UCD IMPROVE Technical Information #301C

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

Interagency Monitoring of Protected Visual Environments
Air Quality Research Center
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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
03/04/21	SRS	All	Separated TI: A-C into individual Tis.
8/23/22	JAG	All	Updated wording and tests to match CSN. Updated tables 1 and 2 to reflect the correct test elements and match wording with CSN. Updated Figures of some webpages to more recent screenshots.

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1. PURPOSE AND APPLICABILITY

The subject of this technical information (TI) document concerns quality assurance/control (QA/QC) steps applied in the elemental mass loading measurements of $PM_{2.5}$ filters. These filters are 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 is required for analysis of samples. Failure in meeting criteria requires further checks/testing for resolution.

Figure 1. The flowchart of calibration verification.

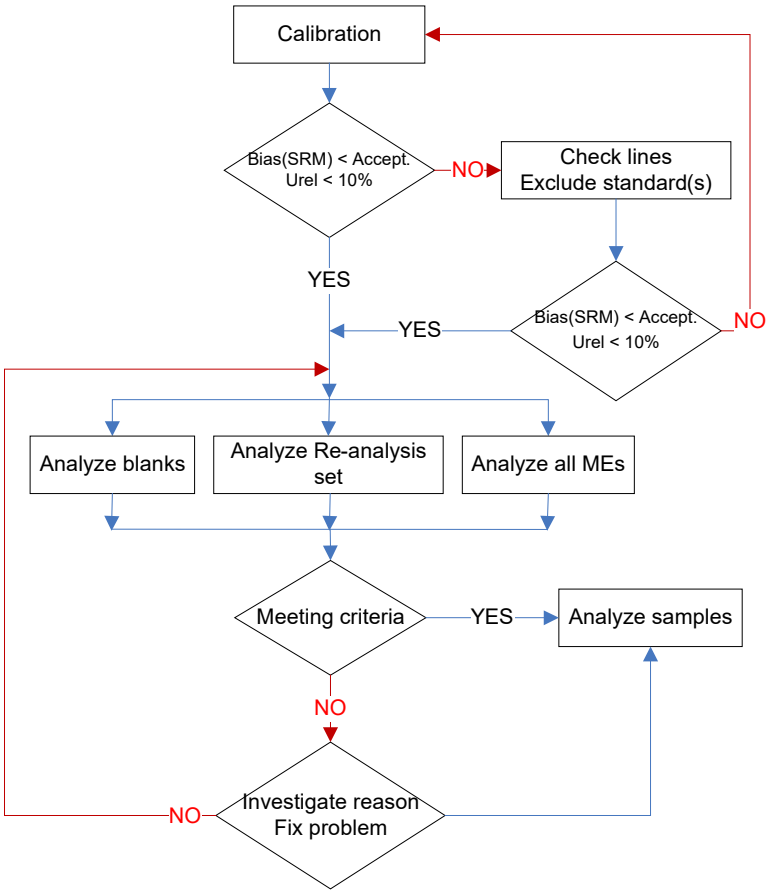


Table 1. The calibration verification activities, criteria, and corrective actions.

Analysis	Criterion	Corrective Action
Correlation of calibration	Correlation coefficient (r^2) of the calibration line for each element is ≥ 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 SRM2783	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
Laboratory Blank	≤ acceptance limits with exceedance of max two elements	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD Multi-element samples	Larger of ± 10% or 3 standard deviations of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	• Check sample for damage/contamination • Further cross-instrumental testing • Replace filter sample as necessary
Reanalysis samples	z-score between ± 1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	

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 any elements not to occur in more than two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing • Reanalyze network samples since last pass QC as needed.
UCD Multi-element sample	Daily	Larger of ± 10% or 3 standard deviations of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of any element not to occur in more than two consecutive days	• Check sample for damage/contamination • Further cross-instrumental testing • Replace QC sample if necessary • Reanalyze network samples since last passing QC as needed.
UCD Multi-element sample	Weekly	Larger of ± 10% or 3 standard deviations of reference mass loadings for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb with exceedance of any element not to occur in two consecutive measurements	
Sample Replicate Measures	Weekly	None at the lab level.	
Reanalysis samples	Monthly	z-score between ± 1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb	
SRM 2783	Monthly	Bias within acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

4.2.1 Daily Analysis

The S trays containing analyzer specific 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:

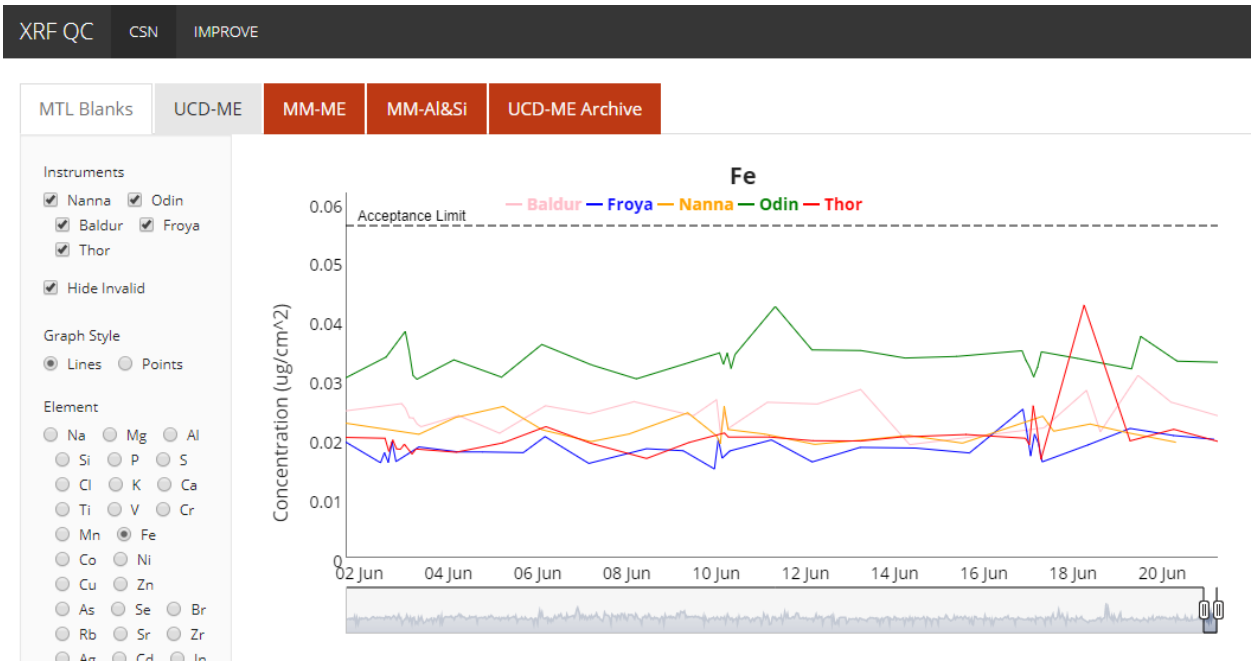
4.2.1.1 QC of Laboratory Blanks

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.

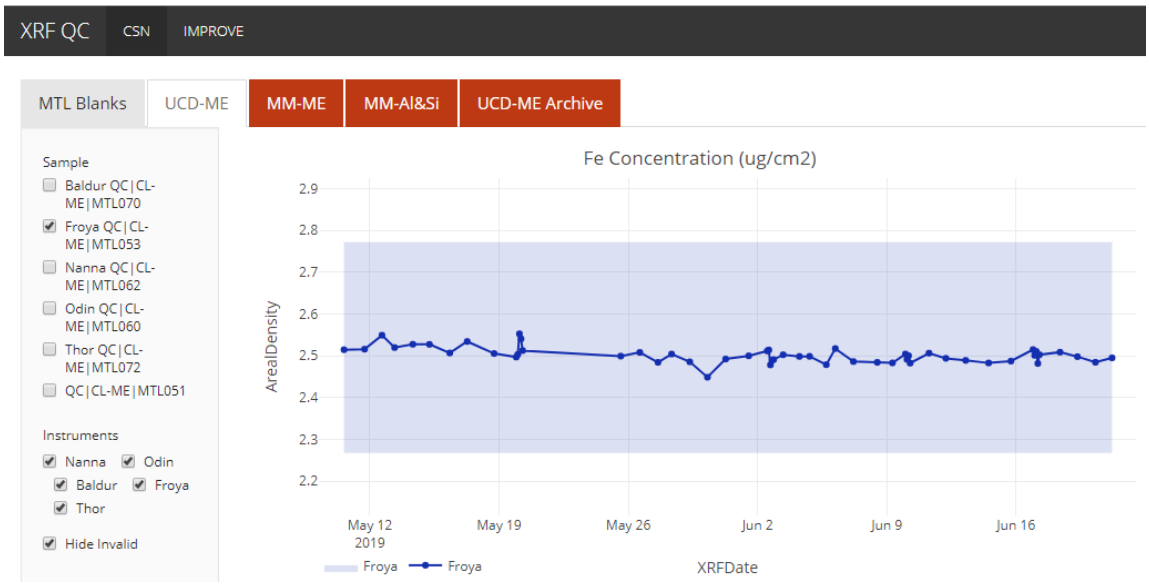
Figure 2. The QC plot of laboratory blanks.



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. The upper and lower bounds of the shaded region are the upper and lower limits for the test.



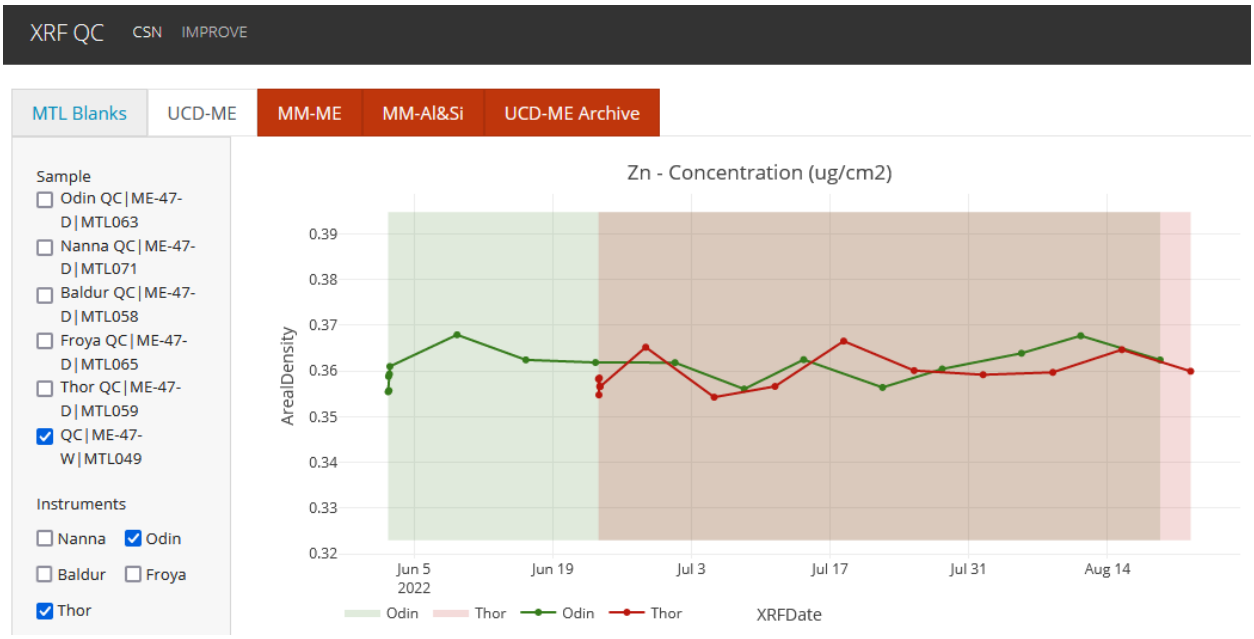
4.2.2 Weekly Analysis

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. The upper and lower bounds of the shaded region are the upper and lower limits for the test.



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. Red dashed lines represent test limits.

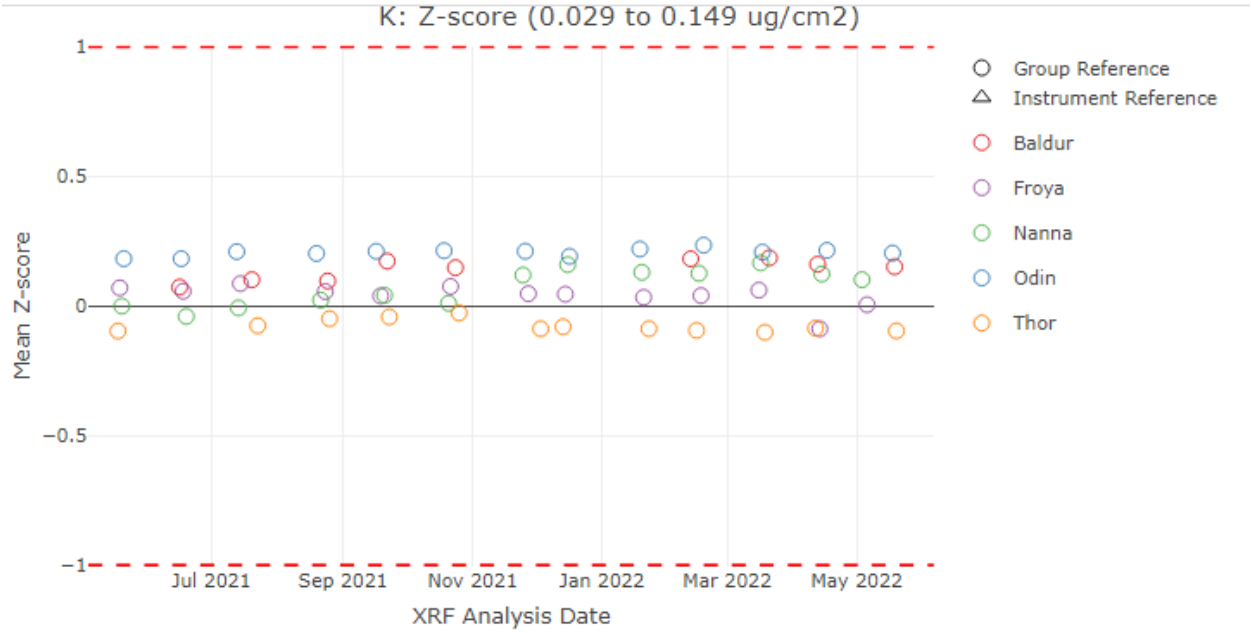
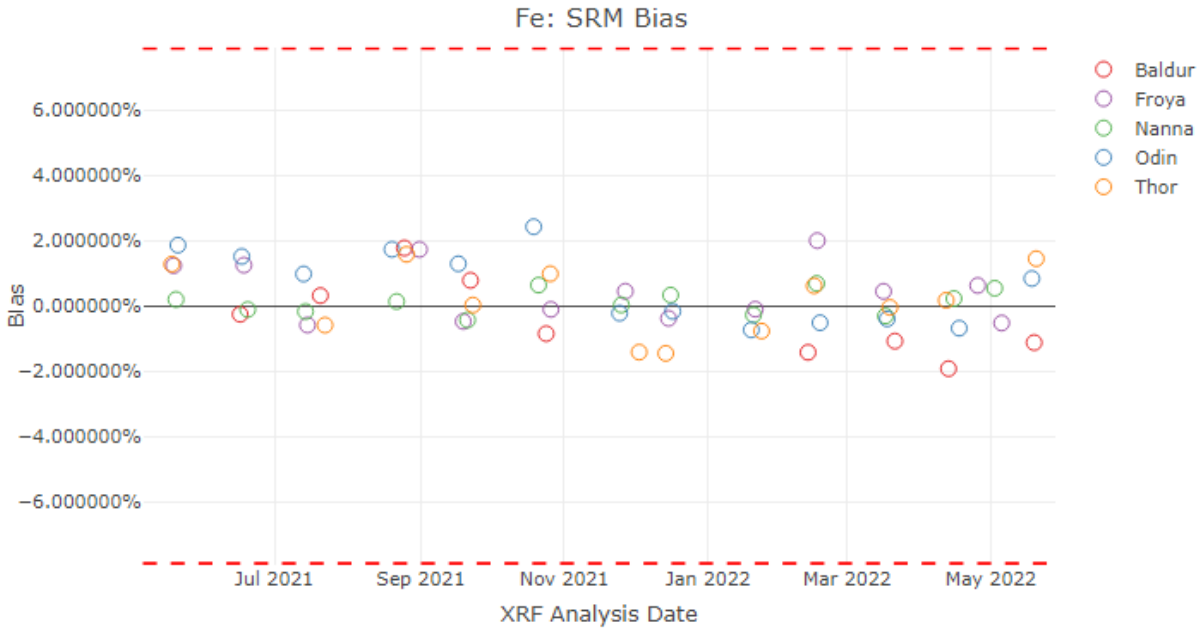


Figure 6. The monthly bias of K from NIST SRM2783. Red dashed lines represent test limits.



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.