UCD CSN Technical Information #302D

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

Chemical Speciation Network
Air Quality Research Center
University of California, Davis

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
04/24/18	MGN	3, 8, 9.2	Fixed spelling errors and updated the QC website URL. Plots updated.
06/20/19	JAG	3, 8, 9	Updated QC acceptance criteria to include appropriate elements for new QC samples. Updated calibration QC criteria to account for values displayed by E5 software. Updated plots and flowcharts to reflect changes to QC tools. Updated z-score and bias calculations to use signed values instead of absolute values.

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1. PURPOSE AND APPLICABILITY

The subject of this technical information (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 Chemical Speciation Network (CSN) and analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) PANalytical Epsilon 5 instruments. The scope 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. A user is required to have access to UC Davis Central Authentication Service.

2. SUMMARY OF THE METHOD

The QA/QC of EDXRF operations involves calibration by certified standards, calibration verification by certified multi-elemental reference materials, and routine performance checks using laboratory blanks, multi-elemental reference materials and CSN samples. All calibration verification and QC results must meet the acceptance criteria.

3. 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 MTL-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 at CSN sites. The checking/examining is performed on the elemental loadings ($\mu g/cm^2$). 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 CSN 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 ten measurements after calibration. Acceptance limits are applied as ± 10 % of the reference loadings.
- **Reanalysis Samples (RA):** A selected set of sixteen multi-elemental samples prepared at UCD with elemental mass loadings approximating the range of expected loadings from CSN. The Reanalysis 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 result of 5 measurements by each E5.

- **z-score:** The ratio of the difference between each result from monthly reanalysis 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/cm^2), c_{ref} is the reference mass loading; U is the expanded uncertainty 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 Standard Reference Material (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 ± root mean squared relative errors (RMSREs; Equation 2) plus three times standard deviations (SDs) from 44 monthly measurements between January 2013 and July 2016.

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

Equation 2

Where, m refers to measurement month.

4. HEALTH AND SAFETY WARNINGS

Not applicable.

5. CAUTIONS

Not applicable.

6. INTERFERENCES

Not applicable.

7. PERSONNEL QUALIFICATIONS, DUTIES, AND TRAINING

Only trained lab personnel designated by the Laboratory Manager may operate the E5 instruments. QC can only be performed by personnel designated and trained by the Laboratory Manager.

8. EQUIPMENT AND SUPPLIES

- Certified standards
- Laboratory blanks, free of contamination.
- Multi-elemental reference materials generated by UCD
- NIST SRM 2783 certified reference materials
- Reanalysis samples

9. PROCEDURAL STEPS

9.1 Calibration 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 lower than 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 CSN samples. Failure in meeting criteria requires further checks/testing for resolution.

Figure 1. The flowchart of calibration verification.

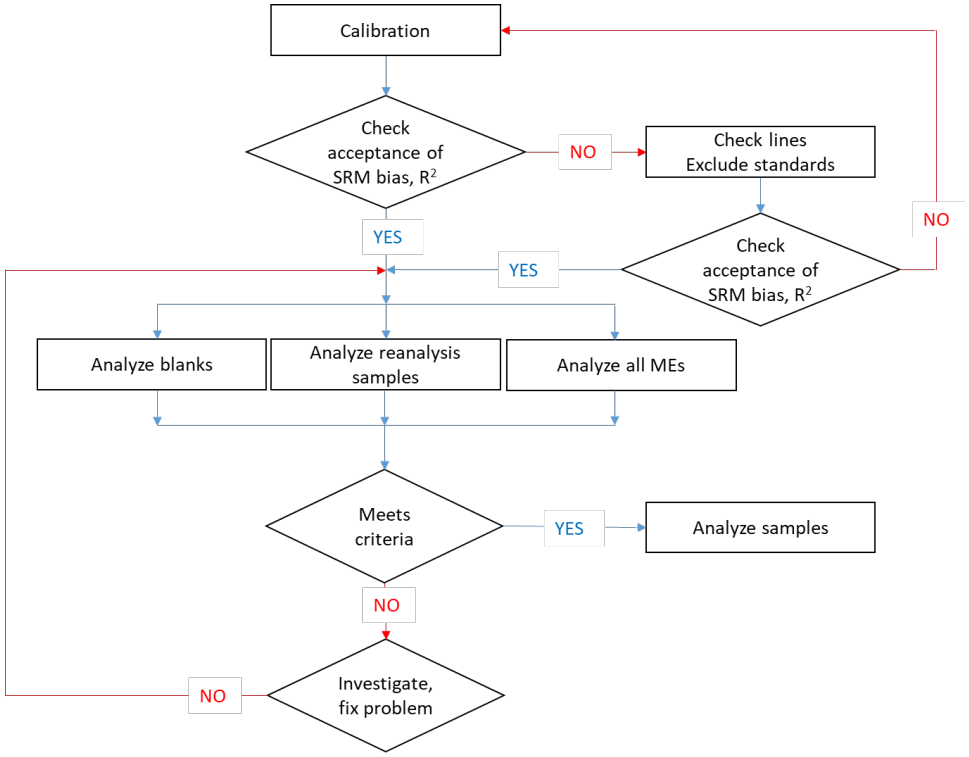


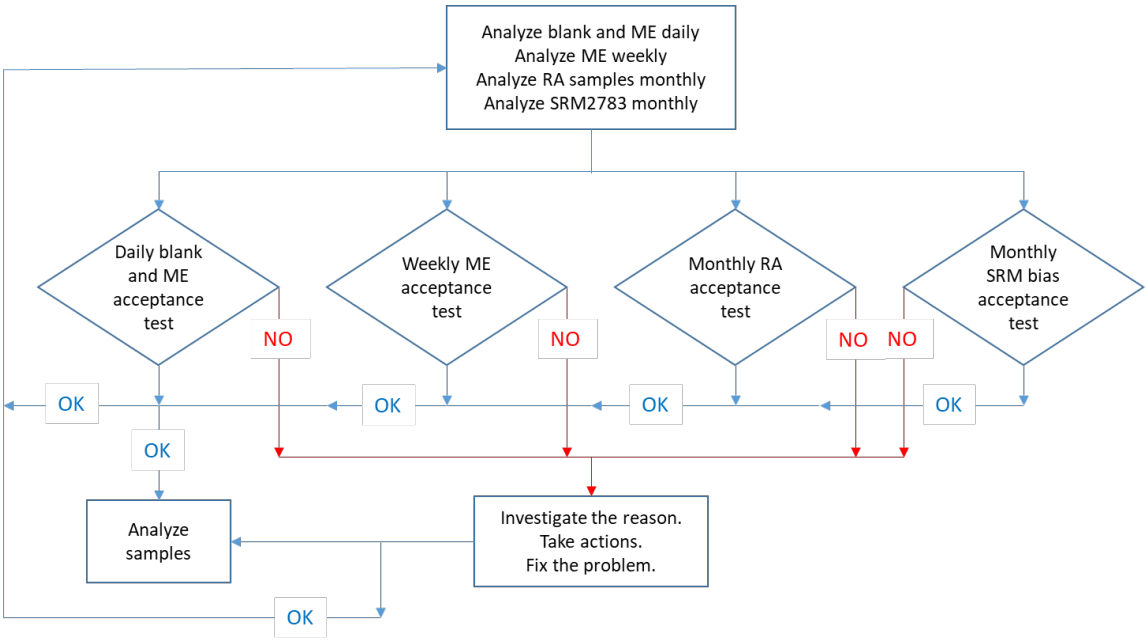
Table 1. The calibration verification activities, criteria and corrective actions.

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	± 10 % 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	

9.2 Routine QC of EDXRF Analyzers

Procedures for routine QC checks of the EDXRF performance are shown in Figure 2.

Figure 2. Routine QC of EDXRF performance.



Routine QA/QC activities, criteria, and corrective actions 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
Laboratory 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
UCD Multi-element sample	Daily	± 10 % 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 sample if necessary
UCD Multi-element sample	Weekly	± 10 % 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	
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	

9.2.1 Daily Analysis

The E5 *S* trays containing analyzer specific TB and UCD-ME are analyzed daily. The samples analyzed must be clean and undamaged. The TB and ME results are migrated to the database (http://analysis.crocker.ucdavis.edu:3838/xrfQC/).

The QC of daily-analyzed samples is performed weekly as described in Section 9.2.1.1 and 9.2.1.2.

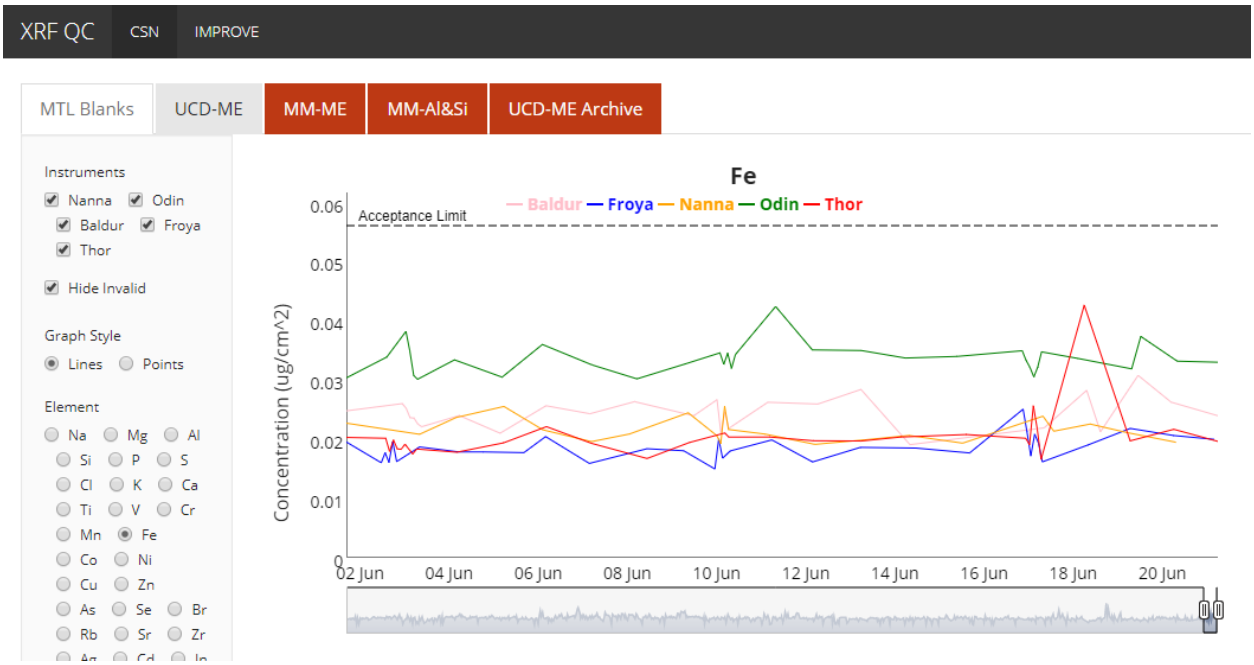
9.2.1.1 QC of Teflon Blanks

The QC plot (Figure 3; http://analysis.crocker.ucdavis.edu:3838/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 TB, 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 TB. If loadings of elements in question decrease, no further action is necessary and the analysis may continue. If not, the TB will be replaced with a new one. If the problem is not resolved, more lab blanks should be analyzed to check for similar increases. An observed increase on clean lab blanks suggests instrument-related contamination, which should be resolved by cleaning the analytical chamber and/or diaphragm. Following cleaning, reanalyze TB and clean lab blanks 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 the 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.

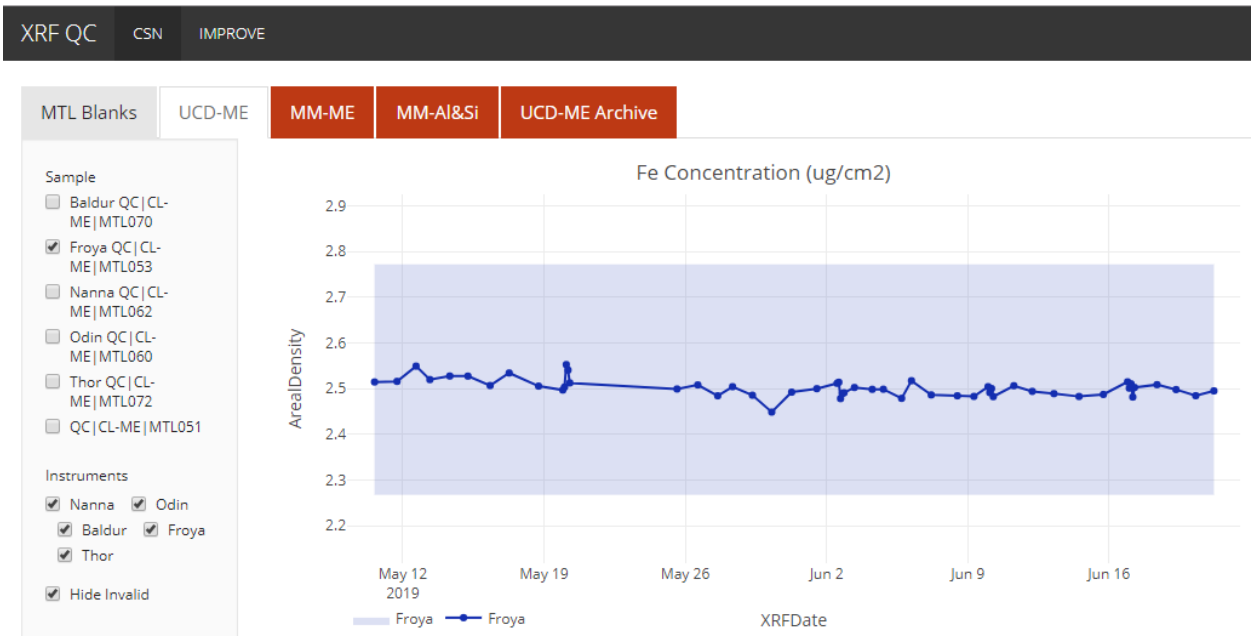
Figure 3. The QC plot of laboratory blanks.



9.2.1.2 QC of daily ME

The QC plots of the daily ME include the mass loadings in real time for each E5 (Figure 4). 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 4. The QC plots of ME.

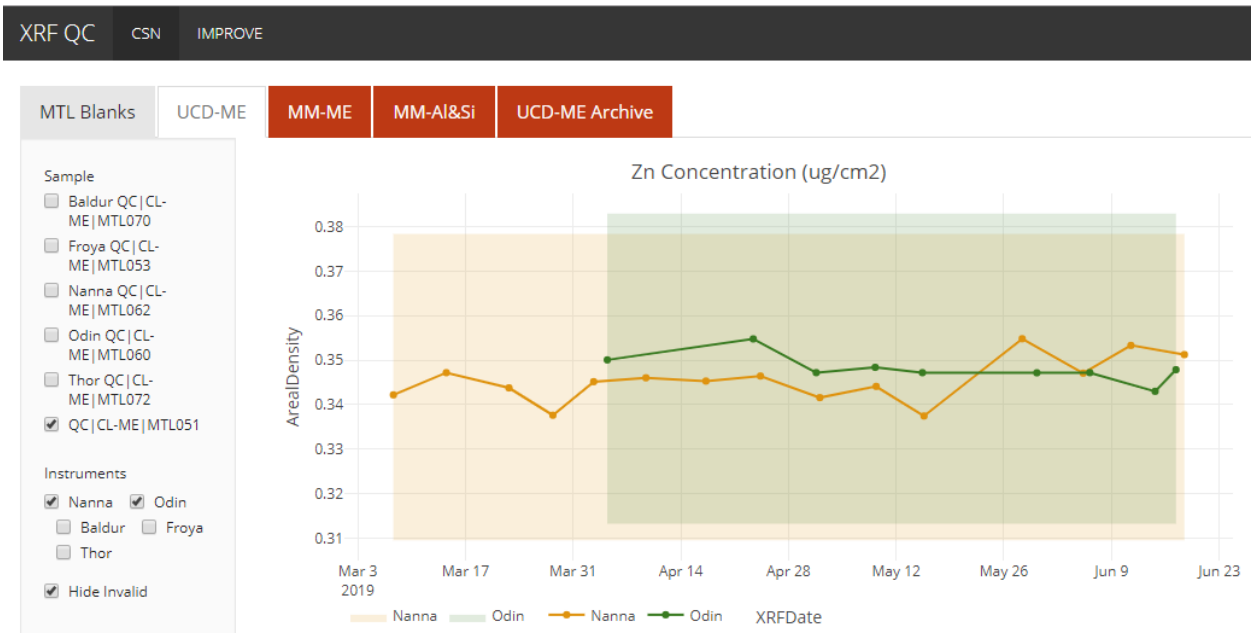


9.2.2 Weekly Analysis

These analyses include a UCD-ME sample to be analyzed on all E5s. 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 6). 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.

Figure 5. The QC plots of weekly UCD-ME.



9.2.3 Monthly Analysis

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

The z-score plot shows the mean z-score values of the reanalysis samples based on the reference loadings (Figure 7). 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 absolute 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 8). Exceedances require further testing to address the problem.

Figure 6. The plot of mean z-score for Reanalysis samples.

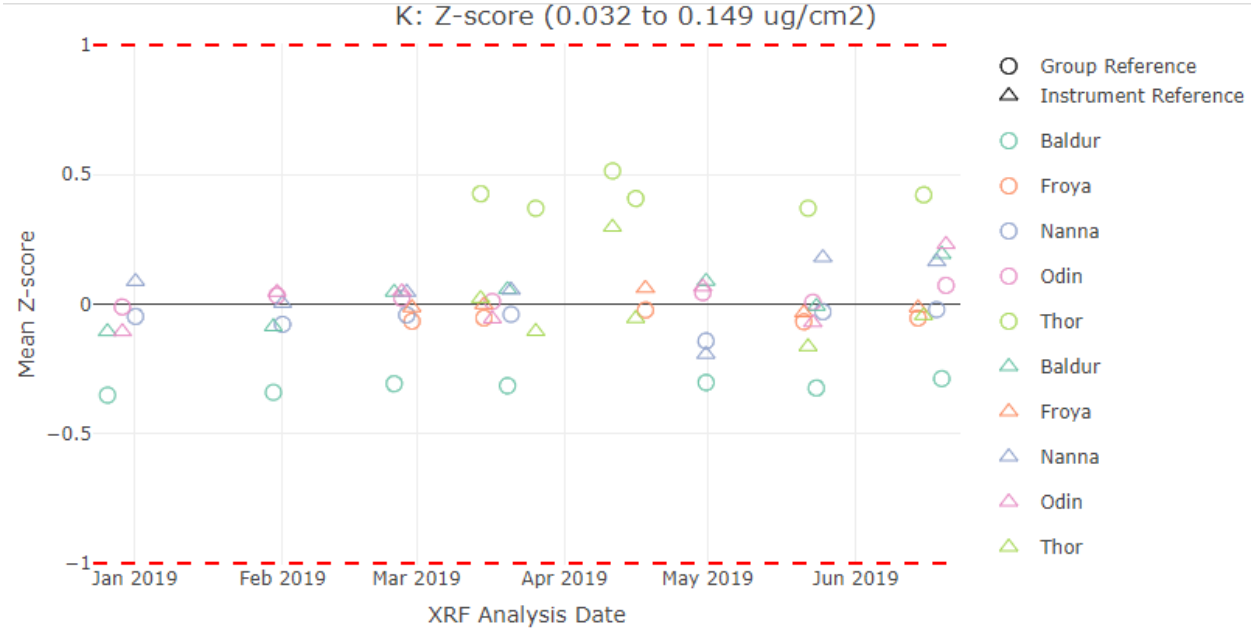
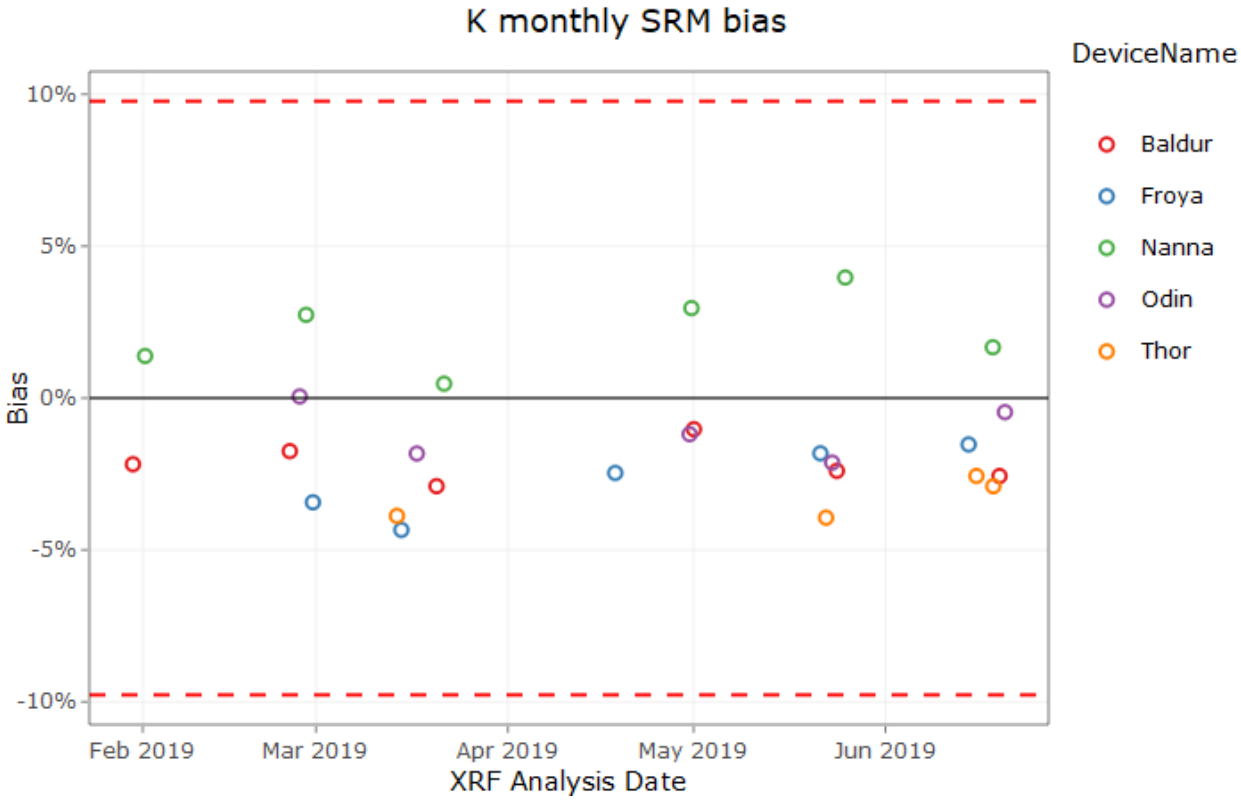


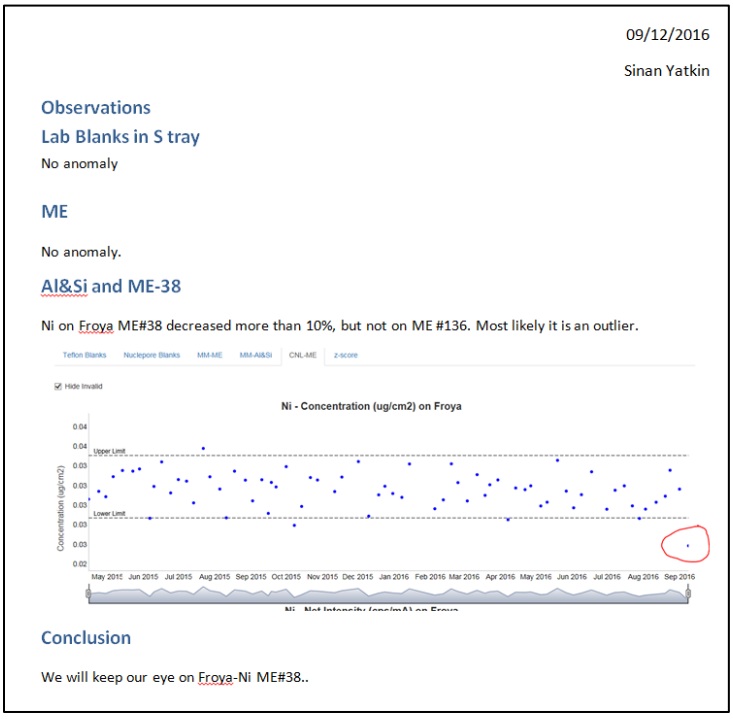
Figure 7. The monthly bias of K from NIST SRM2783.



9.2.4 Reporting

The weekly analyzer performance QC reports, prepared by the Laboratory Manager or 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. Example of weekly QC report for daily and weekly monitoring of analyzers' performance.



10. QUALITY ASSURANCE AND QUALITY CONTROL

All standards, blanks, reference materials, and reanalysis set must be checked regularly for damage. Any damaged or contaminated materials must be replaced.

11. REFERENCES

Not applicable.