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UCD IMPROVE Technical Instruction #301A

LN2 Fills and Detector Calibration

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

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1. PURPOSE AND APPLICABILITY

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

2. SUMMARY OF THE METHOD

The E5 instruments use LN2 to cool the PAN-32 Ge X-Ray Detector. LN2 fills for each Epsilon 5 are performed on a weekly basis. Several hours after the LN2 fill is completed, a detector calibration is performed for each instrument.

3. DEFINITIONS

- LN2: liquid nitrogen
- PPE: Personal protective equipment
- E5: PANalytical Epsilon 5 XRF system

4. HEALTH AND SAFETY WARNINGS

Cryogenic liquids, such as liquid nitrogen, are extremely cold. Contact between cryogenic liquids and exposed skin can produce a painful burn or loss of vision through contact with the eye. Always wear proper personal protective equipment including a buttoned lab coat, cryogenic apron, long pants or a long skirt, heavy leather gloves (or cryogen handling gloves), safety goggles, and a face shield (when the risk of splash is high) whenever handling cryogenic liquids.

Asphyxiation is another hazard when working with cryogenic liquids. If vented into a closed space, a cryogenic liquid will vaporize, displacing oxygen and possibly causing asphyxia. For this reason, never store a container of cryogenic liquid in an enclosed space.

5. CAUTIONS

LN2 dewar must be handled with care in ventilated rooms. Proper personal protective equipment (PPE) must be worn, including a face shield, 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 and the UC Davis SafetyNet 58: Safety Precautions for Cryogenic Liquids (https://safetyservices.ucdavis.edu/safetynet/safety-precautions-for-cryogenic-liquids).

6. INTERFERENCES

Not applicable.

7. PERSONNEL QUALIFICATIONS

T 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 required (https://safetyservices.ucdavis.edu/training/cryogen-safety).

8. EQUIPMENT AND SUPPLIES

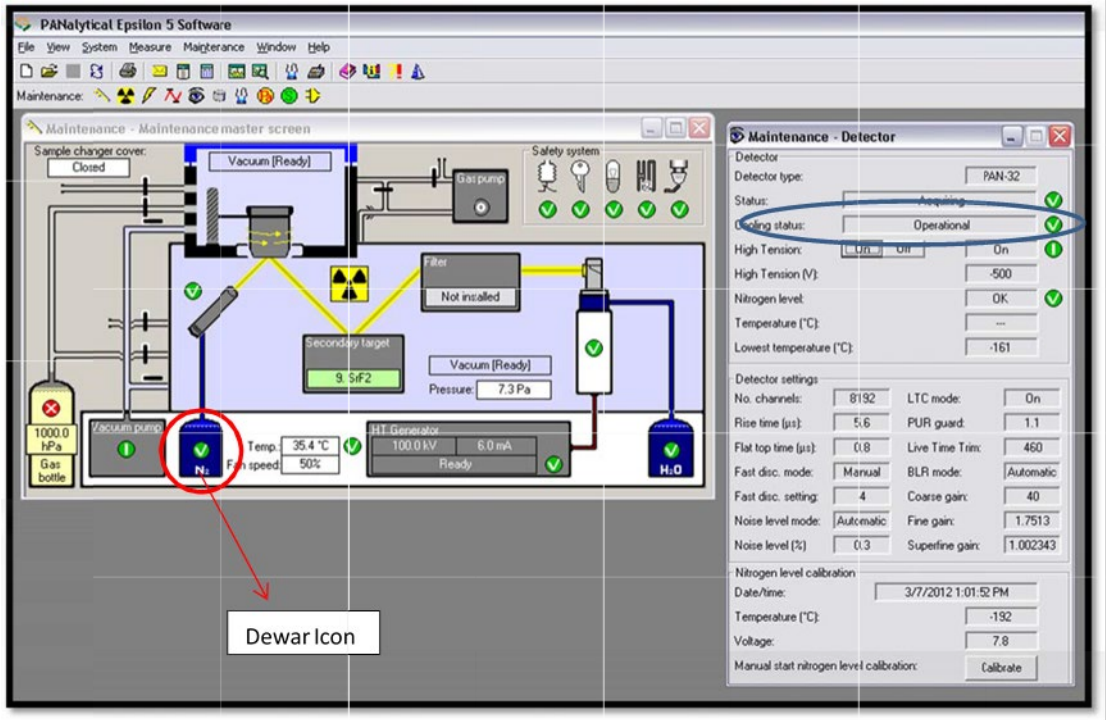
- Liquid nitrogen tank
- Liquid nitrogen tubing
- Adapter
- Safety glasses/face shield
- Cryogenic safety gloves
- Laboratory coat

9. PROCEDURAL STEPS

9.1 Epsilon 5 LN2 Fill

The detector in the Epsilon 5 (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 if it is not already attached.
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, note the time the valve to the LN2 is opened (this will be used to record the length of time required to fill the dewar).
6. During filling, nitrogen gas will exhaust from the dewar vent at the back of the E5.
7. The dewar is full when liquid nitrogen begins to steadily discharge from the rear vent of the E5. Close the valve on the LN2 tank.

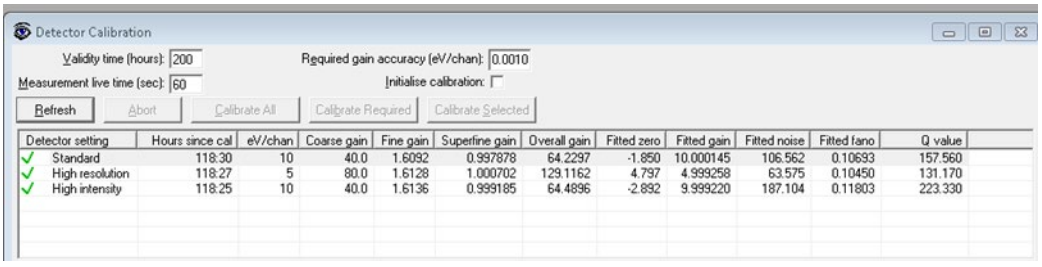
   Record the time required to fill the dewar and the temperature of the cabinet in the corresponding log book.

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**.

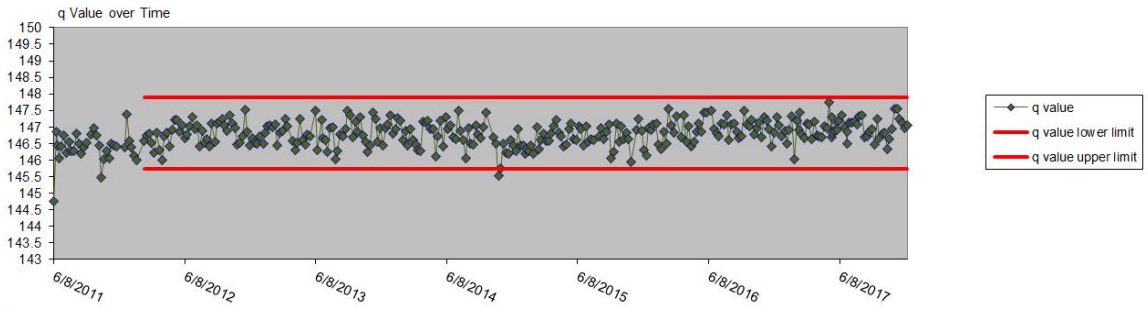
Figure 2. Detector Calibration sub-window.



3. When detector calibration is completed, click the Detector Calibration window to activate window. Press 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", where Name is the name of the instrument being calibrated. Paste the corresponding numbers at the bottom of the data set based on their respective setting.

4. Review the q value and verify all the values are within the acceptable limits, as shown in Figure 3 below. If the values exceed the acceptable limits, repeat detector calibrations starting with step 2 above.

Figure 3. Detector Calibrations Graph, q value over Time.



5. If the values are within the bounds, continue to step 6. If the values exceed the acceptable limits a second time, notify the spectroscopist or lab manager.

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 CTRL+V to paste the screen grab. Save and close the file.

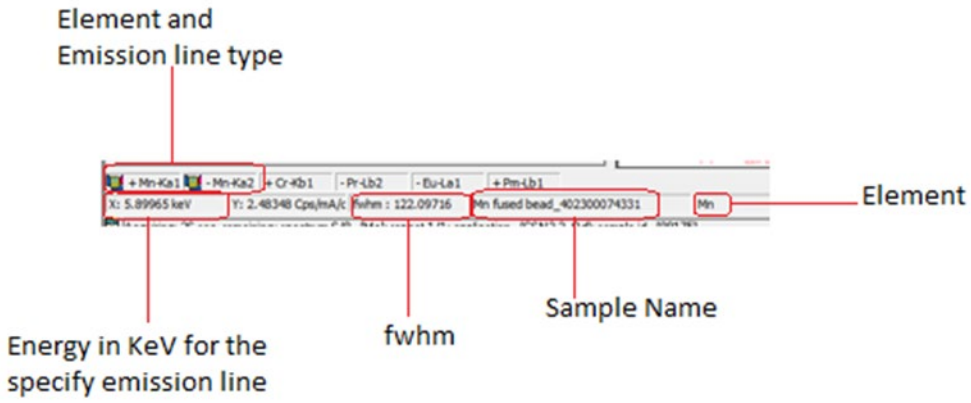
7. In the Epsilon Software, close the sub-windows for the detector and the detector calibrations.

9.3 Resolution Test

1. This test is performed when there is a question about recognition of specific peaks in the spectra. 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.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 and insure the resolution test application is selected.
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.

Figure 4. Resolution Test Information.



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 of the Epsilon 5 during operation are briefly described. The user software displays the cooling status in the detector maintenance window (Figure 1). In addition to the statuses described below each E5 is equipped with an external LN2 alarm. In the event the LN2 is near empty an audible alarm will sound until refilled.

***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 ºC.

***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 has warmed above LN2 temperatures and *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. QUALITY ASSURANCE AND QUALITY CONTROL

Not applicable.

11. REFERENCES

Epsilon 5 EDXRF Spectrometer System User's Guide.

UC Davis SafetyNet 58: Safety Precautions for Cryogenic Liquids (https://safetyservices.ucdavis.edu/safetynet/safety-precautions-for-cryogenic-liquids).

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UCD IMPROVE Technical Instruction #301B

Sample Changes for 8-Position Trays

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

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1. PURPOSE AND APPLICABILITY

The purpose of this technical information (TI) document is to describe the process of loading and unloading samples using standard cups in 8-position trays in the Epsilon 5 (E5) Energy Dispersive X-ray Fluorescence (EDXRF, referred to as XRF) instruments.

2. SUMMARY OF THE METHOD

XRF queue files are generated for each IMPROVE set number, which include the filter barcode, sample identity and application name. The scanning capabilities of the PANalytical software are used to ingest the sample information from the XRF queue file into the sample changer. Filters are transferred from Petri dishes into cups immediately after scanning the barcode. The cups are placed into one of six 8-position trays (as assigned during barcode scanning). The instrument name, assigned tray and position number are recorded on the printed inventory sheet. 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. DEFINITIONS

Not applicable.

4. HEALTH AND SAFETY WARNINGS

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

5. CAUTIONS

Once filters are placed into cups, they may be identified by the filter barcode. In some cases, filters do not have this information; these filters 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. Similar caution must be taken when unloading filters from the cups. Ensure 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 excel log on the U-drive (U:\IMPROVE_Lab\XRF_Epsilon5\Problems). 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 the XRF electronic or physical log records are required for filter issues.

6. INTERFERENCES

Not applicable.

7. PERSONNEL QUALIFICATIONS

The lab manager, spectroscopist, and designated lab technicians perform sample changes on the Epsilon 5 instruments. All users of the XRF systems must have taken and passed the University safety class, "Radiation Safety For Users Of Radiation Producing Machines", and must maintain required refresher trainings.

8. EQUIPMENT AND SUPPLIES

- Sample holder insert
- Sample holder cups
- 8-position sample trays (labeled A-F)
- 4-position sample tray (labeled S)
- Forceps
- XRF queue file generated from IMPROVE web app
- Barcode scanner
- Labeled IMPROVE trays with samples
- Printed inventory list (per tray)
- Log books (physical and electronic)
- Petri dish holder

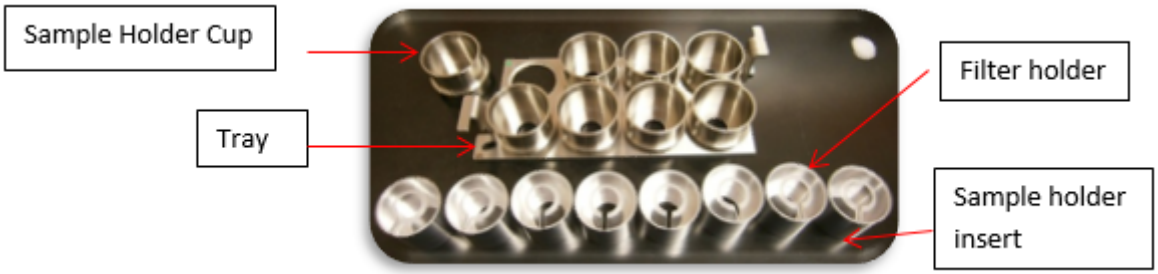
9. PROCEDURAL STEPS

Because the E5 instruments run twenty-four hours a day and seven days a week, trays must be unloaded before 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

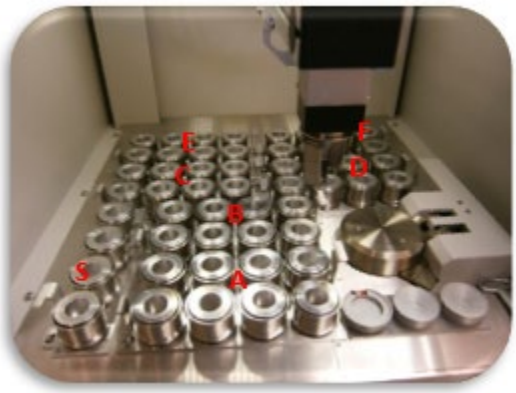
The sample assembly components for loading 25 mm filters are shown in Figure 1.

Figure 1. 8-position tray contents.



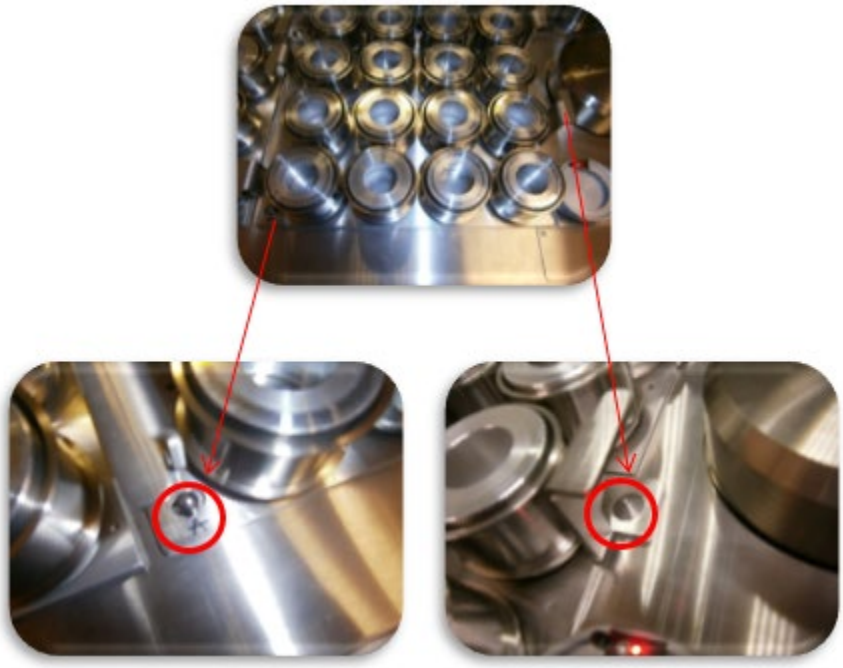
The E5 sample changer compartment holds six 8-position sample trays labeled A-F. Positions in the tray are numbered #1-8. There is also one 4-position tray labeled S. The "S" tray houses the Teflon® blank and a multi-elemental reference filter. Each Epsilon 5 have an assigned "S" tray that is analyzed daily for monitoring sampling performance.

Figure 2. 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.

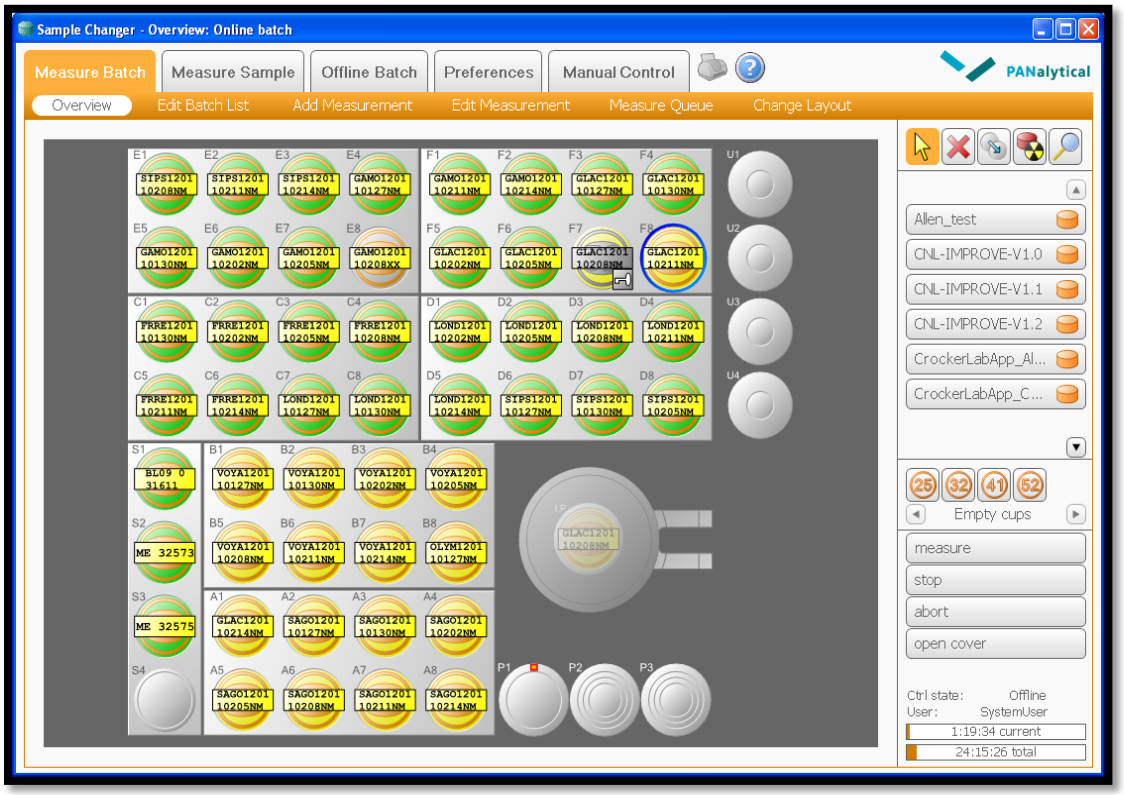
Figure 3. Tray keys.



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 (e.g. E8)
- Yellow/Orange: Queued to be measured (e.g. F8, Tray A, Tray B)
- Green/Orange: Measured and okay (e.g. 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. Green "Free to Open" light.

1) IMPROVE samples are assigned an XRF tray and position during the loading process. At the end of the week a laboratory technician may load a partial tray to maximize the number of samples analyzed over the weekend. Before you begin unloading/loading samples check the printed inventory sheets for notes. Never remove a tray if the instrument is currently analyzing a sample from this tray. Removing an active tray may result in alignment issues, error or a halt in analysis.
2) Note which trays have completed analysis. The trays are unloaded in alphabetical order. After unloading the "F" tray continue with the "A" tray.
3) After checking all eight 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.
4) Set the tray on the desk or sample handling table and close the sample changer cover.
5) Remove the Petri dishes in the corresponding compartment of the Petri dish holder. Begin with the Petri dish on the top of the stack, verify the information on the Petri label matches the filter information on the sample changer screen. Place this Petri dish on the desk/sample handling bench.

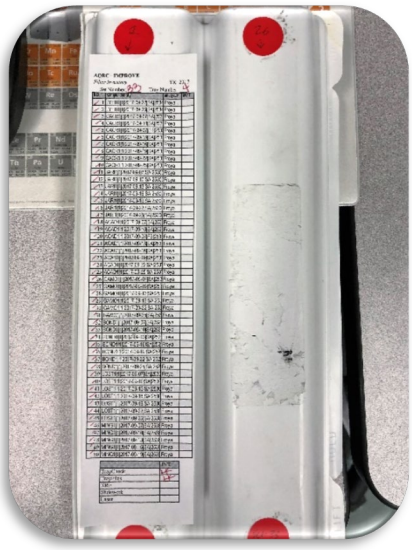
Figure 7. Layout of Petri dishes.

6) Pick up the sample holder cup from position 1 in the tray being unloaded. Place one finger on the inner sample holder insert for support, then turn the sampling cup upside down and place it on the desk/sample handling bench.

Figure 8. Sample holder cup handling and positioning.

7) Remove the sample holder cup by lifting it up and off of the sample holder insert. 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.
8) Place the Petri dish in its white Petri tray (located in the right-hand side of the cabinet for each instrument). Confirm that it is the correct tray by examining the filter inventory label on top of the tray.

Figure 9. Petri tray and inventory label.



9) Place the sample holder insert back into the sample holder cup.
10) Repeat steps 5-9 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 9.9 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.
11) NOTE: Remember that for now, some 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 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 to 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.

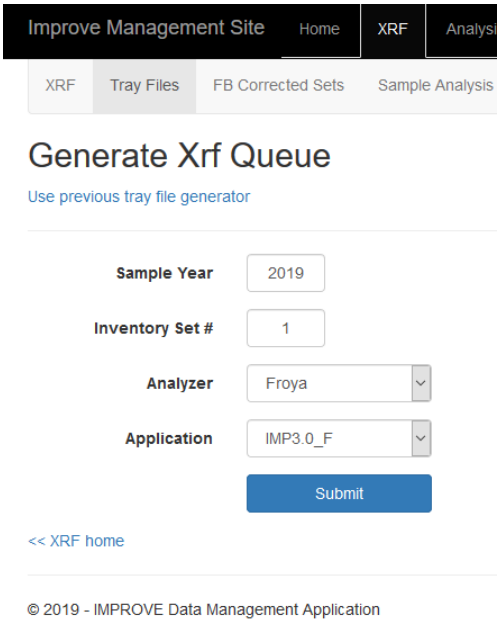
9.4 XRF Queue Generation

An XRF queue file is generated via the IMPROVE web app for all valid IMPROVE samples. Once generated, instrument specific queue files will need to be moved from the U-drive to the local drive on each instrument.

1) Navigate to the IMPROVE web app (*https://improve.aqrc.ucdavis.edu/)* and login in with your credentials.
2) Click on **XRF** at the top of the page.

3) Click on **Tray Files**, loading the Generate XRF Queue page.
4) Fill in the requested information, sample year, Inventory Set #, Analyzer and Application, then click **Submit** (example in figure below).

Figure 10. Generate XRF Queue web page.



5) Save the text file here *U:\IMPROVE_Lab\XRF_Epsilon5\Queue Files*, each instrument has its own subfolder. Before hitting save rename the file adding the set number (example; E5_queue_impset#.txt).
6) Upload the queue file to the instrument in the directory *C:\PANalytical\Epsilon5\Programs\Changer\Barcode Scripts*
7) If there is already a queue file there from a previously analyzed set, replace the file with the new one. The new queue file must be saved as a txt file and named as follows for the PANalytical software to recognize it, *E5_queue.*

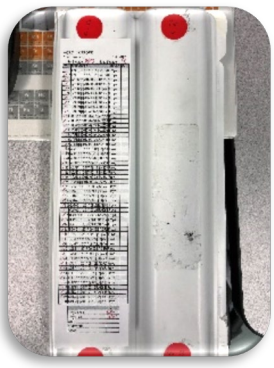
9.5 Generating Inventory Tray Labels and Performing Tray Checks

Before loading samples at XRF, inventory tray labels need to be generated and tray checks must be performed. Inventory tray labels are used to ensure samples are in the same order as the electronic inventory.

9.5.1 Generating Inventory Tray Labels

1) Before generating labels, check the next available filter for analysis in the XRF lab. To do this, locate the “unassigned filters” in the XRF lab. These filters are located on the right-hand side of the white shelving unit labeled “unassigned”.
2) The set of filters up next for XRF analysis will numerically follow the set currently being analyzed. For example, if the current set being analyzed is set 15 then set 16 will be

analyzed next. Locate the first tray in the set and check if it has an inventory tray label or not, see image below for example.



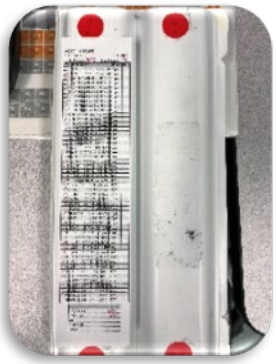
3) When you come across the first tray without an inventory label, open the tray to check the first filter (top, left). Check the corresponding filter inventory sheet (will be folded inside the tray) to verify this is the correct filter and write down the filter information: sampler, sample date and filter ID. Remember to note this information is for the inventory tray label, also write down the set number.
4) From the U:\ drive, open the inventory sheet folder U:\IMPROVE_Lab\XRF_Epsilon5\Labels\Inventory Tray Labels and navigate to the "Printout template". You will paste information found in another file into this template.
5) From the U:\ drive navigate to the "Lab Gravimetric" folder here: *U:\IMPROVE_Lab\Lab_Gravimetric.*
6) Navigate to the Applications and Macros folder: *U:\IMPROVE_Lab\Lab_Gravimetric\Applications and Macros.*
7) Select the **XRF** folder.
8) Click on the folder for the year corresponding to the year you need to print (example 2020 Closed), within the year you will see "Sets", open the excel file for the set you are generating labels for.
9) Copy the information from the "Master List" in columns A-H (starting with Row 2), then paste this information into the "Printout template" under the worksheet "Master". You will paste the information starting in cell B2 (the row is highlighted in yellow).
10) Column J will auto populate once information is pasted into columns B-I.
11) Copy the information from column J and click on the **paste worksheet** and paste the information.
12) Click on the worksheet **print** and verify the information looks correct. You may also want to double check the trays start and end with the correct filter. To do this navigate back to the file you opened in step 8 above. You will see sheet 1-8 for the given set. Check the first filter on sheet 1 matches the first filter on your first label. Then check the 50th filter on sheet 1 matches the 50th filter on your first label. Check those same two positions for the remaining labels. If you find a discrepancy verify it is not a copy and paste error. Once you have verified it was copied/pasted correctly (before printing the labels) you will need to go physically check the filters in the tray to locate the discrepancy.

Once the information is correct, print and save the file to the current year subfolder in the "Inventory Tray Labels" folder in the following format "mm-dd-yyyy (set#) printout".

9.5.2 Performing Tray Checks

After generating inventory tray labels, a physical tray check is performed to ensure the correct filters are assigned and prepared.

1) Printed inventory tray labels are taken to the XRF lab to perform a physical tray check.
2) Trays that are not yet analyzed will be located in the XRF lab on the white shelving unit, right-hand side labeled "unassigned". Locate the tray that corresponds to the first generated inventory tray label, remove this tray from the shelf.
3) Starting with the Petri dish in position 1 (top, left) physically check the Petri dishes (samples) are in the same order as the inventory label.
4) Once all the Petri dishes in a tray have been verified then initial the bottom of the inventory label next to tray check.
5) Place the inventory tray label on the front-left side of the white Petri tray, see figure below.



6) After completing tray checks remove the printed inventory sheet. Place the tray back on the shelf, then move on to the next tray in the set. Gather the inventory sheets for the entire set (should be 8 sheets), hole punch them and place them in the binder for instrument this set is assigned to.

9.6 Adding New Samples with the XRF Queue File

An XRF queue file is generated based on the samples in a set, with 8 trays per set. The set numbers are assigned by the sample handling lab via the IMPROVE web app before reaching XRF. The sample changer software uses the data within the queue file to link the filter barcode ID with the sample identity and the instrument specific application. The filter barcode ID is etched on the support ring of 25 mm Teflon filters.

9.7 Loading New Samples into the Sample Changer

1) Remove the designated 8-position tray from the E5 and place it on the desk or sample handling table.
2) Remove the sample holder inserts from the sample holder cups and place on the desk.
3) Locate the white Petri tray with samples awaiting analysis and remove the next eight filters to be analyzed according to the printed inventory sheet. 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). While the filters can technically be scanned in any order, the best way to maintain an orderly filter inventory is to scan filters in the same order as the filter inventory sheet/label.
4) Click on **handheld scanner** on the sample changer software screen. Then click on the first empty position being loaded, typically position 1 of the tray you will be loading. This will open the "scan barcode for position" popup.
5) Using a 2-D barcode scanner, scan the filter barcode. To do this, remove the lid from the Petri dish. Place the Petri dish with the filter on the designated circle of the loading platform (marked with a small circular groove on the white platform). There is a proximity sensor built into the loading platform and it will trigger the scanner, if successfully scanned the filter sample identity will appear on the sample changer screen (in the position selected in step 4).
6) Verify the information on the screen matches the information on the lid of the Petri dish (site and sample date).
7) Using forceps lift the filter by the outer support ring and place it on the filter holder. The sample side should be face up.
8) Place the sample holder cup over the top of the sample holder insert. Tip the cup slightly and support the sample holder cup and insert by applying gentle pressure on the bottom of the cup/insert. Then, turn the assembly upside down and place it in the first position of the tray.
9) Place the lid back on the empty Petri and set the 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.)
10) Continue with the rest of the samples, moving from positions two through eight.
11) 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.
12) Make sure the green "Free to Open" light is illuminated. Then, open the sample changer cover.

13) 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.
14) Close the sample changer cover and repeat steps 1-14 for the remaining empty trays.
15) Add the newly populated filters to the analysis queue by selecting the symbol (in the "Overview" screen of the "Measure Batch" tab. Then, select the newly-loaded trays. The samples will change from gray to yellow.

9.8 Adding QC Samples utilizing "Add Measurement" function

1) To add Quality Control (QC) samples to the queue, double click on the first position that will be loaded in the sample changer software. This will open the *Add Measurement* screen.
2) The *location* should already be the correct position, it can be manually changed if needed.
3) For *Application*, select the current version of the application being run on the particular Epsilon 5.
4) Place the cursor in the *Sample Identification* box.
5) Type or scan the QC code for each QC sample.
6) Press F8 to save the entry and the program will automatically move on to the next position.

9.9 Analyzing the QC Samples

The "S" tray is analyzed once every day. If the queue needs to be re-ordered for the "S" Tray to be analyzed, refer to Section 10.2 of Additional Checks/Procedures.

9.10 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 with your first initial and full last name. 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 select **Save This New Record**. Close the log.

10. ADDITIONAL CHECKS AND PROCEDURES

10.1 Additional Procedure for Adding New Samples without a Filter Barcode

New samples can be loaded to an XRF instrument by manually typing the sample identification into the sample changer software or through the generation of a QR code label.

10.1.1 Manually Typing Sample Identifications

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.
5) Place the cursor in the "Sample Identification" box. Type in the filter sample identity in the following format SITE1|1|YYYY-MM-DD|SA|#######, for example OLYM1|1|2019-06-08|SA|1722441. The SA stands for sample, if the filter is a field blank this SA is replaced with FB. If the filter is from a 5A module, the |1| is replaced with a |5|. The last 7 digits are the filter id, which can be found on the IMPROVE web app and is not always 7 digits.
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

10.1.2 Adding New Samples with QR Code Labels Generated in Bulk

The following details how to make QR code labels for 80 filters at once:

1) Before generating QR code labels check the next available filter for analysis in the XRF lab. To do this, locate the "unassigned filters" in lab. These filters are located on the right-hand side of the white shelving unit labeled "unassigned".
2) The set of filters up next for XRF analysis will numerically follow the set currently being analyzed. For example, if the current set being analyzed is set 15 then set 16 will be analyzed next. Locate the first tray in the set and open the tray to check for QR code labels starting with the filter in position 1 (top, left). If this sample already has a QR code

label then move to the next sample until you come across the first sample without a QR code label. Write down the sample information; sampler, sample date and filter ID. Remember to note this information is for the QR code labels.

3) From the U:\ drive, open the Petri QR label folder- U:\IMPROVE_Lab\XRF_Epsilon5\Labels\Petri Labels
4) Select the worksheet titled "1-80Barcode_templates.xlsx" you paste information here copied from another file.
5) Select the Applications and Macros folder: *U:\IMPROVE_Lab\Lab_Gravimetric\Applications and Macros*
6) Click on the **XRF** folder
7) Navigate to the folder for the year corresponding to the year you need to print (example 2020 Closed), within the year you will see "Sets", open the excel file for the set you are generating labels for.
8) Click on the **Master List** worksheet within the workbook. Verify the first filter matches the information you recorded in step 2.
9) Copy the information in columns A-H starting with row 2, then paste into the "1-80Barcode_template" worksheet "Master" in B2. Columns I, J and K will auto-populate.
10) Copy the information in column J and click on the **List** worksheet, paste this information into column A. Then copy Column K from "Master" and paste into column B on "List". Then copy column C from "Master" and paste in column C on "List".
11) Verify the information is correct and then select the **Barcode** worksheet and click **Add-ins**. This will open the TbarCode Panel add-in. From the TbarCode submenu click **Select all Barcodes**, then **Refresh all Barcodes**.
12) From the barcode tab select print from the menu.
13) Copy the next 80 samples from the "Master" worksheet you generated in step 9 and repeat steps 10-12 until all QR code labels are printed for the set being analyzed. The only difference is you will copy the information for the next 80 filters each time you print the previous 80.
14) When you have finished printing all the labels for a set save the file, this will only retain the last 80 QR codes generated.
15) Printed QR code labels are then taken to the XRF lab to label samples.
16) Find the sample that matches the first QR code on the printed sheet.
17) Verify the site name and sample date match the label already on the Petri before adding the QR code label (these labels are placed on the sample by the Sample handling lab). Place the Petri dish back in the tray in the same place you removed it from. Repeat with the rest of the filters.
18) Once the entire tray is labeled place the tray back on the shelf and continue labeling with the next tray.
19) The labeled filters can now be scanned into the sample changer software with a barcode scanner, by clicking on the position you want to load the filter to and selecting "Add-measurement". Verify the location is the position you just clicked on and that "type" is set to routine.

20) For "Application", select the current version of the application being run on the particular Epsilon.
21) Place the cursor in the "Sample Identification" box and scan the QR code label, verify the information is correct for the sample and click **next**. Repeat this step for any additional filters being loaded with QR codes.

10.1.3 Adding New Samples when Generating Individual QR Code Labels

1) If generating labels for less than 80 filters the lab technician can manually update the barcode worksheet.
2) From the U:\ drive, open the Petri QR label manual template- U:\IMPROVE_Lab\XRF_Epsilon5\Labels\Petri Labels\Barcode_templatemanual.xlsx
3) On the list tab the only entry in the sample identity column should be in Row 2, this is an example of the format needed for making QR code labels manually.
4) Open the IMPROVE web app (https://improve.aqrc.ucdavis.edu), and from the homepage click on **Filters**.
5) Click on the **filter results** icon to open the filter search criteria screen.
6) Type in the 4-letter site code in the sampler box and select the dates needed from the start and end date boxes.
7) Click on the **Module Type Code** box and select **A-PM2.5 Mass/XRF** from the dropdown menu.
8) Click on **search**. This will load all A filters within the set date range from the selected site.
9) Click on the **view filter details** icon to see the filter ID number, listed as "Id" at the top of the filter details page. Copy the "Id".
10) Return to the Barcode_templatemanual.xlsx worksheet and paste the "Id" into the last portion of the 1st entry in column A, currently filled in as "FilterID".
11) Next type in the site name, module #, date and filter type, making sure you maintain the required format.
12) In column B of the same row type in the site name and date in the specified format.
13) In column C only update the module for 1A if the filter being analyzed is from a 5A module.
14) Repeat steps 21-30 for any additional QR code labels needed.
15) Click on the **barcode** tab. From the ribbon select **Add-ins** and click on **TBarCode** Panel, opening the barcode add-in.
16) On the barcode software sub-menu click on **select all barcodes**, then click **refresh all barcodes**. This will update all the QR codes on the sheet.
17) Before printing, if there are additional barcodes on the screen that are not linked to a label being generated delete them before printing.
18) From the barcode tab select print from the menu, close the file without saving.
19) Place the generated labels on the Petri dishes

20) The labeled filters can now be scanned into the sample changer software with a barcode scanner, by clicking on the position you want to load the filter to and selecting **Add-measurement**. Verify the location is the position you just clicked on and that "type" is set to routine.
21) For "Application", select the current version of the application being run on the particular Epsilon.
22) Place the cursor in the "Sample Identification" box and scan the QR code label. Verify the information is correct for the sample and click **next**. Repeat this step for any additional filters being loaded with QR codes.
23) Queue the filters after verifying the information is correct.

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

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

10.3 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.

10.4 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.

10.5 Weekly Check of Blank Identities-only Applicable if Blank Subtraction is Utilized

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, select **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. Select 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.

10.6 Changing Inserts in Sample Holder Cups

The filter holder inserts in the sample holder inserts are changed as needed. 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 the XRF lab. Exchange used inserts for clean inserts, place the clean inserts in the sample holder inserts, and continue with the sample change.

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UCD IMPROVE Technical Instruction #301C

Quality Assurance/Quality Checks (QA/QC) of XRF Performance

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

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1. PURPOSE AND APPLICABILITY

The subject of this technical instruction (TI) document is the quality assurance/control (QA/QC) steps applied in the elemental mass loading measurements of $PM_{2.5}$ filters collected in the IMPROVE network and analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) PANalytical Epsilon 5 instruments. The purpose is to ensure good laboratory practices including calibration, verification of calibration, and routine quality control checks (daily, weekly and monthly). The intended audience must have fundamental knowledge of XRF operations and data.

2. 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:** 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 $PM_{2.5}$ sampling. The quality control is performed on the elemental loadings (µg/cm2). The acceptance criteria are calculated as three times the standard deviations added to the mean of the laboratory 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 acceptance limits are applied as ± 10% or ± 3 standard deviations, whichever is larger, of the reference loadings depending on the elemental concentration on the UCD-ME.
- **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 the difference between each result from monthly re-analysis and reference loadings to accompanying uncertainty for element i (Equation 1):

$$z_i = \frac{C_{E5,i} - C_{ref,i}}{\sqrt{U^2(C_{E5,i}) + U^2(C_{ref,i})}}$$

Equation 1

where, c_{E5} is the mass loading measured (µg/cm2), c_{ref} is the reference mass loading; U is the expanded uncertainties of measured (c_{E5}) and reference (c_{ref}) mass loadings. The z-score should remain between ± 1 (inclusive) 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 (%). Urel is estimated by the summation of contributions from the calibration function, repeatability and uncertainty of calibration standards.
- **Bias:** Ratio of the difference between measured and certified loading of NIST SRM 2783 to certified loading (%). The 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 the certified loading ± root-mean-squared-relative-errors (RMSREs; Equation 2) plus three times standard deviations (SDs) from a set of SRM measurements:

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

Equation 2

where, m refers to measurement month.

3. CAUTIONS

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.

4. PROCEDURAL STEPS

4.1 Calibration and Verification

The calibration verification activities are performed as summarized in Figure 1 and Table 1.

The bias of SRM 2783 must be within acceptance limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb for acceptance of the calibration. The correlation coefficient for each element′s calibration line must be ≥ 0.98. If the correlation coefficient is less than 0.98, calibration lines and spectra are examined to determine the cause of the reduced correlation. Further testing and checks (i.e., checking the calibration lines of corresponding elements from other E5s) are also performed to determine the reason for exceedance. If similar deviations are observed on the other E5s, the orientation of the standard must be examined. If the orientation is correct, the quality of corresponding standards may be compromised and they can be excluded from calibration. If the problem is not resolved by excluding standard(s), calibration with the current standards shall be reprocessed. If recalibration does not show changes from the previous one, the Laboratory Manager will be notified for further instructions (e.g., stop analysis, order new standards, etc.).

The finalized calibration lines are verified by analyzing blanks, multi-element reference materials and reanalysis samples. Meeting the criteria (i.e., being within acceptance limits for

laboratory blanks and UCD-MEs, z-score between ± 1, and SRM biases being within the limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb) is required for analysis of samples. Failure in meeting criteria requires further checks/testing for resolution.

Figure 1. The flowchart of calibration verification.

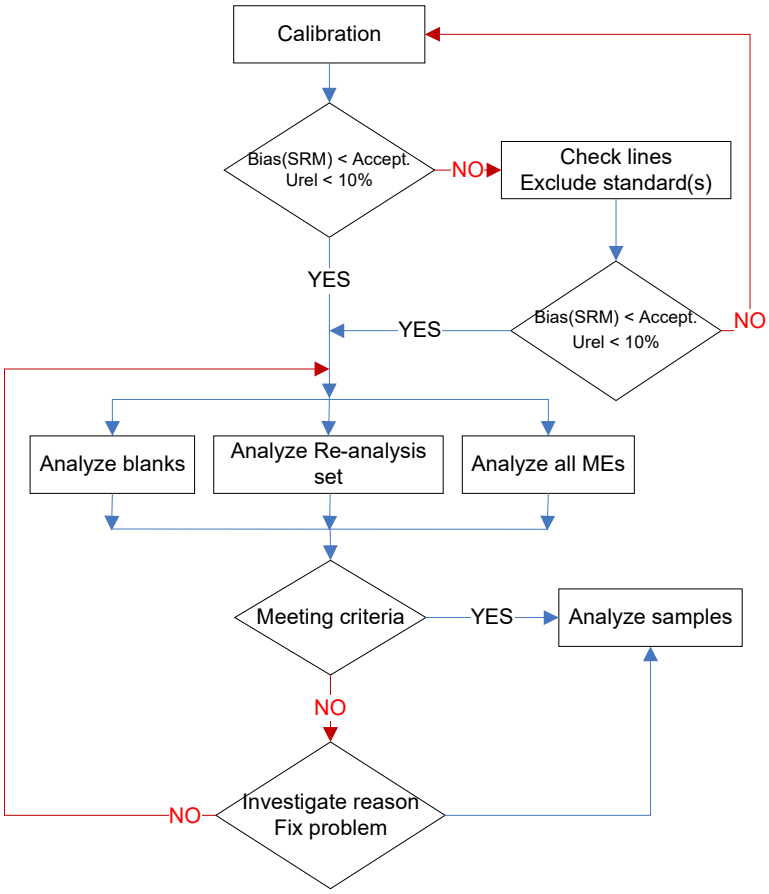


Table 1. The calibration verification activities, criteria and corrective actions.

Analysis	Criterion	Corrective Action
Uncertainty and correlation of calibration	Urel≤10% for stoichiometric standards. Correlation coefficient of calibration ≥ 0.98	• 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 SRM 2783	Bias within 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 an element not to exceed two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing

UCD-MEs	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	• Check sample(s) for damage/contamination • Further cross-instrumental testing • Replace sample(s) as necessary
Re-analysis set	-1≤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 summarized in Table 2.

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 adjusts the energy channels
PTFE Blank	Daily	≤ acceptance limits with exceedance of an element not to exceed two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD-MEs	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
UCD-MEs	Weekly	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Sample Replicate Measures	Weekly	None at the lab level.	
Re-analysis set	Monthly	-1 ≤ z-score ≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Bias within acceptance limits 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 laboratory blanks and UCD-MEs are analyzed daily using the instrument's Chemical Speciation Network CSN application. The IMPROVE application is a subset of the CSN application, therefore, the CSN application is used for QC procedures to cover both network analyses. The samples analyzed must be clean and undamaged.

The laboratory blank and UCD-ME results are migrated to the database. The plots can be examined via web browser at https://shiny.aqrc.ucdavis.edu/xrfQC/

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

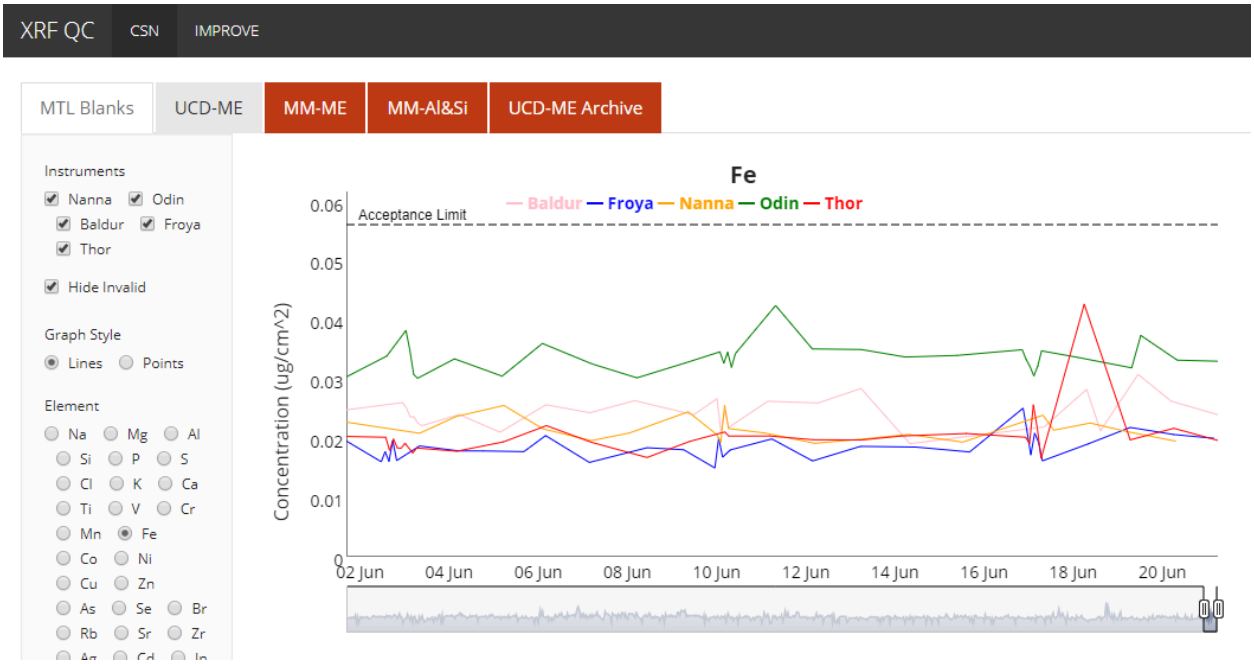
4.2.1.1 QC of Laboratory Blanks

The QC plot (Figure 2; https://shiny.aqrc.ucdavis.edu/xrfQC/is monitored, and any element exceeding the limits for more than two consecutive days constitutes failure. Gradual and small increases for some elements (e.g., Ca, S, and Cl) is most likely caused by atmospheric contamination of laboratory blanks, while increase in Cu and Zn likely originates from the instrument (e.g., abrasion of rubber materials inside the analytical chamber). If the QC fails, the first action is to airbrush the laboratory blank. If loadings of elements in question decrease, no further action is necessary and the analysis may continue. If not, the laboratory blank will be replaced with a new one. If the problem is not resolved, more laboratory blanks should be analyzed to check for similar increases. An observed increase on clean laboratory blanks suggests instrument-related contamination, which should be resolved by cleaning the analytical chamber and/or diaphragm. Following cleaning, reanalyze the laboratory blank for confirmation. If the problem is not resolved with cleaning, stop analysis and perform additional tests to address the issue. For example, in case of sudden increase in loadings, 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 analyzed sample.
- Sample filter off center during analysis, which can be indicated by Zn spikes in the spectra due to the beam interaction with the ring of the filter.

The analysis must be stopped until the problem is resolved. All samples analyzed during the time period in question must be reanalyzed.

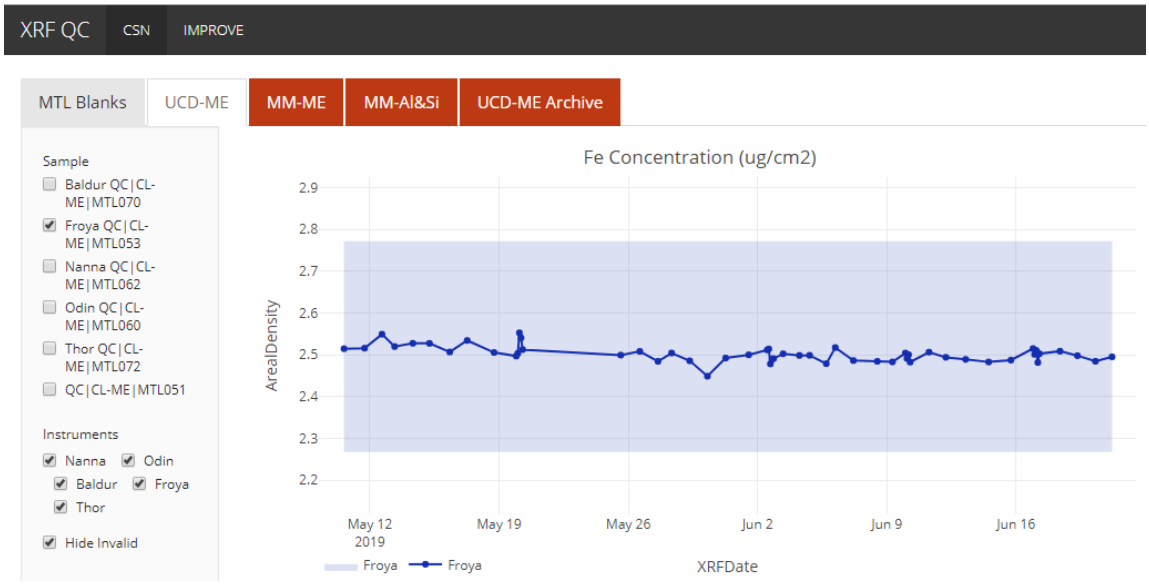
Figure 2. The QC plot of laboratory blanks.



4.2.1.2 QC of daily UCD-ME

The QC plots of the daily ME include the mass loadings in real time for each E5 (Figure 3). Elements monitored for QC are Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb. If an element exceeds its acceptance limits for more than two consecutive days, an investigation (including cross-instrument analysis, analysis of other ME samples, analysis of single element standards, and other additional tests) is initiated to address the issue.

Figure 3. The QC plots of UCD-ME.



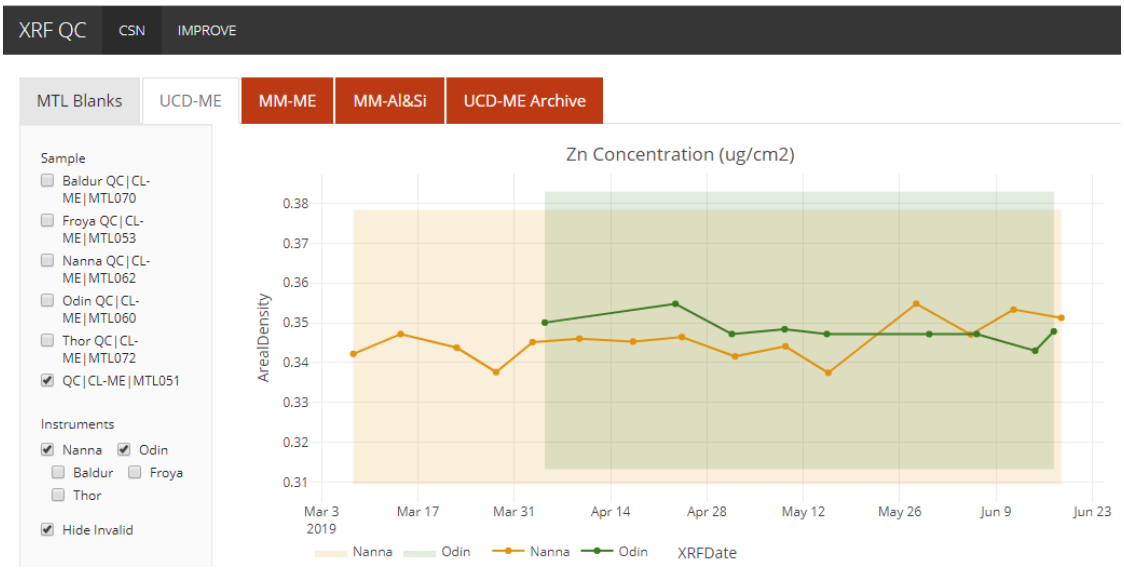
4.2.2 Weekly Analysis

These analyses include a UCD-ME sample to be analyzed on all E5s once a week. The analyzed sample must be contamination free and undamaged.

The weekly UCD-ME plot includes mass loading plots in real time for each instrument (Figure 4). Elements monitored for QC are Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb. If the acceptance limits are exceeded for more than two consecutive measurements, an investigation (including cross-instrument analysis, analysis of other ME samples, analysis of single element standards, and other additional tests) is initiated to address the issue.

Replicate sample analyses are performed over the weekend. Each XRF analysis takes approximately an hour, therefore performing replicate analysis is difficult to fit into the analytical procedures. However, a full load of samples over the weekend will typically end before the following Monday morning. So, one tray of samples is queued to repeat analysis over the weekend. Timing is never certain so the number of replicates which are performed is not constant, but should be something like 8 samples per week per instrument. There are no laboratory level acceptance tests for the replicate measurements yet. As data is collected, these tests will be determined and implemented here in this TI.

Figure 4. The QC plots of weekly analyzed UCD-ME.



4.2.3 Monthly Analysis

The reanalysis samples are analyzed monthly on all E5s using the CSN XRF application.

The z-score plot shows the mean z-score values of the reanalysis samples based on the reference loadings (Figure 5). The satisfactory level (z within ± 1) is checked for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb. If limits are exceeded, additional tests are implemented to address the problem.

The SRM biases of Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb are checked to be less than or equal to the element-specific limits (Figure 6). Exceedances require further testing to address the problem.

Figure 5. The plot of z-score for Re-analysis samples.

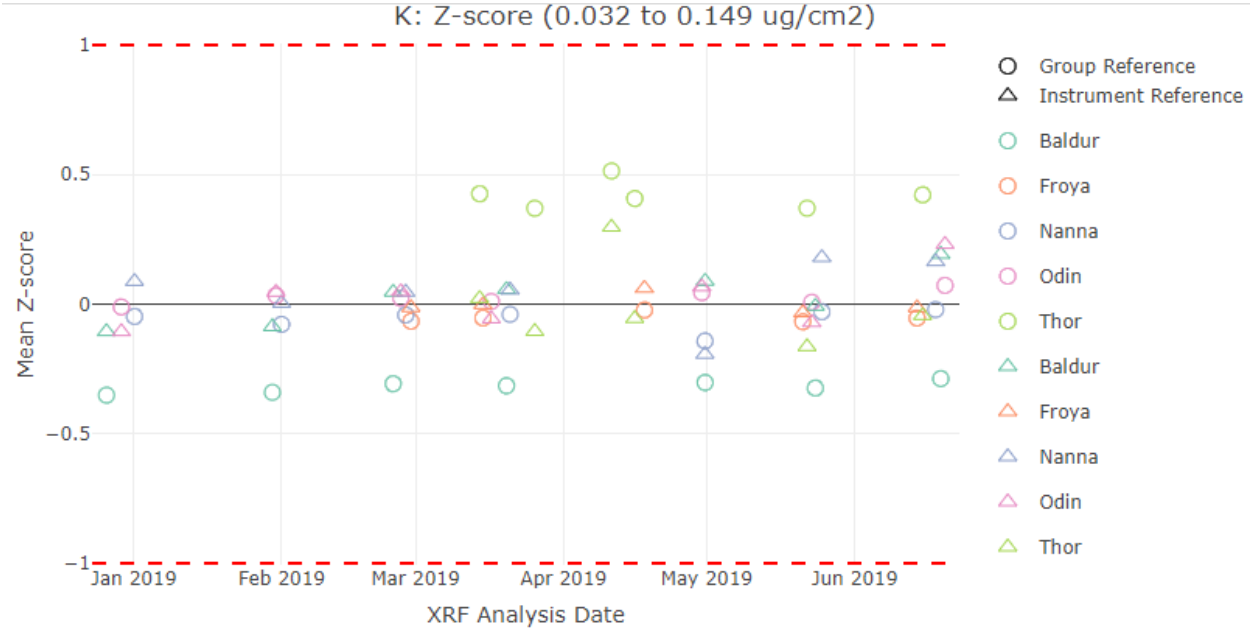
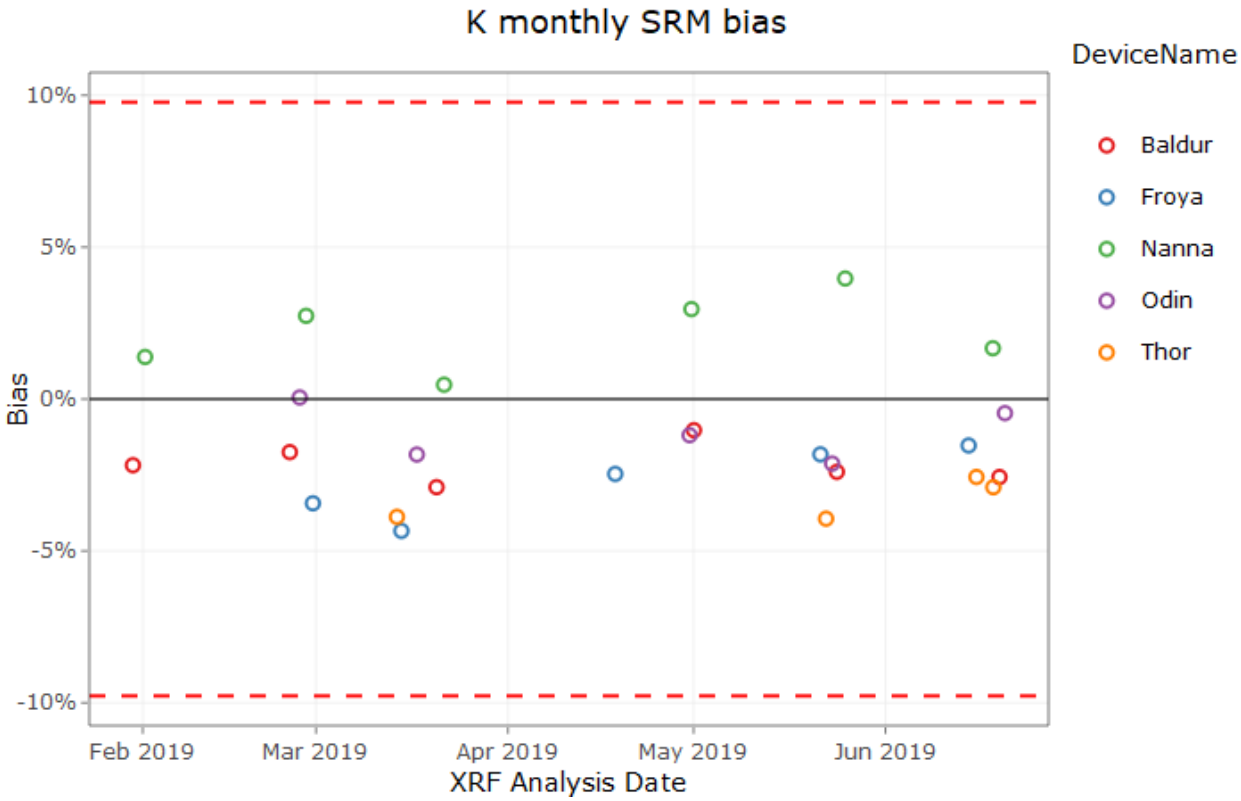


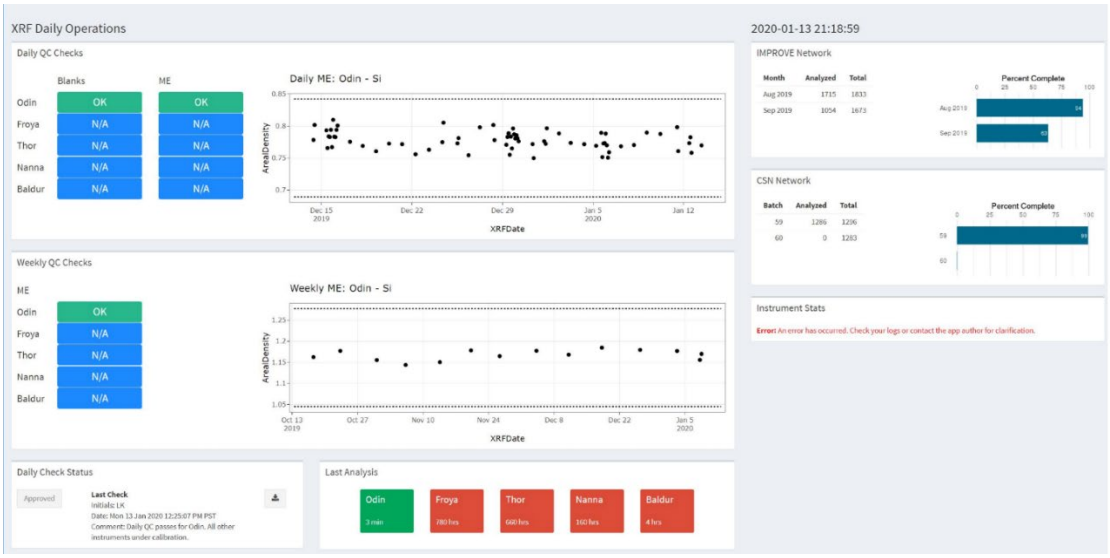
Figure 6. The monthly bias of K from NIST SRM2783.



4.2.4 Reporting

Daily analyzer performance is monitored via the XRF Daily Operations page as shown in Figure 8, https://shiny.aqrc.ucdavis.edu/xrfDailyOps/. The XRF Daily Operations page is displayed on a touchscreen in the XRF laboratory. Trained laboratory personnel review daily and weekly QC results for laboratory blanks and MEs. If results for all analyzers meet acceptance criteria, then they are approved for the day by clicking the approve button. The approver will be prompted to input their initials and any additional comments. If any analyzer fails acceptance criteria for two consecutive days, the laboratory manager is notified immediately and decides corrective action.

Figure 7. XRF Daily Operations Page.



The weekly analyzer performance QC reports, prepared by the Spectroscopist or Laboratory Manager designee, include the results of daily and weekly monitoring (Figure 9; *U:\IMPROVE_Lab\XRF_Epsilon5\QA\QC_Reports*). The results of reanalysis samples and SRM bias are reported to the Laboratory Manager.

Figure 8. An example of a weekly QC report for daily and weekly monitoring of analyzers' performance.

09/12/2016

Sinan Yatkin

Observations

Lab Blanks in S tray

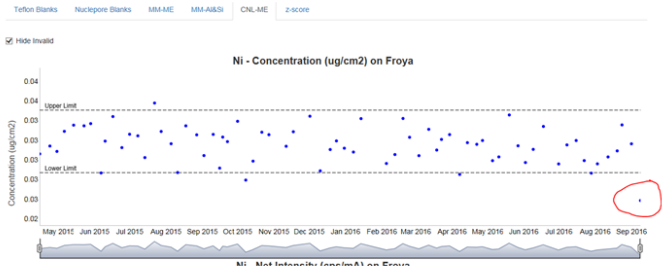
No anomaly

ME

No anomaly.

Al&Si and ME-38

Ni on Froya ME#38 decreased more than 10%, but not on ME #136. Most likely it is an outlier.



Conclusion

We will keep our eye on Froya-Ni ME#38..