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

September 28, 2017
Version 1.0

Prepared By: M J Navarro Date: 10/16/17

Reviewed By: [signature] Date: 10/16/2017

Approved By: Nicole Hyslop Date: 10/16/17

UCDAVIS
AIR QUALITY RESEARCH CENTER

DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications

Table of Contents

List of Figures

List of Tables

1. PURPOSE AND APPLICABILITY

The subject of this technical instruction (TI) is the quality assurance/control (QA/QC) steps applied in the elemental mass loading measurements of $PM_{2.5}$ filters collected in the CSN network and analyzed using EDXRF (Panalytical Epsilon5). The scope is to ensure good laboratory practice 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 contains steps of calibration by certified standards, calibration verification by certified multi-elemental reference material, and routine performance checks by laboratory blanks, multi-elemental reference materials and CSN samples. All calibration verification and QC results shall meet the acceptance criteria.

3. DEFINITIONS

- **Laboratory Blanks (TB):** These are MTL-Teflon filters placed in the *S* trays of each Epsilon 5 (E5) for daily analysis. Unexposed filters selected from batches of filters used for regular $PM_{2.5}$ sampling at CSN sites. The checking/examining is performed on elemental loading ($\mu g/cm^2$) basis. The Method Detection Limits (MDL), is calculated as three times standard deviations of a set of laboratory blanks. The acceptance criteria are calculated as 3 times standard deviations added to the mean of lab blanks 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 designated UCD-ME is analyzed weekly on all E5s for inter-instrumental comparison. The reference loadings are calculated as the average of the first five measurements after calibration. Acceptance limits are applied as ±10% of the reference loadings.
- **Al & Si Samples from Micromatter (MM-Al&Si):** These samples contain Al and Si, and are analyzed weekly. The reference loadings are calculated as the average of the first five measurements after calibration. The deviations of ±5% and ±10% from reference loadings serve as warning and acceptance limits, respectively.
- **Reanalysis Samples (RA):** A selected set of sixteen real samples, a UCD-ME and a NIST SRM2783 (#1720). 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 first instrument specific reference loadings of CSN samples and UCD-ME have been assigned as the mean results of 5 measurements

by each E5; the second ones have been calculated as the average of all instruments reference values. The reference values of NIST SRM2783 are the certified mass loadings. The average absolute z-score of the reanalysis set must be ≤1 for selected elements. The absolute bias of selected elements in NIST SRM2783 must meet the criteria for calibration verification.

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

$$z = \frac{\left|C_{ij} - C_{ij(ref)}\right|}{\sqrt{U_{C_{ij}}^{\ 2} + U_{C_{ij}(ref)}^{\ 2}}} \qquad \text{Equation 1}$$

Where, C_{ij} is the mass loading element i measured using analyzer j (µg/cm^2), C_{ij}(ref) is the reference mass loading of analyzer j, U_{Cij} and $U_{Cij(ref)}$ are the expanded uncertainties of measured (C_{ij}) and reference ($C_{ij(ref)}$) mass loadings. The z-score should remain ≤1 for specified elements.

- **Relative Expanded Uncertainty (Urel)**: The ratio of uncertainty estimated by the propogation of contributions of each factor effective on the measurement to the result (%). Urel is estimated by the summation of contribution from the calibration function, repeatability and uncertainty of calibration standards.
- **Absolute Bias:** The absolute ratio of difference between measured and certified loading of NIST SRM2783 to certified loading (%). The absolute bias for selected elements (Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb) must remain within element-specific acceptance limits determined as root-mean-squared-relative-errors (RMSREs; Equation 2) plus three times standard deviations (STDs) from 44 monthly measurements between January 2013 and July 2016.

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

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 Epsilon 5 instruments. The QC can only be performed by a personnel designated and trained by the Laboratory Manager.

8. EQUIPMENT AND SUPPLIES

- Certified standardards
- Laboratory blanks, free of contamination.
- Multi-elemental reference materials generated by UCD
- Al&Si samples generated by Micromatter
- 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 absolute bias of SRM 2783 must be equal to or less than 10% for Al, Si, K, Ca, Ti and Fe for acceptance of the calibration. The relative expanded uncertainty (Urel) of each element's calibration function is estimated using the designated excel sheet (see ..\..\CSN\QC\uncertainty-Calibration2016.xlsx for 2016 calculations). The Urel must be equal to or less than 10% for stoichiometric standards of CSN reported elements. If the Urel is higher than 10%, calibration lines and spectra are examined to detect the reason for the elevated Urel. Further testing and checks (i.e. checking the calibration lines of corresponding elements at 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 needs to 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 cannot be solved with excluding standard(s), calibration with the current standards shall be redone. If recalibration does not show changes from previous one, the Laboratory Manager shall be notified for further instructions (e.g. stop analysis, order new standards, etc.).

The finalized calibration lines are verified by analyzing blanks, multi-element reference materials and reanalysis samples. Meeting the criteria (i.e. being lower than acceptance limits for Teflon blanks and UCD-MEs, z-score ≤ 1, and SRM absolute biases being lower the limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb) is needed for analysis of CSN samples. Failure in meeting criteria requires further checks/testing for resolution.

Figure 1. The flowchart of calibration verification.

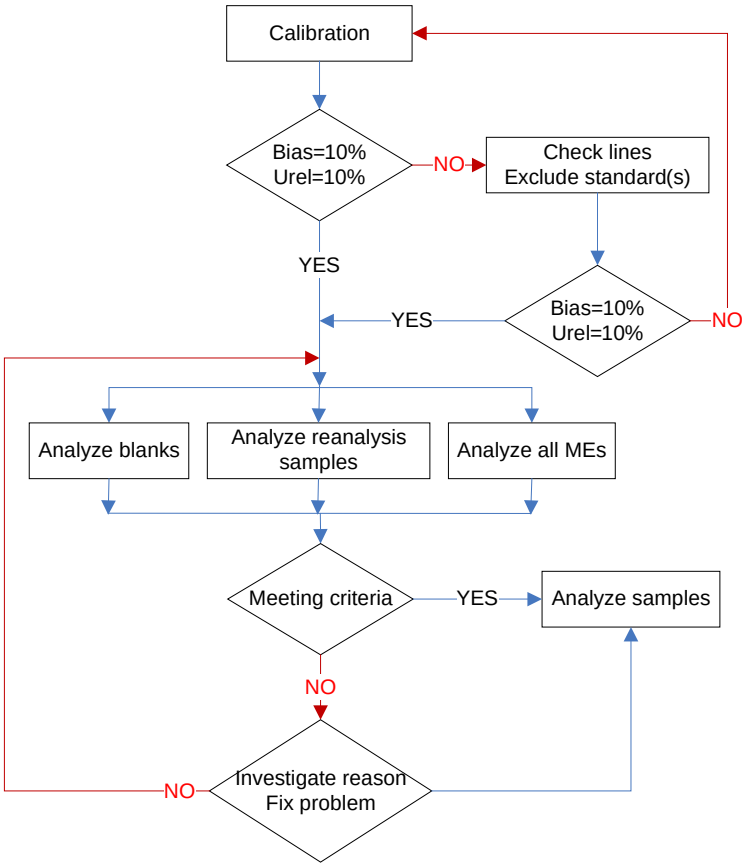


Table 1. The calibration verification activities, criteria and corrective actions.

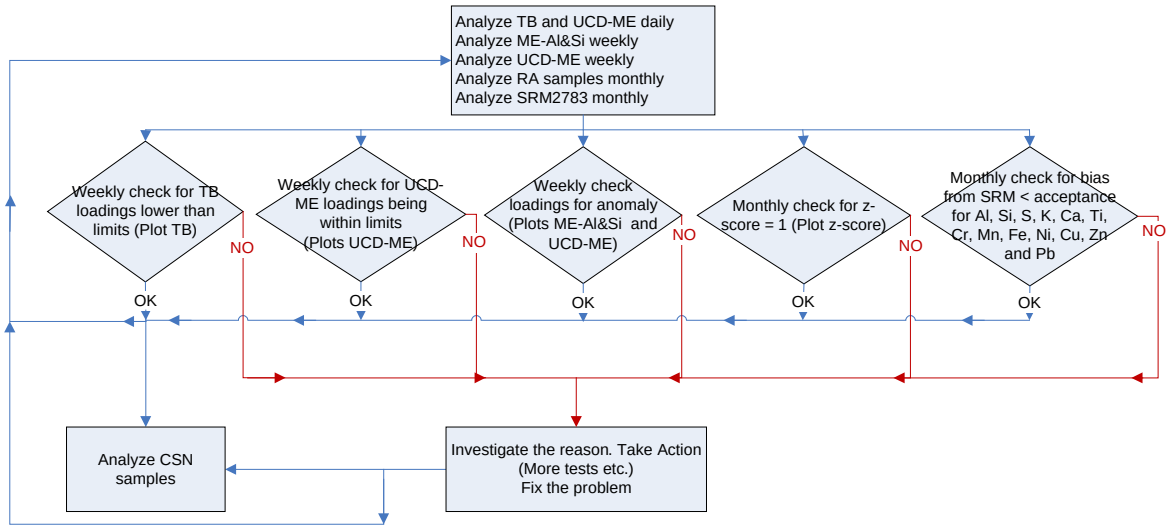
Analysis	**Criterion**	**Corrective Action**
Uncertainty of calibration	Urel≤10% for stoichiometric standards and with loadings≥3*MDL	• Check calibration line and spectra • Check standard(s) for damage/contamination • Exclude standard(s) from calibration line • Further cross-instrumental testing

		• Recalibration with current or new standards
NIST SRM2783	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	• Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards
Teflon 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	• Check sample for damage/contamination • Further cross-instrumental testing • Replace filter sample as necessary
Micromatter Al&Si sample	±10% of reference mass loadings	
Reanalysis samples	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	

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 adjust the energy channels
Teflon Blank	Daily	≤ acceptance limits with exceedance of any elements at least in 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	• Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
Micromatter Al&Si sample	Weekly	±10% of reference mass loadings	
UCD Multi-element sample	Weekly	±10% of reference mass loadings	
Reanalysis samples	Monthly	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

9.2.1 Daily Analysis

The *S* trays containing analyzer specific TB are analyzed daily. The samples analyzed must be clean and undamaged. The TB and ME results are migrated to the database (http://169.237.146.119:3838/xrfQC/).

The QC of daily-analyzed samples is performed weekly as described in Section 4.2.1.1 and 4.2.1.2.

9.2.1.1 QC of Teflon Blanks

The QC plot (Figure 3; http://169.237.146.119:3838/xrfQC/) is monitored, and exceedance of the limits for at least 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 (abrasion in analytical chamber). If the QC fails, first replace the TB with a clean one. If loadings of elements in question decrease, no further action is necessary and the analysis may continue. If not, more lab blanks should be analyzed to check for similar increase. Observed increase on clean lab blanks suggests the 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 (Zn spikes in the spectra due to the beam interaction with the ring of the filter).

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

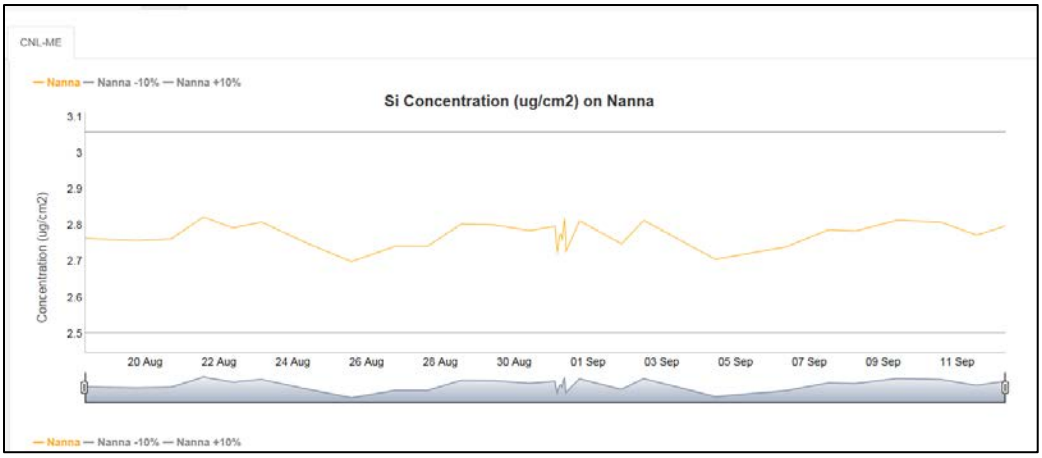
Figure 3. The QC plot of Teflon blank.

9.2.1.2 QC of ME

The QC plot includes the mass loadings in real time for each E5 (Figure 4). If the acceptance limits are exceeded (with exception of Br and Cl) for at least two consecutive days, an investigation (including cross-instrument analysis, analysis of other ME

samples, analysis of single element standards, and some of the additional tests) is started to address the issue.

Figure 4. The QC plots of ME.

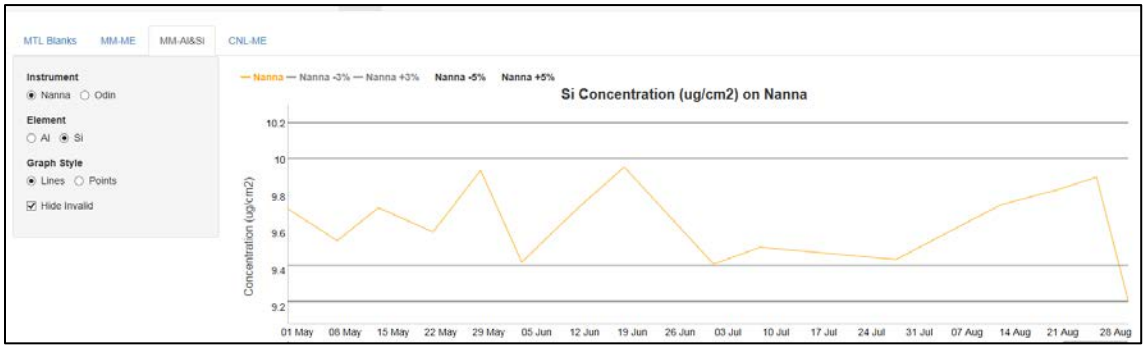


9.2.2 Weekly Analysis

These analyses include instrument specific MM-Al&Si samples and a UCD-ME sample to be analyzed on all E5s with corresponding blank. The analyzed samples must be contamination free and undamaged. No special blank is required for MM-Al&Si sample.

The MM-Al&Si plot includes the Al and Si intensities and mass loadings in real time for each instrument (Figure 5). If acceptance limits are exceeded for two elements, an investigation (including cross-instrument analysis, analysis of other ME samples, analysis of single element standards, and some of the additional tests) is started to address the issue.

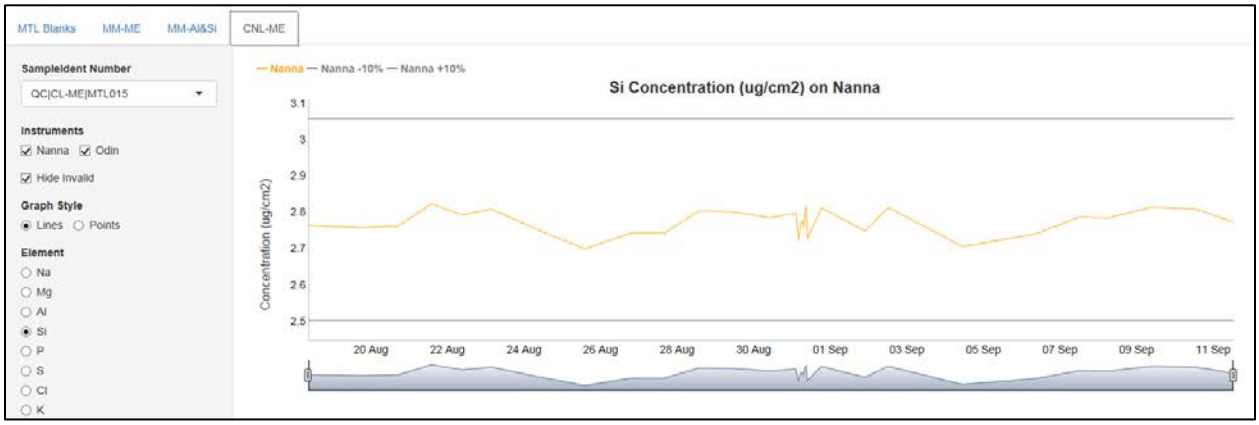
Figure 5. The QC plot of MM-Al&Si.



The UCD-ME plot includes mass loadings plots in real time for each instrument (Figure 6). If the acceptance limits are exceeded (with exception of Br and Cl) for at least two consecutive days, an investigation (including cross-instrument analysis, analysis of other

ME samples, analysis of single element standards, some of the additional tests) is started to address the issue.

Figure 6. The QC plots of UCD-ME.



9.2.3 Monthly Analysis

The reanalysis samples are analyzed monthly on all E5s using the regular CSN application. A dedicated blank (for blank subtraction) is analyzed with the reanalysis samples.

The z-score plot shows mean z-score values of 17 samples based on any reference loadings (Figure 7). The satisfactory level ($z \leq 1$) is checked for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr (..\..\CSN\QC\Reanalysis_GUM.xlsm). 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 equal to or lower than the element-specific limits (Figure 8; ..\..\CSN\QC\SRM2783.xlsm). Exceedance requires the further testing to address the problem.

Figure 7. The worksheet of z-score for Reanalysis samples.

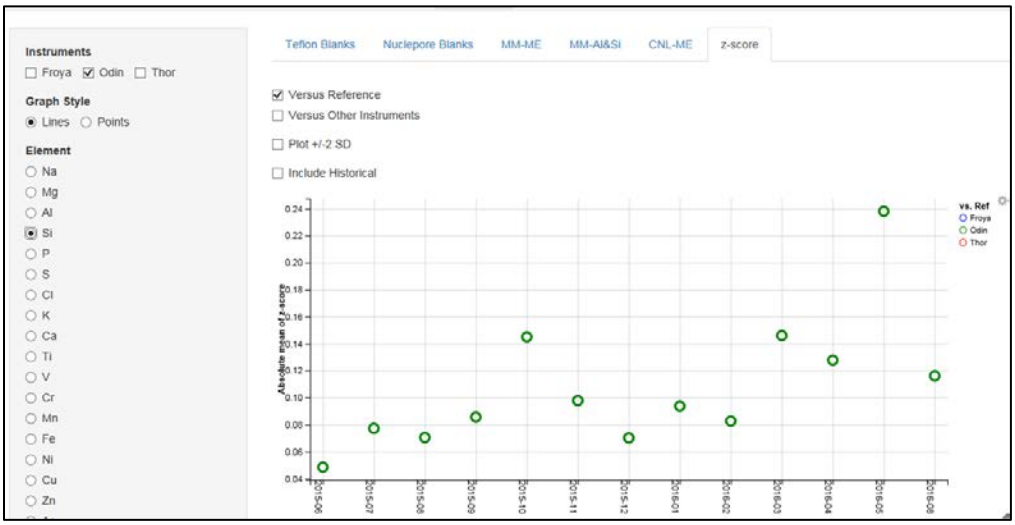
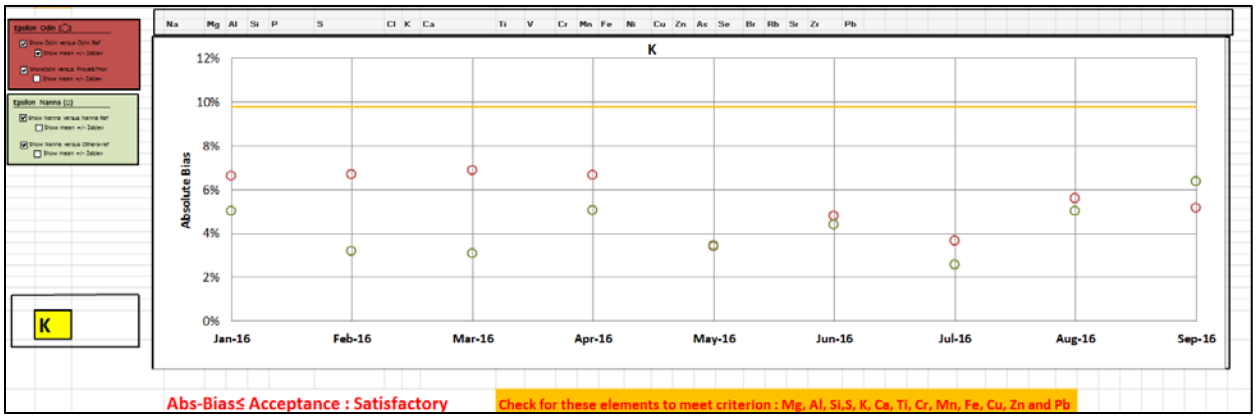


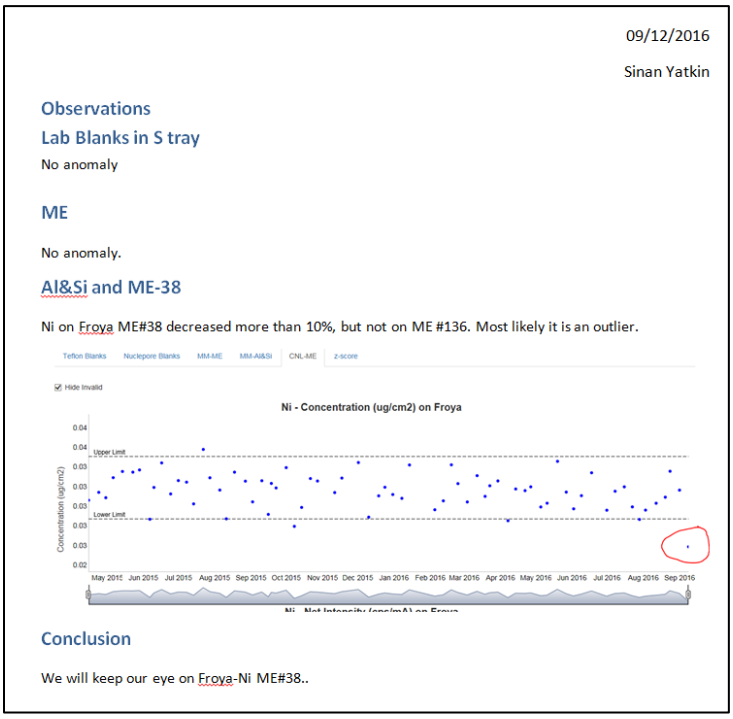
Figure 8. The monthly absolute bias of K from NIST SRM2783.



9.2.4 Reporting

The weekly analyzer performance QC reports prepared by the Laboratory Manager include the results of daily and weekly monitoring (Figure 9; U:\IMPROVE_Lab\XRF_Epsilon5\QA\QC_Reports). The results of RA samples are reported to the Laboratory Manager in case of a need for further analysis.

Figure 9. 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. The damaged/contaminated ones must be replaced.

11. REFERENCES

Not applicable.