TI 301E- Quality Assurance/Quality Checks (QA/QC) of XRF Performance

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1. PURPOSE AND APPLICABILITY

The subject of this standard operating procedure (SOP) is the quality assurance/control (QA/QC) steps applied in the elemental mass loadings measurements of $PM_{2.5}$ loaded filters collected in IMPROVE network using EDXRF systems, namely Panalytical Epsilon5. The scope is to ensure good laboratory practice of measurements of elements on $PM_{2.5}$ loaded filters including calibration, verification of calibration and routine quality control checks (daily, weekly and monthly), which are analysis of blanks, multi-elemental reference materials and selected IMPROVE samples, later referred to as "Reanalysis".

2. DEFINITIONS

Lab Blanks: These are Teflon (TB) and Nuclepore (NB) filters placed in the S trays of each Epsilon 5 (E5) to be analyzed daily. TBs are selected from previously accepted batch of filters for regular $PM_{2.5}$ sampling at IMPROVE sites. The monitoring is performed on elemental loadings (µg/cm^2) and intensity (cps/mA) bases for TB and NB, respectively. The TB loadings are compared to be lower than the acceptance limits determined as three times standard deviations added to mean loadings of a set of lab blanks (at least 20 filters).

Multi-Element Samples from Micromatter (MM-ME): These samples contain Fe, Si, Zn, Te, Cs, Br, K and Cl deposited on Nuclepore filters. The samples are analyzed daily (S-tray location) on each of the E5. The first results determined on each instrument serve as reference values. The deviations of ±3% and ±5% serve as warning and acceptance limits, respectively**.**

Al&Si Samples from Micromatter (MM-Al&Si): These samples contain Al and Si deposited on Nuclepore filters to be analyzed weekly on 3 E5s. The loadings are monitored for unusual difference from the long-term measurement results; no specific acceptance criteria are set up at this time.

Multi-Element Sample generated at CNL (CNL-ME): The sample generated from certified multi-elemental solutions contains majority of IMPROVE reported elements, plus Molybdenum. The reference loadings were calculated based on elemental ratios in the certified solutions and EDXRF-K measurements. The mass loadings for all elements present in CNL-ME are monitored in weekly intervals on each E5. No acceptance limits are applied; the weekly results are compared to the long-term measurements at any given E5 as well as between each other for any anomaly.

Reanalysis Samples: This is a selected set of sixteen IMPROVE samples 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 IMPROVE reported elements for each sample obtained each month are compared to pre-determined reference loadings.

z-score: The ratio of absolute difference between each result from monthly reanalysis and reference value to accompanying uncertainty. z-score should remain ≤1 for specified elements.

Relative Expanded Uncertainty (Urel): The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%). Urel is estimated by the summation of contribution from the lack-of-fit of calibration function, repeatability and uncertainty of calibration standards.

Bias: The ratio of difference between measured and assigned (reference) value to assigned value (%).

3. GENERAL GUIDELINES

This document is intended to guide users for verifying the calibration to ensure starting of analyzing samples as well as checking the performance of EDXRF instruments routinely, including analysis of blanks and samples, checks of the results and the action required in case of detected malfunction. 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 (CAS).

4. PROCEDURES

4.1 Calibration Verification

The procedure of the calibration verification is shown in Fig.1 and is summarized in Table 1.

The calibration is performed following instructions. The 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 ..\Uncertainty_GUM\uncertainty-Calibration2015_OrhReg.xlsx for 2015 calculations). The Urel is checked to be equal to or less than 10% for stoichiometric standards of IMPROVE reported elements. In case Urel for stoichiometric standards of IMPROVE reported elements is higher than 10%, calibration lines and spectra are examined to detect the reason of higher Urel. Further testing and checks, i.e., checking the calibration lines of corresponding elements at other E5s, are performed to figure out the reason of exceedance. In case similar deviations are observed on the other E5s, the orientation of the standard needs to be examined. If the orientation is correct, one can suspect the quality of corresponding standards and exclude them 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 (16 preselected IMPROVE samples) and a NIST SRM2783. Meeting the criteria, i.e., acceptance limits for Teflon blanks and MM-ME and z-score equals to or lower than 1 and SRM biases lower than 10% for Al, Si, K, Ca, Ti and Fe, assures the analysis of IMPROVE samples. Failure in meeting criteria requires further checks/testing to resolve it.

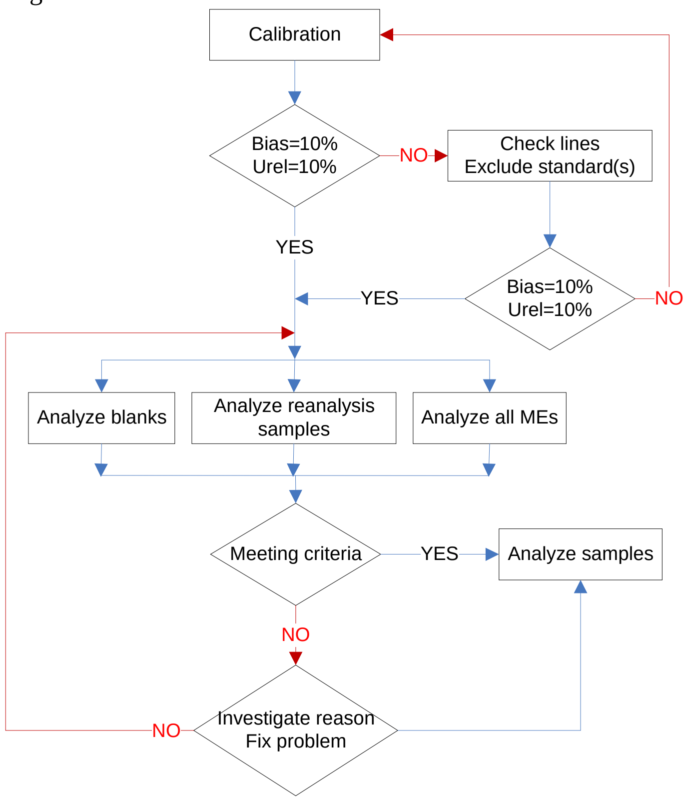

Fig.1. The flowchart of calibration verification.

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

Analysis	Criterion	Corrective Action
Uncertainty of calibration	Urel≤10% for stoichiometric standards	• 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≤10% for Al, Si, K, Ca, Ti, and Fe	• Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards
Teflon Blank	< mean+3sd of pre-set mass loadings for at least two elements	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
Nuclepore Blank	Difference from long-term trend	
Micromatter Multi-element sample	±5% of pre-set mass loadings for Fe, Si, Zn and K	• Check sample for damage/contamination • Further cross-instrumental testing
Micromatter Al&Si sample	Difference from long-term trend	
CNL Multi-element sample	Difference from long-term trend	
Reanalysis samples	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 shown in Fig.2.

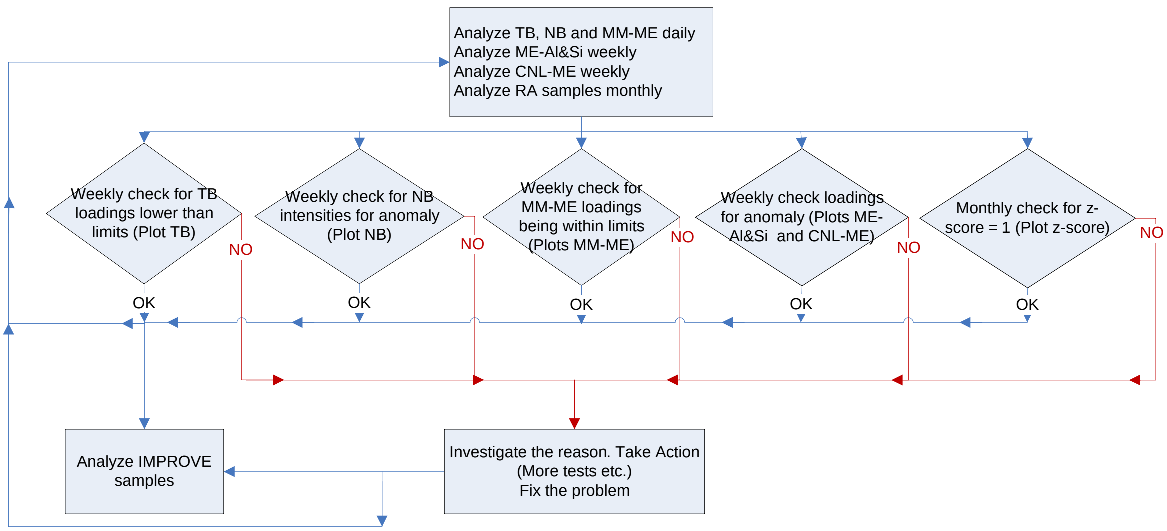

Fig.2. The flowchart of routine QC of EDXRF instruments' performance.

The 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	< mean+3sd of pre-set mass loadings for at least two elements	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
Nuclepore Blank	Daily	Difference from long-term trend	
Micromatter Multi-element sample	Daily	±5% of pre-set mass loadings for Fe, Si, Zn and K	• Check sample for damage/contamination • Further cross-instrumental testing
Micromatter Al&Si sample	Weekly	Difference from long-term trend	
CNL Multi-element sample	Weekly	Difference from long-term trend	
Reanalysis samples	Monthly	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	
SRM 2783	Monthly	Bias≤10%f or Al, Si, K, Ca, Ti, and Fe	

4.2.1 Daily Analysis: The S trays containing analyzer specific TB and MM-ME is analyzed daily using the same application of IMPROVE samples. The samples analyzed must be clean and undamaged.

The TB and MM-ME results are migrated to the database. The plots can be examined at http://169.237.146.119:3838/xrfControlCharts/

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

4.2.1.1 QC of Teflon Blanks: The plot at http://169.237.146.119:3838/xrfControlCharts/ (Fig.3) must be checked for exceedance the limits for at least two elements for failure. The gradually small increase for few elements, e.g., Ca, S and Cl, most likely means atmospheric contamination of TB while increase in Cu and Zn is likely to mean an instrument originate, i.e. abrasion in analytical chamber. The first action is to replace TB with clean one. If loadings of elements exceeding the limits decrease, no further action is necessary and the analysis may continue. If not, the field blanks analyzed in a close time must be checked at U:\IMPROVE_Lab\XRF_Epsilon5\QA\Field Blanks\field_blank_monitoring_updated.xlsm for similar increase. Observed increase on FBs would suggest the instrument related contamination. In this case cleaning the analytical chamber and/or diaphragm should solve the issue. Reanalyzing TB and FB should follow for confirmation. If, however, the problem is not solved, the analysis needs to be stopped and the additional testing needs to be performed to address the issue. For example, in case of sudden huge increase in loadings for few elements, the following are the possible causes:

- Change in geometry (most likely tube or detector distance/angle)
- Filter (or other material) presents in the chamber in addition to analyzed sample
- Sample filter of 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 in the period in question must be reanalyzed.

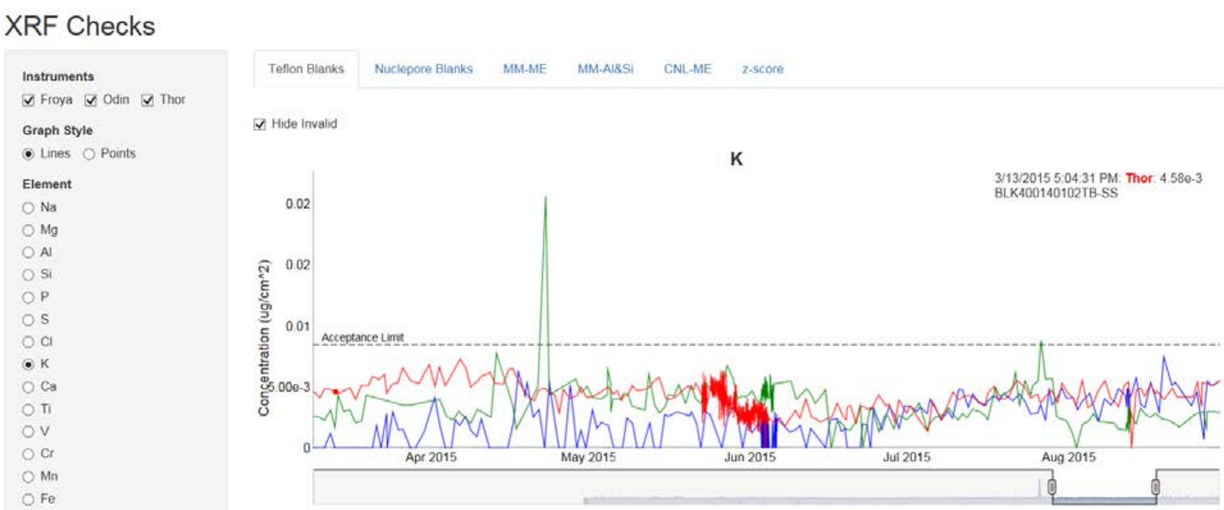

Fig.3. The QC plot of Teflon blank.

4.2.1.2 QC of Nuclepore Blanks: No specific criteria are applied to evaluate the exceedance (Fig.4). The NBs are typically not replaced unless they show consistent contamination. There are small increasing trends observed for few elements, e.g. Cl, S, Ca, Cu, Zn, and sometimes, spikes of Cu and Zn intensities. The possible reasons are investigated. Ultrasonic cleaning of NB using water helped to decrease the contamination of many elements.

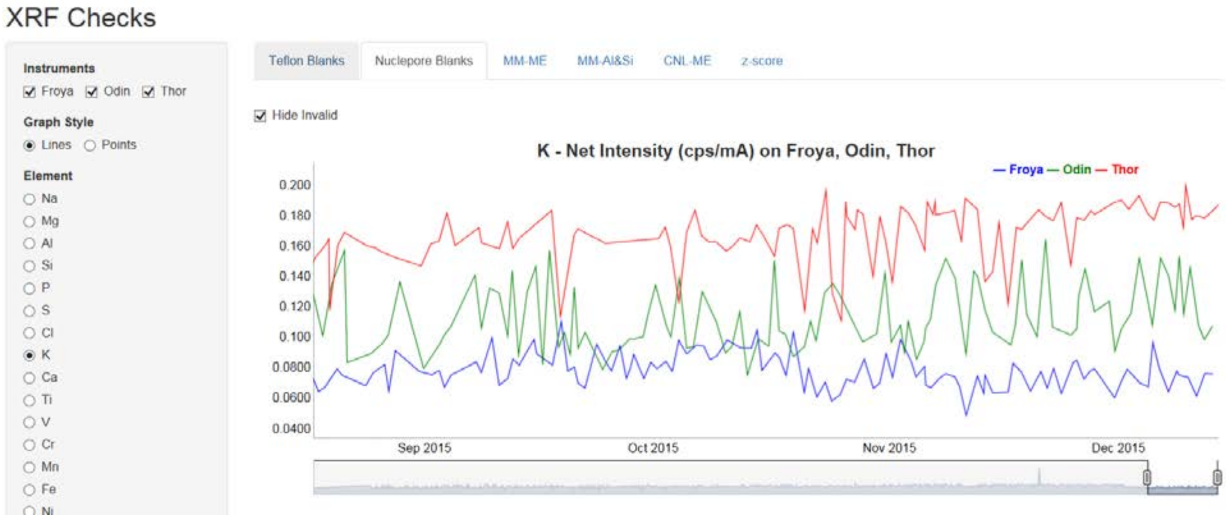

Fig.4. The QC plot of Nuclepore blank.

4.2.1.3 QC of MM-ME: The QC plot includes the intensity and mass loadings in real time for each instrument, see Fig.5. The limits are setup to be ± 3% and ± 5% based on the first measurements of given MM-ME. These reference values may change if any changes to the instruments were performed (i.e. new X-ray tube, new detector, etc.).

If the 5% loading limits are exceeded for number of elements (with exception of Br and Cl), the investigation is started. The cross-instrument analysis, analysis of other ME samples and analysis of single element standards are some of the additional tests performed to address the issue.

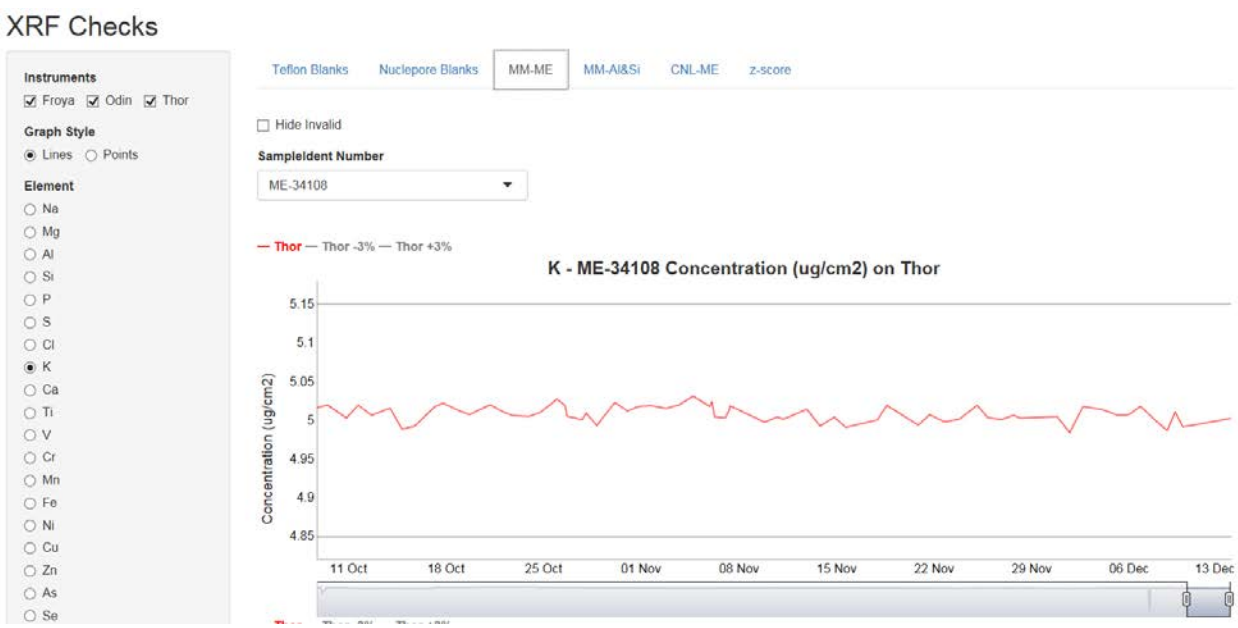

Fig.5. The QC plots of MM-ME.

4.2.2 Weekly Analysis: These analyses include instrument specific Al&Si-ME samples and a CNL-ME sample to be analyzed on three E5 with corresponding blank. The analyzed samples must be contamination free and undamaged. No special blank is required for Al&Si-ME sample.

The MM-Al&Si plot includes the Al & Si intensities and mass loadings in real time for each instrument, see Fig.6. There is no criterion to check for compliance with, but, the mass loadings are inspected and if any discrepancies, the additional testing is implemented.

Note: For consistency, samples should be analyzed with the same application; introduction of “short” application may result in inappropriate quantification due to Br correction for Al and Rb&Sr correction for Si.

Fig.6. The QC plot of Al&Si-ME.

The CNL-ME plot includes intensities and mass loadings plots in real time for each instrument, see Fig.7. There is no criterion to check for compliance with. The ±10% differences from reference loadings are shown in the plot to guide the inspector for any discrepancies, which requires the further testing to resolve the problem.

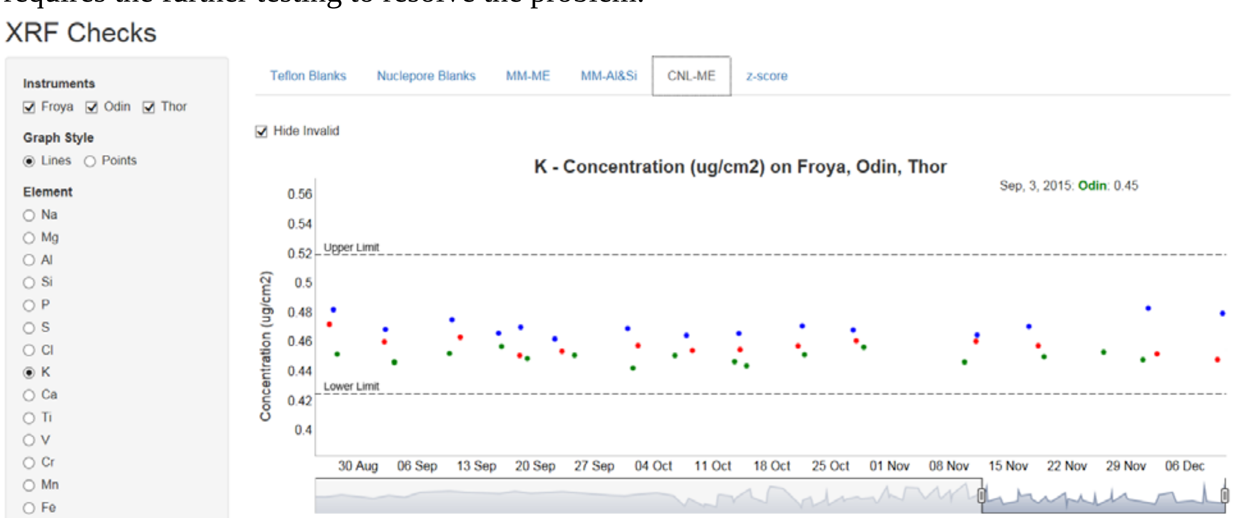

Fig.7. The QC plots of CNL-ME.

4.2.3 Monthly Analysis: The Reanalysis samples are analyzed monthly on three instruments using regular IMPROVE application. A dedicated blank is analyzed along the samples to be utilized for blank subtraction.

z-score is calculated using the following equation:

$$z = \frac{\left| C_j - C_{j(ref)} \right|}{\sqrt{U_{C_j}{}^2 + U_{C_{j(ref)}}{}^2}}$$

where C_j is the mass loading measured using analyzer j (µg/cm^2), $C_{j(ref)}$ is the assigned reference mass loading of analyzer j, U_{Cj} and $U_{Cj(ref)}$ are the expanded uncertainties of measured (C_j) and reference ($C_{j(ref)}$) mass loadings.

The plots include z-score values of three instruments in real time based on two reference values ($C_{j(ref)}$): first instrument specific reference values have been assigned as the mean IMPROVE loadings of 10 measurements by each E5; the second have been calculated as the average of other two instruments reference values, e.g. each month's Odin results are compared to Odin's reference values and the average of Thor's and Froya's reference values. The reference values of NIST SRM2783 are the certified mass loadings.

The z-score plot shows mean z-score values of 17 samples based on any reference values, see Fig.8. The satisfactory level ($z \leq 1$) is checked for each element. As seen in the notes in Fig.8 highlighted in red, there are few exceptions that must be considered. In case of exceedance of the limit, additional tests need to be implemented to address the problem. An excel workbook at..\QA\Reanalysis\Inter_Instruments\2015\Reanalysis_2015.xlsx has links to instrument specific workbooks in the same folder, which provide calculations and graphs of the regression slopes, intercepts and R^2 between monthly results and two reference values (see Fig.9a). In addition, the relative expanded uncertainties based on the error propagation are calculated and plotted in element specific worksheet (see Fig.9b). The unusual slopes than different from long-term ones and R^2 as well as uncertainty must be further investigated. When available, the biases from SRM2783 must be evaluated for unusual cases. The *Sheet1* contains summary and plots of annual variation of slopes.

The same excel files contain the SRM 2783 biases of certified elements. The biases of Al, Si, K, Ti, Ca and Fe shall be checked to be equal to or lower than 10%. Exceedance requires the further testing to address and resolve the problem.

Fig. 8. The plot of z-score for Reanalysis samples.

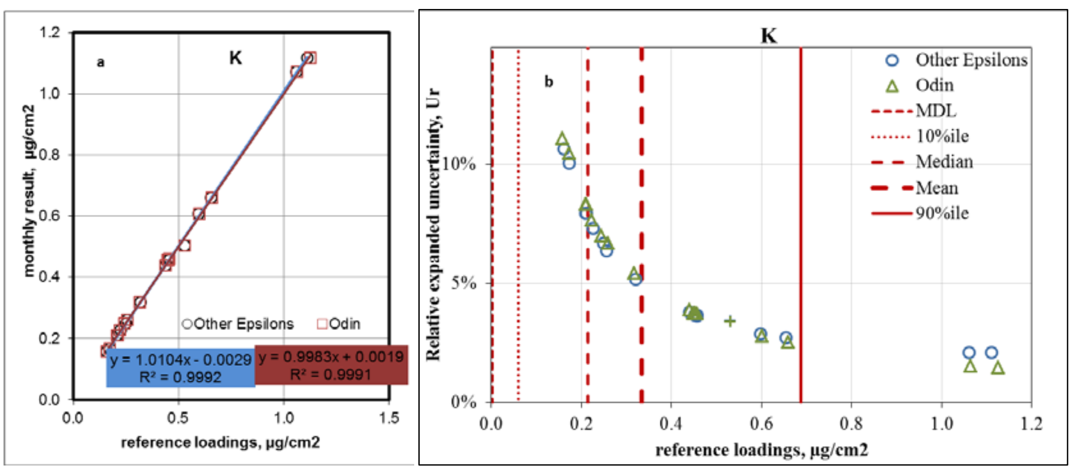

Fig.9.a) The comparison of monthly results of Reanalysis samples with the reference loadings, Odin is reference loadings of Odin; Other Epsilons is the mean reference loadings of Thor and Froya; b) Relative expanded uncertainty at the reference loadings

4.2.4 Reporting: The weekly QC reports about the analyzer performance including the results of daily and weekly monitoring are prepared for the check by the Laboratory Manager. These reports are placed in U:\\IMPROVE_Lab\XRF_Epsilon5\QA\QC_Reports. An example is given in Fig.10. The results of RA samples are reported to the Laboratory Manager in case of a need for further analysis.

07/07/2015
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Observations

Lab Blanks in S tray

TB-Cl on Froya has a small increasing trend just over the limit. Cu-NB-Thor spiked on 4/7/15 and came back to original level.

MM-ME

After PM, all the elements are within their acceptance limits. However, Odin Si, S, K and Fe intensities decreased ~2% after PM in June, 2nd.

MM-Al&Si and CNL-ME

Al&Si ME are normal. ME-38 Odin concentrations of K and S decreased ~2% while Fe and Si are variable. Nevertheless 2% decrease in all elements is more likely.

Conclusion

None.

Fig.10 An example of weekly QC report for daily and weekly monitoring of analyzers' performance