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

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1.0 PURPOSE AND APPLICABILITY

The purpose of this technical instruction (TI) is to describe the procedure used for the liquid nitrogen (LN2) fill, liquid nitrogen calibration, and detector calibration for the Epsilon 5 (E5) instruments.

2.0 SUMMARY OF THE METHOD

The E5 instruments use LN2 to cool the PAN-32 Ge X-Ray Detector. LN2 fills for each Epsilon are performed on a weekly basis. Several hours after the LN2 fill is completed, detector calibration is performed for each instrument.

3.0 DEFINITIONS

Not Applicable.

4.0 HEALTH AND SAFETY WARNINGS

Not Applicable.

5.0 CAUTIONS

LN2 dewar 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 UCD SOP #301: Attachment 1 on liquid nitrogen safety.

6.0 INTERFERENCES

Not Applicable.

7.0 PERSONNEL QUALIFICATIONS, DUTIES AND TRAINING

Only trained lab personnel designated by the laboratory manager may perform LN2 fills. A course offered on the UC Davis campus, “Safe Use of Cryogenic Liquids,” is highly recommended (http://safetyservices.ucdavis.edu/tr/cd/suoclcd).

8.0 EQUIPMENT AND SUPPLIES

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

9.1 Epsilon 5 LN2 Fill

The detector in the E5 must be cooled with LN2. To keep the level of LN2 consistent, the dewar is filled on a weekly basis. Under special circumstances such as holidays, the dewar can be filled on a different schedule with prior Laboratory Manager approval.

Figure 1. Maintenance Master Screen and Detector Maintenance Window.

1. The E5 has several potential values for “Cooling status” that are displayed on the Maintenance screen (Figure 1, circled in blue). The statuses 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 dewar with LN2. Check this by clicking on the picture of the LN2 dewar (Figure 1, circled in red). Refer to section 9.4 Detector States for additional information.

2. Open the LN2 fill access door on the right-hand side of the E5.

3. Connect the LN2 tubing to the adapter.

4. Connect the tubing to the LN2 tank and then carefully insert the adapter into the E5 dewar.
5. Slowly open the valve on the LN2 tank while ensuring that the line from the LN2 tank into the dewar fill tube does not come apart. In addition, start the timer the moment the he valve to the LN2 tank is open.

6. Note the time required to fill the dewar and the temperature of the cabinet in the corresponding log book. Create a new entry with the same information in the Microsoft Access log on the desktop.

9.2 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 beam stop is utilized to perform the measurements. The software automatically performs the energy calibration calculations.

1. Click on the System drop-down menu, then Detector Calibration.

2. Select Calibrate All.

Figure 2. Detector Calibration sub-window.

3. When detector calibration is completed, click the Detector Calibration window to activate window. Using the keyboard Ctrl +P, verify the data is set to “copy to the clipboard” in a “delimited” format, and click OK. Open the desktop folder named “Detector and LN Calibrations”, then open the excel sheet “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 3). If the values exceed the acceptable limits, repeat detector calibrations (Step 2 above) and notify the Laboratory Manager.
Figure 3. Detector Calibration Graph, q value over time.

5. If the values are normal, continue to step 6 below. If the values exceed the acceptable limits a second time, continue to step 9.3 Resolution Test.

6. In the E5 software, copy the screen using the snipping tool, then open the folder “Detector and LN Calibrations”. Type the date and press \texttt{CTRL+V} to paste the screen shot. Save and close the file.

7. In the Epsilon Software, close the sub-windows for the detector and the detector calibrations.

9.3 Resolution Test

The purpose of the resolution test is to gauge the method’s ability to differentiate detected peaks from individual X-rays. This is especially important in regions of the X-ray spectra where characteristic X-ray peaks overlap. The test measures the full width half max (FWHM) of the Mn Kα peak, which is the standard peak for this purpose. The measured FWHM should be less than the manufacturer’s specification of 140 eV. Only approved personnel may perform the resolution test. Check with the Lab Manager and/or Spectroscopist.

1. Verify the Resolution application has been installed on the instrument. Notify the Spectroscopist if the application needs to be created.
2. Locate Petri slide containing the Mn pellet.
3. Select the Resolution test application
4. Go to “Add Measurement”. Type “Mn fused bead 402300074331” in SampleID.
5. Place the Mn pellet in a stainless steel cup and load to the instrument.
6. Queue the sample for analysis.
7. To review the results, open the resolution test application.
8. Highlight the result file and open the spectra window. To view the spectra select the spectra button on the lower right hand corner.
9. Check the fwhm value in the lower left corner, see Figure 4.
10. Verify the energy for Mn Kα has not shifted. The energy calibration is automatic, a shift is not expected.

11. Notify the Laboratory Manager and spectroscopist of the resolution test results.

### 9.4 Epsilon 5 Detector Cooling Status

The different detector cooling statuses that may be encountered by the user during operation are briefly described. The user software displays the cooling status in the detector maintenance window (Figure 1).

**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 LN2.

**Cooling:** After the LN2 level sensor has detected more than 20 degrees temperature decrease due to filling the dewar, the user must wait 6 hours before switching on the detector high tension in order to allow the crystal and the FET to cool down to -178°C.

**Pre-operational:** The system is available for normal use. As the LN2 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 LN2 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 LN2 as soon as possible. There are 100 hours (4 days) left to refill the dewar.

**Forced heat-up:** The detector crystal must be brought to room temperature. This can be done by waiting for the status to reach ‘filling allowed’. Additionally, acceleration of this procedure can be achieved by blowing with dry air into the liquid nitrogen fill opening.

### 10.0 QUALITY ASSURANCE AND QUALITY CONTROL

Not applicable.
11.0 REFERENCES

Not applicable.

TI 301B: Tray File Web Creation

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1.0 PURPOSE AND APPLICABILITY

The purpose of this technical information (TI) is to describe the process of generating tray files using the IMPROVE web app. Tray files are a set of procedures that are used to queue samples to the Epsilon 5 (E5) software.
2.0 SUMMARY OF THE METHOD
Tray files are generated by utilizing the tray file generator on the IMPROVE web app. After tray files are generated, the files are saved on the U:\ drive, which can be accessed when they are ready for use. The tray files are transferred to the respective XRF instrument for use.

3.0 DEFINITIONS
Not Applicable.

4.0 HEALTH AND SAFETY WARNINGS
Not Applicable.

5.0 CAUTIONS
Pay close attention when making modifications to tray files. The information in a tray file must follow a specified format in order for the LIMS program (see TI 301C) to translate the file properly.

6.0 INTERFERENCES
Not applicable.

7.0 PERSONNEL QUALIFICATIONS, DUTIES AND TRAINING
The lab manager, spectroscopist, and designated lab technicians can generate tray files. Permissions to access and work with the IMPROVE web app are granted by the IMPROVE Database Manager, or any member of the IMPROVE Software Development Team.

8.0 EQUIPMENT AND SUPPLIES
- Tray file labels

9.0 PROCEDURAL STEPS

9.1 Tray Files
Written in .XML format, tray files are used to queue samples to the E5 software. A diagram depicting the composition of a typical 8-position tray file is shown in Figure 1.
9.2 Preparation Before Generating Tray files

9.2.1 Creating Tray Files

1) Go to the IMPROVE web app - https://improve.aqrc.ucdavis.edu/
2) Under the XRF Menu, click on Tray files sub-menu.
3) On the first form, specify position cup format, # of files to generate, 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 an integer)
   • **Sample Year**: indicate what Sample Year to analyze (input in YYYY format)
   • **Analyzer**: select which analyzer for the tray files (Odin, Froya, Thor, Baldur, Nanna)
4) Click on **Continue**.
5) 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)

6) Click on .

7) To download the .xml files and save, click on . The files are saved in the analyzer specific folder located in U:\IMPROVE_Lab\Trayfiles.

### 9.2.2 Generating Tray Labels


2) Open XRF Analysis Lab and click Sample Analysis Tray File List.

3) From the U:\ drive, open the last tray file label created - U:\IMPROVE_Lab\XRF_Epsilon5\Cruz\trayfilestickers_working\archived

4) Use the .xml file to look up the first sample in the tray file 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) Verify the information is correct on the print tab, save the file with the current date, and print the labels.

### 9.2.3 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 tray file will not be re-generated. If a sample needs to be re-analyzed, a copy of the original tray file 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.

### 9.2.4 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 UCD SOP #301: X-ray Fluorescence Analysis on PTFE Filters section 9.2, “Calibration”. In special cases, a user may contact the IMPROVE Software Development Team e-mail (cnldevteam@ad3.ucdavis.edu) for possible work-around.
9.2.5 Tray Checks

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

1) Printed tray file 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 room 116 on the shelves labeled “unassigned”. Locate the tray that corresponds to the first generated tray file 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, initial the bottom of the inventory label next to tray check.

5) Place the tray file inventory label on the front-left side of the white Petri tray (Figure 2).

Figure 2. 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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1.0 PURPOSE AND APPLICABILITY
The purpose of this technical information (TI) is to describe the process of loading and unloading samples using standard cups in 8-position trays in the Epsilon 5 (E5) EDXRF instruments.

2.0 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 E5 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.

3.0 DEFINITIONS
Not Applicable.

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

5.0 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 E5 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 E5 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.

6.0 INTERFERENCES
Not Applicable.

7.0 PERSONNEL QUALIFICATIONS, DUTIES AND TRAINING
The lab manager, spectroscopist, and designated lab technicians perform sample changes on the Epsilon 5 instruments.

8.0 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

9.0 PROCEDURAL STEPS
Because the E5 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.

9.1 Overview and General Definitions
The following picture outlines the terms given to each element that houses the samples:
The E5 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 have an assigned “S” tray that is analyzed daily for monitoring sampling performance.

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.
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 4. 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). 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 5. Petri dish holder.
9.2 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 6. “Free to Open” light.](image)

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 7. Layout of petri dishes.](image)

5) Pick up the sample retaining cup from position 1 in the tray being unloaded. 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. Verify the sticker on the Petri matches the information on the Epsilon sample changer software.

**Figure 8.** Sample retaining cup handling and positioning.

6) 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 9.** 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.

9.3 Removing the Analyzed Filters from the Queue

After removing the analyzed filters, they need to be deleted from the Epsilon sample changer software. Towards the right side of the sample changer window, there is a \( \mathbb{R} \) 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.

9.4 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 301D QA/QC of XRF Analysis for more information.

9.5 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.
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) Go to the “Manual Control” tab, in the sample changer window, 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 10. Sample tray file.
9.6 Loading New Samples into the Sample Changer

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.

9.7 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.

9.8 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.

10.0 ADDITIONAL CHECKS AND PROCEDURES

10.1 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 “Tray files”. Select all the relevant tray files from the analyzer specific tray file folder found on the U drive and copy them to the tray file folder on the analyzers desktop.

10.2 Adding 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.

10) Queue the samples

10.3 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.

10.4 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.

10.5 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.
10.6 Creating Tray Files

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

10.7 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) Select 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.

10.8 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 drawer in room 116. 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 purpose of this technical instruction (TI) is to convey the quality assurance/control (QA/QC) steps applied in the elemental mass loadings measurements of PM$_{2.5}$ loaded filters. These filters are collected via IMPROVE network using EDXRF systems, namely Panalytical Epsilon 5. The scope is to ensure good laboratory practice of element measurements on PM$_{2.5}$ loaded filters including calibration, verification of calibration, and routine quality control checks (daily, weekly and monthly). This creates an analysis of blanks, multi-elemental reference materials and selected IMPROVE samples, later referred to as “Re-analysis set”.

2.0 DEFINITIONS

- **NIST Standard Reference Material (SRM):** a certified reference material issued from the National Institute of Standards and Technology, used to institute quality assurance and control.
- **Laboratory Blanks (TB):** These are Teflon filters placed in the S trays of each Epsilon 5 (E5) for daily analysis. Unexposed filters are selected from batches of filters used for regular PM2.5 sampling at IMPROVE sites. The checking/examining is performed on the elemental loadings (µg/cm²). The Method Detection Limit (MDL) floors, are calculated as three times the standard deviations of a set of laboratory blanks. The acceptance criteria are calculated as three times the standard deviations added to the mean of lab blank’s loadings.
- **Multi-Element Reference Materials generated at UCD (UCD-ME):** UCD-ME samples are generated from certified multi-elemental solutions and contain the majority of IMPROVE reported elements. Instrument specific UCD-MEs are analyzed daily while a designated UCD-ME is analyzed weekly on all E5s for inter-instrumental comparison. The reference loadings are calculated as the average of the first five measurements after calibration. Acceptance limits are applied as ±10% of the reference loadings.
- **Al & Si Samples from Micromatter (MM-Al&Si):** These samples contain Al and Si, and are analyzed weekly. The reference loadings are calculated as the average of the first five measurements after calibration. The deviations of ±5% and ±10% from reference loadings serve as warning and acceptance limits, respectively.
- **Re-analysis Samples (RA):** A selected set of sixteen UCD-made multi-elemental samples with elemental mass loadings approximating the range of expected loadings from the IMPROVE network. The Re-analysis set is analyzed on all E5s every month to provide long-term reproducibility and inter-instrumental compatibility records. The mass loadings for all reported elements for each sample obtained each month are compared to pre-determined reference loadings. The reference loadings are determined as the mean results of 5 measurements by each E5.

- **z-score:** The ratio of absolute difference between each result from monthly re-analysis and reference loadings to accompanying uncertainty for element i (Equation 1).

\[ z_i = \frac{|c_{E5,i} - c_{ref,i}|}{\sqrt{U_{cE5,i}^2 + U_{cref,i}^2}} \]

Equation 1
where \( c_{E5} \) is the mass loading measured (\( \mu g/cm^2 \)), \( c_{ref} \) 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 \( z \)-score should remain \( \leq 1 \) for specified elements.

- **Relative Expanded Uncertainty (Urel):** The ratio of uncertainty estimated by the propagation of contributions of each factor effective on the measurement to the result (%). \( U_{rel} \) is estimated by the summation of contributions from the calibration function, repeatability and uncertainty of calibration standards.

- **Absolute Bias:** Ratio of the absolute difference between measured and certified loading of NIST SRM 2783 to certified loading (%). The absolute bias for selected elements (Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb) must remain within element-specific acceptance limits determined as root-mean-squared-relative-errors (RMSREs; Equation 2) plus three times standard deviations (SDs) from 44 monthly measurements between January 2013 and July 2016.

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

Equation 2

Where \( m \) refers to measurement month.

### 3.0 GENERAL GUIDELINES

This document is intended to guide users for verifying calibration in order to begin analyzing samples, as well as checking the performance of EDXRF analyzers routinely, including analysis of blanks and samples, double checking results, and appropriate response to 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 and Verification

The procedure for calibration verification is shown in Figure 1, and is summarized in Table 1. The absolute bias of SRM 2783 must be equal to or less than the documented 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 must be equal to or less than 10% for stoichiometric standards of IMPROVE reported elements. In cases where Urel is higher than 10%, calibration functions and spectra are re-examined to determine the cause of issues. Further investigation, e.g., checking the calibration lines of corresponding elements from other E5s, is performed until the reason of the exceedance has been identified. If similar deviations are observed on other E5s, the orientation of the standard will be examined. If the orientation is correct, the quality of the corresponding standards is suspect and will be excluded from calibration. If the problem is not resolved by excluding disqualified standard(s), calibration with the currently selected standards will be performed a second time. If recalibration does not show changes from the original calibration, the Laboratory Manager will
be notified for further instructions. Possible corrective actions may include halting analysis and ordering new standards.

The finalized calibration functions are verified by analyzing blanks, multi-elemental reference materials and a re-analysis set. Meeting the quality control criteria assures the integrity of analysis for IMPROVE samples. Failure to meet these criteria requires further investigation to resolve all identified issues.

**Figure 1.** The flowchart of calibration verification.
Table 1. The calibration verification activities, criteria and corrective actions.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Criterion</th>
<th>Corrective Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncertainty of calibration</td>
<td>$U_{rel} \leq 10%$ for stoichiometric standards</td>
<td>• Check calibration line and spectra&lt;br&gt;• Check standard(s) for damage/contamination&lt;br&gt;• Exclude standard(s) from calibration line&lt;br&gt;• Further cross-instrumental testing&lt;br&gt;• Recalibration with current or new standards</td>
</tr>
<tr>
<td>NIST SRM 2783</td>
<td>Absolute bias $\leq$ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb</td>
<td>• Check sample and blank for damage/contamination&lt;br&gt;• Further cross-instrumental testing&lt;br&gt;• Recalibration with current or new standards</td>
</tr>
<tr>
<td>PTFE Blank</td>
<td>$\leq$ acceptance limits with exceedance of two elements at least in two consecutive days</td>
<td>• Change/clean if contaminated/damaged&lt;br&gt;• Clean the diaphragm, if necessary&lt;br&gt;• Further cross-instrumental testing</td>
</tr>
<tr>
<td>MM-Al&amp;Si</td>
<td>$\pm 10%$ of reference mass loadings</td>
<td>• Check sample(s) for damage/contamination&lt;br&gt;• Further cross-instrumental testing&lt;br&gt;• Replace sample(s) as necessary</td>
</tr>
<tr>
<td>UCD-ME</td>
<td>$\pm 10%$ of reference mass loadings</td>
<td></td>
</tr>
<tr>
<td>Re-analysis set</td>
<td>$z$-score $\leq 1$ for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr</td>
<td></td>
</tr>
</tbody>
</table>

4.2 Routine QC of EDXRF Analyzers

The procedures of the routine QC of the EDXRF analyzers’ performance are shown in Figure 2 and is summarized in Table 2.

Figure 2. The flowchart of routine QC of EDXRF instruments’ performance.
Table 2. The routine QC activities, criteria and corrective actions.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Frequency</th>
<th>Criterion</th>
<th>Corrective Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector Calibration</td>
<td>Weekly</td>
<td>None (An automated process done by XRF software)</td>
<td>• XRF software automatically adjust the energy channels</td>
</tr>
<tr>
<td>PTFE Blank</td>
<td>Daily</td>
<td>≤ acceptance limits with exceedance of two elements at least in two consecutive days</td>
<td>• Change/clean blank if contaminated/damaged</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Clean the diaphragm, if necessary</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Further cross-instrumental testing</td>
</tr>
<tr>
<td>UCD-made ME-RMs</td>
<td>Daily</td>
<td>±10% of reference mass loadings with exceedance of any element not to occur in more than two consecutive days</td>
<td>• Check sample for damage/contamination</td>
</tr>
<tr>
<td>Micromatter Al&amp;Si RMs</td>
<td>Weekly</td>
<td>±10% of reference mass loadings</td>
<td>• Further cross-instrumental testing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Replace sample if necessary</td>
</tr>
<tr>
<td>UCD-made ME-RMs</td>
<td>Weekly</td>
<td>±10% of reference mass loadings with exceedance of any element not to occur in more than two consecutive days</td>
<td></td>
</tr>
<tr>
<td>Re-analysis set</td>
<td>Monthly</td>
<td>z-score≤1 for Al, Si, K, Ca, Ti, Mn, Fe, Zn, Se and Sr</td>
<td></td>
</tr>
<tr>
<td>SRM 2783</td>
<td>Monthly</td>
<td>Absolute bias ≤ acceptance for Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb</td>
<td></td>
</tr>
</tbody>
</table>

4.2.1 Daily Analysis

The S trays containing analyzer specific TB and UCD-ME are 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 via web browser at [http://analysis.crocker.ucdavis.edu:3838/xrfQC/](http://analysis.crocker.ucdavis.edu:3838/xrfQC/)

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

4.2.1.1 QC of TBs

The plot posted at [http://analysis.crocker.ucdavis.edu:3838/xrfQC/](http://analysis.crocker.ucdavis.edu:3838/xrfQC/) (Figure 3) must be checked for any exceedances, where two or more elements out of bounds result in failure. A small and gradual increase for low Z elements, e.g., Ca, S and Cl, typically indicates atmospheric contamination of TB while increases in Cu and Zn are likely due to instrument contamination, e.g., abrasion of rubber components in the analytical chamber. The first action is to airbrush the outlying TB filters. If loadings of elements exceeding the limits decrease to normal levels, no further action is necessary and the analysis may continue. If not, the anomalous TB filters are replaced with new ones. Repeated failure would suggest analyzer related contamination. In that case, cleaning the analytical chamber and/or diaphragm should solve the issue. The TB filters are then reanalyzed to determine the effectiveness of the cleaning. If the problem is not resolved, analysis on that instrument is halted and additional testing must be performed to identify and address...
the issue. For example, in cases of sudden, large increases in loadings for few elements, the following are possible causes:

- Change in geometry (most likely tube or detector distance/angle)
- Filter (or other material) present in the chamber in addition to the analyte
- Sample filter off center during analysis, indicated by Zn spikes in the spectra due to the beam interaction with the filter support ring

The analysis must be halted until the problem is resolved and all samples analyzed within the period in question must be reanalyzed.

Figure 3. The QC plot of TB.

4.2.1.2 QC of UCD-ME

The QC plot shown in Fig. 4 includes the intensity and mass loadings in real time for each instrument. Acceptance limits may change slightly after calibration and when any changes are made to the instruments (e.g. new X-ray tube, new detector, etc.).

If the QC limits are exceeded for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb in more than two consecutive days, an investigation is initiated. The cross-analyzers check, analysis of other ME samples, analysis of single element standards, and a subset of the tests listed in Table 2 are performed to address the exceedences, which may have been the result of damage to the ME or contamination (particularly Zn, Cu and Ca).

It should be noted that UCD-MEs may tear after ~250 analyses. Therefore, multiple MEs at certain levels must be generated to assure availability in case of damage.
4.2.2 Weekly Analysis

Weekly analyses include instrument specific MM-Al&Si and a UCD-ME to be analyzed on three E5s. The analyzed samples must be free of contamination 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 are designated on the MM-Al&Si plot). The UCD-ME plot is examined for inter-analyzer comparison, since that sample is analyzed on three E5s. If limits are exceeded for the elements listed above in more than two consecutive measurements, further testing as listed in Table 2 is required to determine the issue.

The weekly analyzed samples are loaded manually each time; therefore, special attention must be paid to analyze with the active IMPROVE application as well as correct sample identifier. Results must be invalidated if either of these parameters are incorrect.
Figure 5. The QC plot of MM-Al&Si.

Figure 6. The QC plots of weekly analyzed UCD-ME.
4.2.3 Monthly Analysis

The Re-analysis set is analyzed monthly on analyzers using the active IMPROVE application. SRM 2783 must be blank subtracted for comparison with certified mass loadings. Since the blank of SRM 2783 has shown highly repeatable results over years, that blank is analyzed only once in each calibration. When SRM 2783 is analyzed every month, the SRM blank is subtracted manually in an Excel spreadsheet for comparison with certified loadings.

The z-score plot (currently stored at U:\IMPROVE_Lab\XRF_Epsilon5\QA\Reanalysis\Inter_Instruments\Reanalysis_NewSet_GUM.xls while web-app plots are in development) shows mean z-score values of 17 samples based on any reference values, see Figure 7. The satisfactory level (z≤1) is checked for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr. If the limits are exceeded, additional tests must be implemented to address the problem. The folders located at ..\QA\Reanalysis\Inter_Instruments contain analyzer-specific workbooks for each year, which provide calculations and graphs of regression slopes, intercepts, and $R^2$ between monthly results and two reference values (see Figure 8a). In addition, the relative expanded uncertainties based on the error propagation are calculated and plotted in element specific worksheets (see Figure 8b). Any unusual results that differ from long-term trends must be investigated further. The Sheet1 of these workbooks contains a data summary and plots of the annual variation of slopes.

Figure 7. The plot of z-score for Re-analysis set.
Figure 8. a) The comparison of monthly results of Re-analysis 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 SRM 2783 (Figure 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 must be equal to or less than the acceptance limits. In cases of exceedance, the actions in Table 2 must be taken to address the issue. Over 4 years of data show that SRM results are very repetitive, but sample specific. This means that in case #1720 is changed, the acceptance limits must be re-determined. The most probable causes of failure in meeting the criteria are upside-down analysis and improper placement on the insert of the sample cup. Special care must be taken for proper filter loading.

Figure 9. The plot of absolute bias for SRM 2783 (#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 3. An example of weekly QC report for daily and weekly monitoring of analyzers’ performance.
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: The XRF Data Management Pages are webpages related to the administration and processing of XRF data (http://webapp.improve.crocker.ucdavis.edu/Xrf/Home).

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, 10th, 50th and 90th 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 vs Si, but calculates and plots for Ti;
Fe vs Ti 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 the 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.
4.1 Creating Set on Web App

The monthly XRF data set is created on the web app 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 mismatch, 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/](http://webapp.improve.crocker.ucdavis.edu/) →XRF→Reports→Reporting Services. This will open a new web page 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, select the Open button to retrieve 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 (https://improve.aqrc.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 https://improve.aqrc.ucdavis.edu/Xrf/CorrectedSets is clicked. In the next screen, Valid must be unselected ( Valid ).

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.