# UCD CSN Technical Information #302D

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

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UCDAVIS
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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. |
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## 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

- **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 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 UCD-made multi-elemental samples with elemental mass loadings approximating the range of expected loadings from the CSN network. 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 results of 5 measurements by each E5.

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

$$z_i = \frac{|c_{Es,i} - c_{ref,i}|}{\sqrt{U^2_{cEs,i} + U^2_{cref,i}}}$$

Equation 1

where $c_{E5}$ is the mass loading measured (µg/cm$^2$), $c_{ref}$ is the reference mass loading; $U_{cE5}$ and $U_{cref}$ are the expanded uncertainties of measured ($c_{E5}$) and reference ($c_{ref}$) mass loadings. The z-score should remain ≤1 for specified elements.

- **Relative Expanded Uncertainty (Urel)**: The ratio of uncertainty estimated by the propagation of contributions of each factor effective on the measurement to the result (%). Urel is estimated by the summation of contributions from the calibration function, repeatability and uncertainty of calibration standards.
- **Absolute Bias:** Ratio of the absolute difference between measured and certified loading of NIST 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 (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 Epsilon 5 instruments. The QC can only be performed by a 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
- 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 laboratory 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 required for analysis of CSN samples. Failure in meeting criteria requires further checks/testing for resolution.

Figure 1. The flowchart of calibration verification.

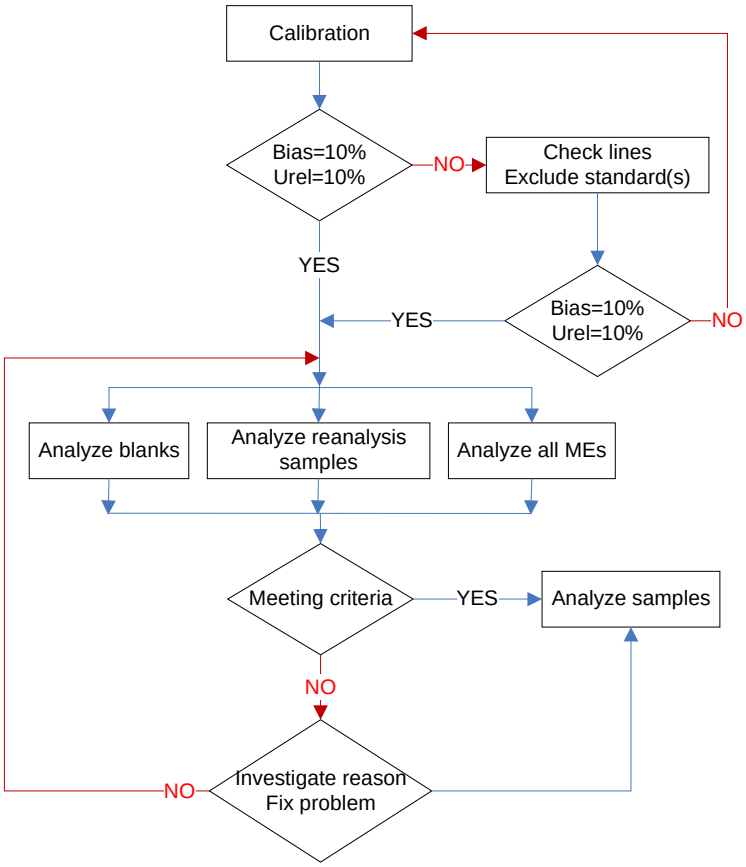


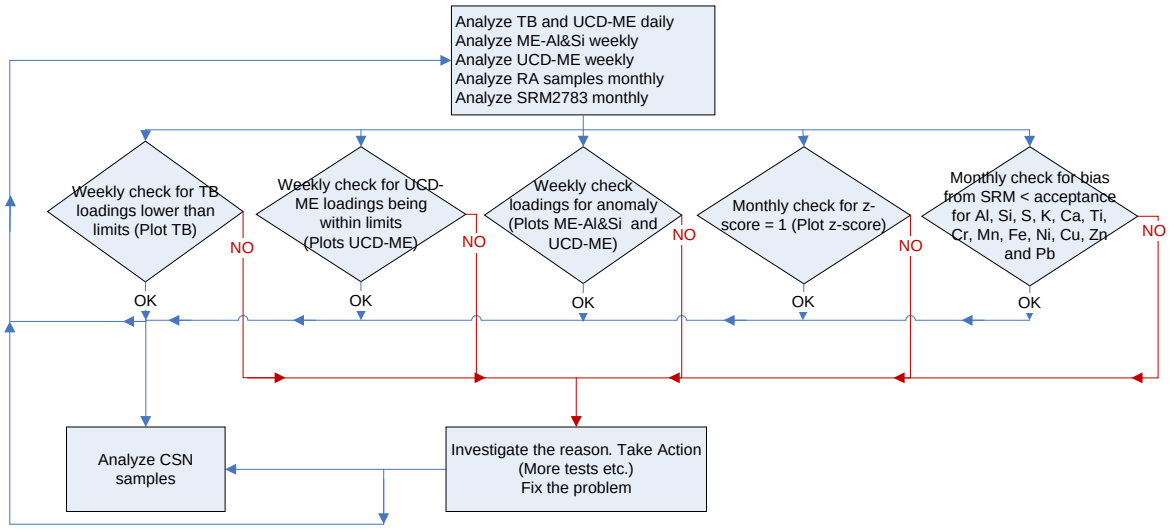
Table 1. The calibration verification activities, criteria and corrective actions.

| Analysis | Criterion | Corrective Action |
|---|---|---|
| Uncertainty of calibration | Urel≤10% for stoichiometric standards and with loadings≥3*MDL | • Check calibration line and spectra<br>• Check standard(s) for damage/contamination<br>• Exclude standard(s) from calibration line<br>• Further cross-instrumental testing<br>• 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<br>• Further cross-instrumental testing<br>• Recalibration with current or new standards |
| Laboratory Blank | ≤ acceptance limits with exceedance of max two elements | • Change/clean blank if contaminated/damaged<br>• Clean the diaphragm, if necessary<br>• Further cross-instrumental testing |
| UCD Multi-element samples | ±10% of reference mass loadings | • Check sample for damage/contamination<br>• Further cross-instrumental testing<br>• 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 |
| 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<br>• Clean the diaphragm, if necessary<br>• Further cross-instrumental testing |
| UCD Multi-element sample | Daily | ±10% of reference mass loadings with exceedance of any element not to occur in more than two consecutive days | • Check sample for damage/contamination<br>• Further cross-instrumental testing<br>• Replace sample if necessary |
| Micromatter Al&Si sample | Weekly | ±10% of reference mass loadings | |
| UCD Multi-element sample | Weekly | ±10% of reference mass loadings with exceedance of any element not to occur in two consecutive measurements | |
| 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 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 (abrasion in analytical chamber). If the QC fails, the first action to take 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. In case the problem is not resolved, more lab blanks should be analyzed to check for similar increase. 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 (Zn spikes in the spectra due to the beam interaction with the ring of the filter).

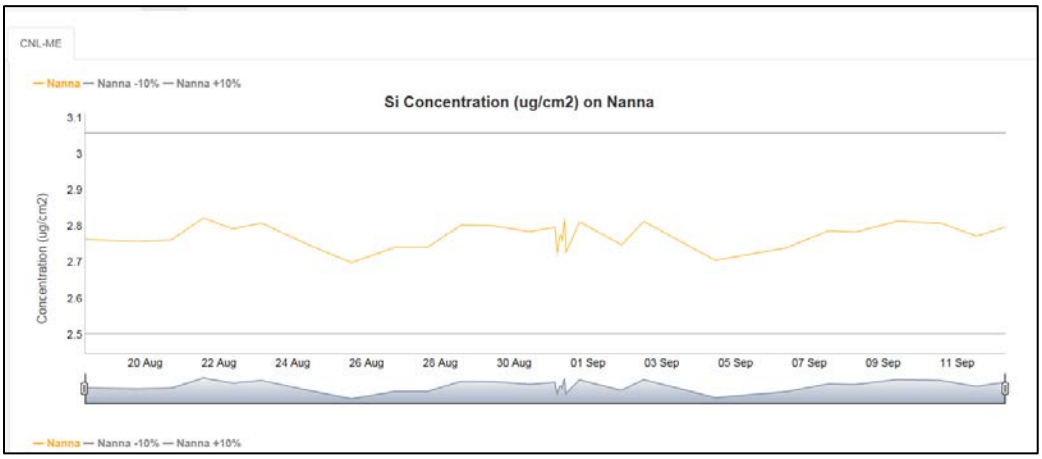
The analysis must be stopped until problem is solved and all samples analyzed during the time period in question must be reanalyzed.

Figure 3. The QC plot of 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). If an element exceeds its acceptance limits (with exception of Br and Cl) 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 started to address the issue.

Figure 4. The QC plots of ME.

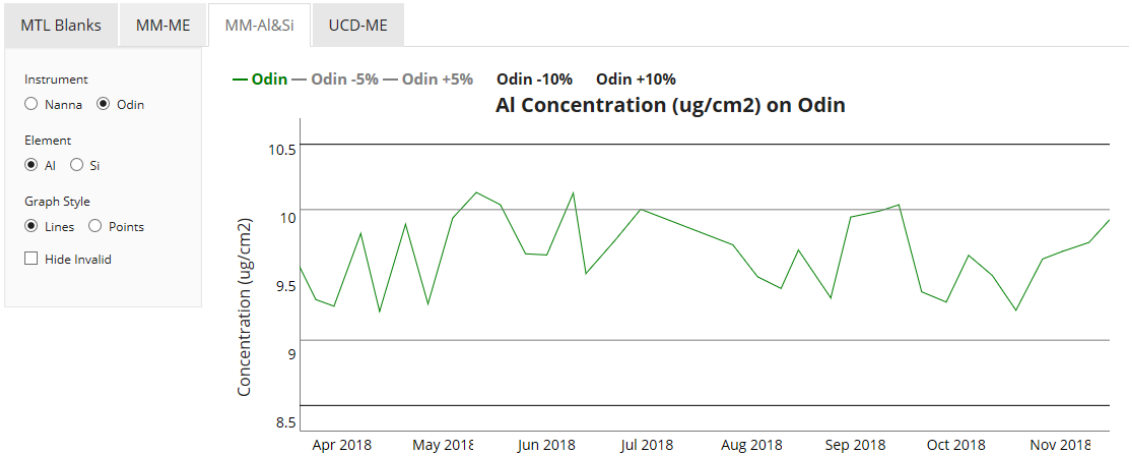



## 9.2.2 Weekly Analysis

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.

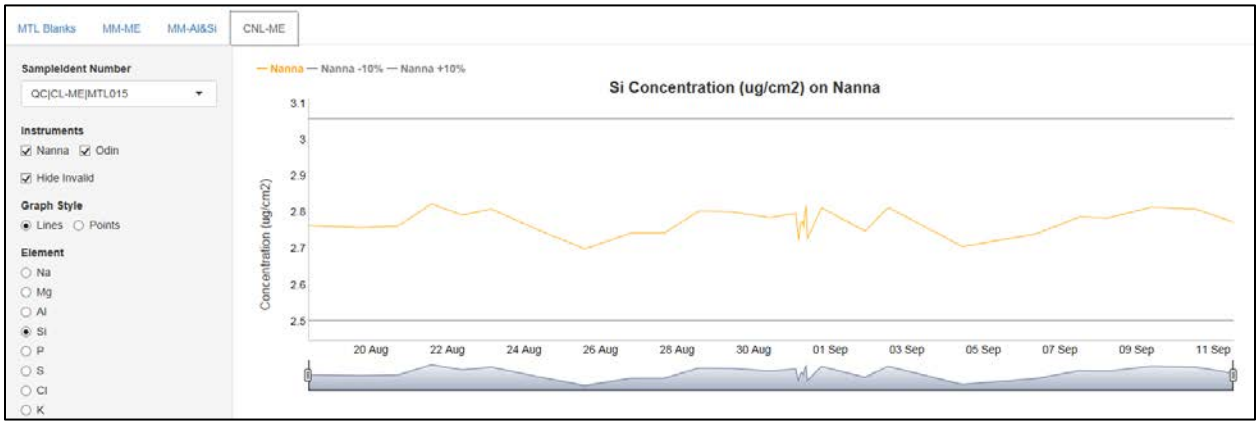
The MM-Al&Si plot includes the Al and Si intensities and mass loadings in real time for each instrument (Figure 5). If acceptance limits are exceeded, an investigation (including cross-instrument analysis, analysis of other ME samples, analysis of single element standards, and other additional tests)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

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




The weekly UCD-ME plot includes mass loading plots in real time for each instrument (Figure 6). If the acceptance limits are exceeded (with exception of Br and Cl) 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 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.

The z-score plot shows the mean z-score values of the reanalysis samples based on the reference loadings (Figure 7). The satisfactory level ($z \leq 1$) is checked for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr (..\..\CSN\QC\Reanalysis_GUM_CSN-ME.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). Exceedances require further testing to address the problem.

Figure 7. The plot of mean absolute z-score for Reanalysis samples.

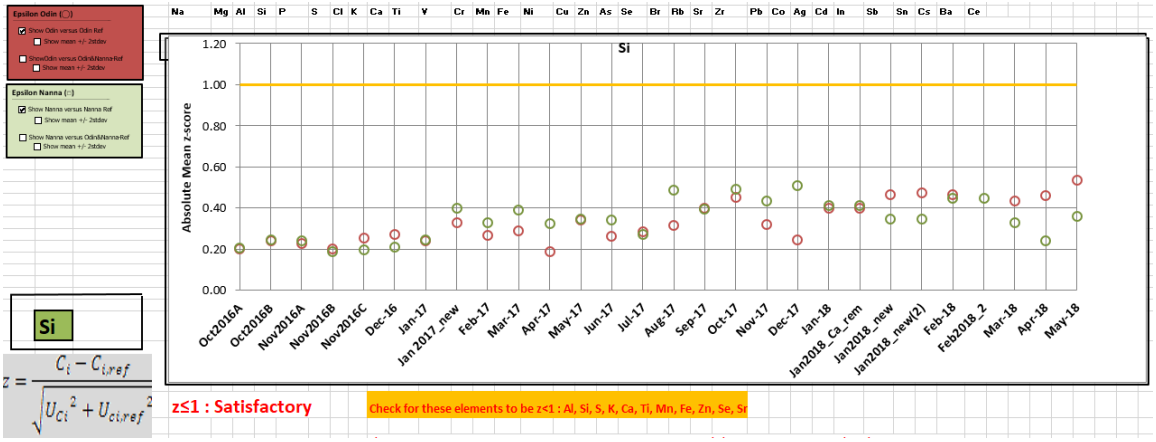
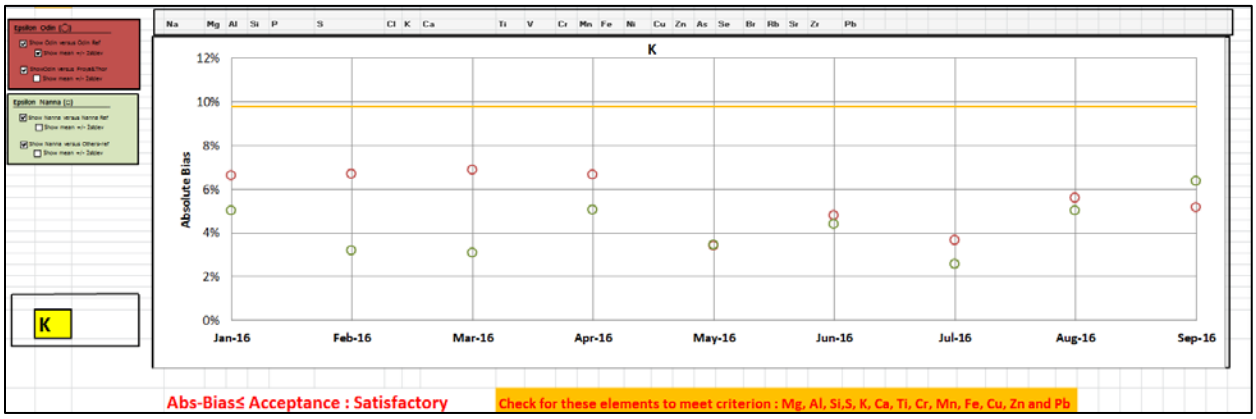


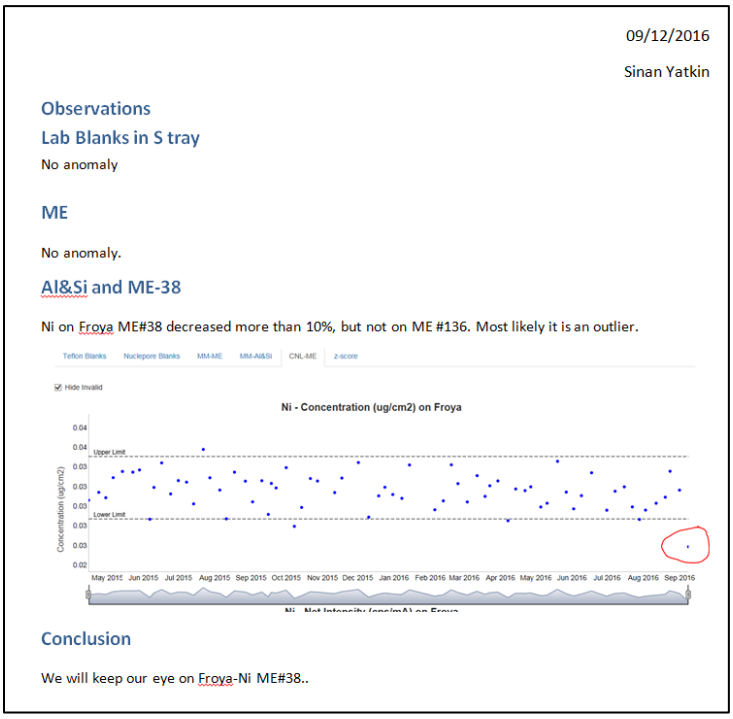

Figure 8. The monthly absolute bias of K from NIST SRM2783.




### 9.2.4 Reporting

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