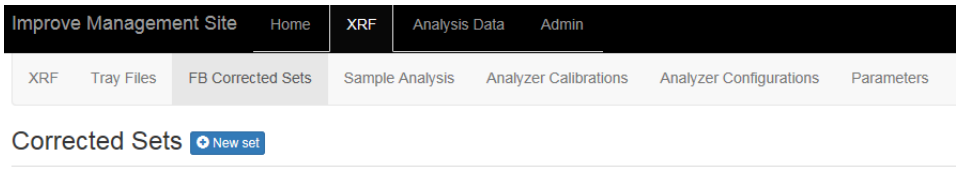
The flowchart of procedures for XRF Level I validation is shown in Figure 1.

Figure 25. The flowchart of procedures for XRF Level I validation of monthly XRF data.

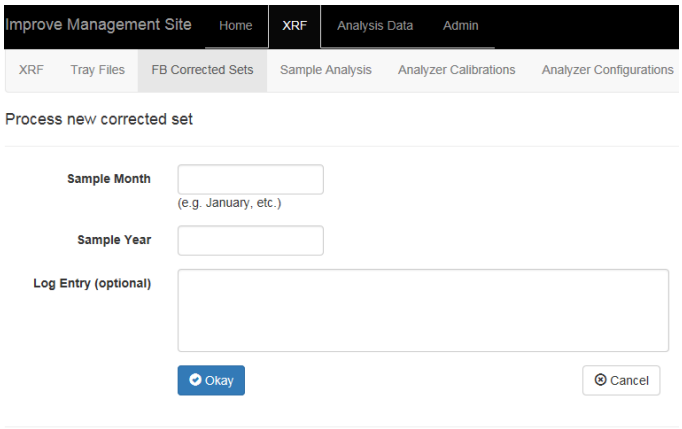


4.1 Creating Set on Webapp

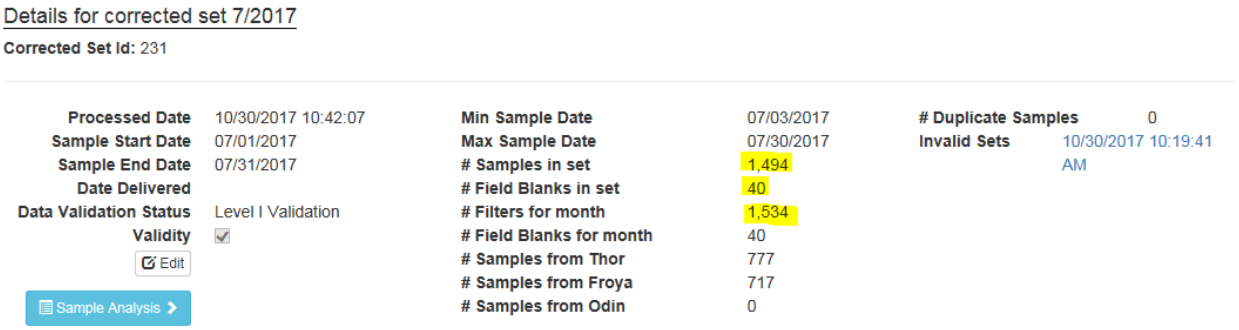
The monthly XRF data set is created on webapp XRF Data Management Pages. Click on FB Corrected Sets → _New set.



Select Month and Year, and click Okay.

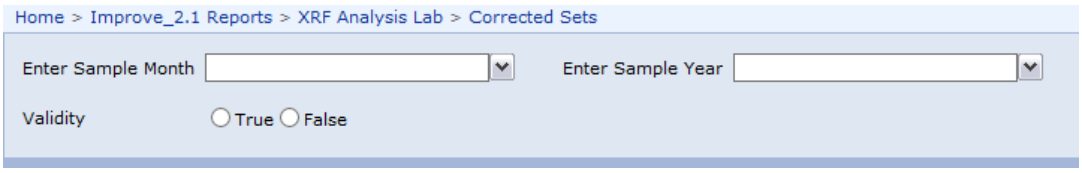


Check sample integrity of the generated set. The sum of "# Samples in set" and "# Field Blanks in set" must match "# Filters for month". Note if there are any repetitions in set. In case of mis-match, investigate the reason and provide resolution.

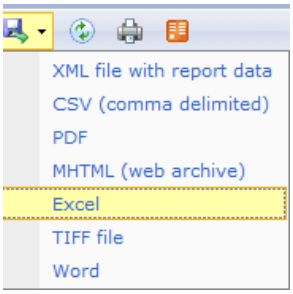


4.2 Accessing the XRF data on cl-sql

To pull the XRF data out, click on http://webapp.improve.crocker.ucdavis.edu/ →XRF→Reports→Reporting Services. This will open a new webpage on SQL Server Reporting Services (by Nov2017, Version Improve_2.1) Click on XRF Analysis Lab → Corrected Sets. Sample Month, Year and Validity (True) are selected on this screen:



Then, View Report button on right corner is clicked. In the next screen, the Set ID is clicked. The report can be viewed in the new screen. The Save button is clicked to select xls data view form.



In the next screen, the Open button is clicked to open the data in xls form.

The xls file must be modified before copy/paste action to the QA template excel file. Perform the following actions:

1) Delete the first row in generated xls file
2) Unmerge column F
3) Delete column G
4) Insert a column between L and M. Name it “Filter comments”
5) In M2, concatenate K and L to place the comments about samples in one column
6) Copy/paste formula of M2 along M column to the end.
7) Copy entire M column and paste as “values”
8) Delete columns K and L.
9) Check the number of samples if matches the sum of samples and FB in the created XRF data set. In case of repetition(s) in set, delete the repetition(s) to match the number. (repetitions in any set can be viewed at Home > Improve_2.1 Reports > Repetitions in Corrected set)

After those modifications, copy the entire sheet and paste into U:\IMPROVE_Lab\XRF_Epsilon5\QA\QAtemplate_Final2017.xlsm sheet “All” (Excel template workbook will be updated/renamed every year).

4.3 Work in QAtemplate xls file

The template file, QATemplate_FinalYYYY.xlsm in U:\IMPROVE_Lab\XRF_Epsilon5\QA, is opened and saved as “MonthYear-work.xlsm” (e.g. Jan2017-work). The copied XRF data in 4.2 is pasted into sheet-*all*. The following steps are employed to check the data:

4.3.1 Data Integrity Check

The macro (Macro1) in the workbook must be first run (The macro in opened excel file must be selected, otherwise excel will stop operating). This macro will update the sheets

NMQD and *FB.* The next step is to check the data integrity. The number of samples with NM and QD is shown in cell A11 of sheet-*NMQD*. This number must be the same as the one in the data set created on webapp (Step 4.1). If not, the inconsistency must be cleared with the laboratory assistant and lab personnel. In case of any missing sample(s), i.e. samples in the logs but not XRF analyzed (supposedly must be XRF analyzed), the created data set is invalidated and the missing sample(s) are analyzed to complete the data set. When the data set is invalidated, the clear comment must be entered to explain why the data set invalidated. The FB integrity also must be checked. When the data integrity is assured, the data check steps are followed starting from checking the IMPROVE network statistics located in the cell DC1 of sheet NMQD. The QC checks are performed for all elemental mass loadings higher than 3 times their reported detection limits.

4.3.2 Correlations

The monthly correlated elements are compared with the historical values (for long term data) (2011-until previous year) in the sheet-*Correlations*. The monthly correlations located in cell BB11 and long-term correlations located in cell CC11 are highlighted in dark for r>0.95 and in light for r between 0.5-0.949. Normally, crustal elements, e.g., Al and Si, are highly correlated. The unusual correlations, e.g. Cu and K, must be noted for any further checks (e.g. *PMvsK* and *basic_check*). The plots in this sheet should be examined for unusual case, e.g. Al vs Si, sample(s) deviation from Mason ratio in high concentrations. The detailed check of these plots will be performed in the sheets *AlvsSi, SivsFe, AlvsFe, AlvsTi, FevsTi, PMvsS* and *PMvsK.*

4.3.3 Mass Ratios

In this sheet, the ratio of sum_of_elements determined by XRF to particulate mass determined by gravimetric measurement is calculated for each sample. Based on the historical data, these ratios are expected to fall between 4 and 49%.

Sorting the cell AI12 by descending will list the samples outside the acceptance criteria, highlighted in dark for ratio>49% and in light for ratio<4%. The outliers must be checked sample by sample. Generally, the cases of ratios over than 49% result from contribution of sea salt to PM, thus, these cases must be checked for increase in Na and Cl. The cases of ratio lower than 4% are typical for some sites, e.g., FRES, PHOE, BYIS, BIRM or results from fire around the site. Increase in K loadings is a good sign of fire around the site in question. In addition, color of such samples will be brownish, which results from brown carbon in biomass. In case K is low and ratio <4%, samples must be visually inspected to look for dark thick deposition resulted from organic carbon (Typical for FRES and BYIS). The ratio over 100% is a good sign of filter swap. In such cases, filters in question must be reweighed to clarify the possible swaps. Sometimes, filters with ratio>100% can be very low loaded (generally <10 ug), which makes the weighing questionable. In such cases, the other samples of the same site must be checked for similar PM and elemental loading profiles. If the sample in question is different from the rest, then neighboring sites must be checked for the same sampling date sample in question. If it is different, and the re-weighing confirms the post weight, the sample must be reported to Level II validation (comment must be put in the sample editing on webapp). The Comments column on sheet-*all* can be checked for samples in question.

4.3.4 AlvsSi

This sheet plots the measured Si versus reconstructed Si based on the Al measurements and Al/Si ratios of, a) long-term (all 2011-up-to-date data), and b) long-term studied month (e.g., Jan2011, 2012, 2013….). Two Si-measured versus Si-constructed plots will be updated automatically except the monthly one linked to column-Q. The column-Q calculates and plots monthly data, and default is linked to slopes of Jan2011-2014 located in sheet-*Correlations,* column-DF. The *Correlations!$DF$11* term in the formula of column-Q must be replaced with studied month (e.g. *Correlations!$DG$11* for Feb), which can be easily done with CTRL+H function of Excel while selecting all column-Q. The blue highlighted cells correspond to values for all data while red ones do for month_2011-YYYY data. The plots set linear regression lines with intercepts zero (blue solid lines), upper acceptance limit (red dotted lines) and lower acceptance limit (green dotted lines). The acceptance limits are calculated as 10% of range of Si-measured (cell P29). Sorting descending the cell T31 (outlier according to all data) will list the outliers. Generally the outliers fall close to the acceptance limits. If sample(s) observed very far from the acceptance limits, the reason must be investigated checking the other samples of the same site and samples of neighboring site collected in the same date of sample(s) in question. If the situation cannot be clarified, this should be noted to the Level II validation.

4.3.5 SivsFe

This sheet plots measured vs constructed Fe based on Si measurements, similar to *AlvsSi* in 4.3.4. The same steps of 4.3.4 must be followed to perform this step. The only difference in 4.3.5 than 4.3.4 is the different Si vs Fe pattern of few sites: BIRM, FRES, PHOE, and BYIS. By the filtering of cell J30, the above listed sites must be unselected to obtain representative plot for the other sites. Generally, more outliers are observed than *AlvsSi* check.

4.3.6 AlvsFe

This is the same as 4.3.5, plotting measured vs constructed Fe based on Al measurements.

4.3.7 AlvsTi

The sheet plots the measured Ti versus reconstructed Ti based on the Al measurements. The only difference than other scatterplots is that it checks the outlier with acceptance limits based on the 15% of the range, due to relatively worse Al vs Ti association than Al vs Si, and Fe.

4.3.8 TivsFe

This plots measured vs constructed Fe based on Ti measurements.

4.3.9 PMvsS

This plots measured vs constructed S based on PM2.5 mass measurements. It checks the outlier with acceptance limits based on the 30% of the range, due to poor association. The samples with high PM but low S must be checked for high K (possible fire) and color by visual inspection. Such filters should not have dark color, either brownish (fire) or grey (crustal contribution).

4.3.10 PMvsK

This plots measured vs constructed K based on PM2.5 mass measurements. It checks the outlier with acceptance limits based on the 30% of the range, due to poor association. The samples with low PM but high K must be checked possible fire by visual inspection. Such filters should have brownish color. In the New Year's eve samples, unusually high K (together with Cu and Sr) can be observed.

4.3.11 Basic_Checks

The samples with S zero, Fe negative, and trace elements (Cu, Zn, Pb, Cr and Ni) with unusually high loadings should be listed here. The reason of zero S must be investigated. Normally, Fe with negative loadings is no more than 10-20 samples. If more, they should be checked. Normally the trace elemental loadings in BYIS, FRES and PHOE are much higher than the other sites. If unusually high loadings are observed in the other sites, the remaining samples must be checked for similar high loadings. If unusually high loadings are observed randomly (only one sample in a month), the Level II validation must be notified (comment must be put in the sample editing on webapp).

4.3.12 Outliers

This sheet is only informative, and lists automatically all the outliers from *MassRatio* and elemental plots' sheets.

4.3.13 FB

This sheet contains the FB results. If any FB has at least two elements higher than 3 times of detection limit, the Level II validation must be notified (comment must be put in the sample editing on webapp). In case a repetitive contamination of FBs from the same site is observed, the Lab Manager must be notified for further checks and maintenance group should be informed of possible site contamination (need for the site maintenance, instrument malfunction, etc.).

4.3.14 QA_change

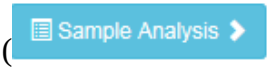
Contains the list of all samples with their changed validity codes. All validity changes implemented during Level I validation will have explanations placed in comments (webapp), visible to Level II validation.

4.3.15 Checks&Changes

Contains the list of all samples need to be checked, i.e. re-weighing, checking PM2.5/PM10 mass, color etc. These samples must contain comments/findings/actions of Level I validator to facilitate the investigation.

4.4 Changing Validity of Samples and Invalidating the Set

On webapp, the samples in the studied set must be accessed to change the validity, if any. If no change/comment requires, no further action is needed, and the set is ready for Level II validation.

To change validity or/and comment, the View Record Details () in corrected set (http://webapp.improve.crocker.ucdavis.edu/Xrf/CorrectedSets) is clicked. Then, Sample Analysis button (

) is clicked. The required validity changes or/and

commenting is done on the samples listed in 4.3.12, if any. After changing/commenting, the current data set must be invalidated (Commenting is optional). To do that, Edit button () in http://webapp.improve.crocker.ucdavis.edu/Xrf/CorrectedSets is clicked. In the next screen,

Valid must be unselected ().

As the last step, the data set must be re-created, and the changes/comments made must be checked. Once new data set is created, validators are notified and the data set is ready for Level II validation.