

UCD IMPROVE Standard Operating Procedure #301

X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
06/11/21	SRS	All	Reformatted to fit document guidelines.
06/14/21	JAG	3, 11.3	Updated UCD ME-RM acceptance limits and added routine replicate sample analysis.
8/2/2022	LMK	All	Updated wording.
8/19/2022	JAG	6, 7, 9, and 10	Minor updates in 6 and 7. Updates in 9 and 10 to reconcile with CSN SOP for parts that are the same in both. Also, updated version to 2.5 as last year's version was mistakenly not updated to 2.4 as it should have been.

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1. PURPOSE AND APPLICABILITY

This standard operating procedure (SOP) provides an overview of the principles of X-Ray Fluorescence (XRF) spectrometry, describes the application of this technique to determine and quantify the elemental composition of IMPROVE aerosol samples using the PANalytical Epsilon 5 (E5) XRF analyzer, and outlines the laboratory procedures. The procedures cover operational safety, analyzer calibration and monitoring, filter preparation, handling and analysis, data acquisition, and quality control for all IMPROVE aerosol filter samples.

The body of this document gives only the outline of how samples are handled and analyzed and how data are processed and validated. Each step in the filter analysis process has a specific function and a set of procedures. A detailed explanation of each of these steps is required and provided in the Technical Information (TI) documents that are referenced within this SOP. The E5 analyzer manual is referenced for more specific instructions on certain processes.¹

Five E5 XRF analyzers are housed with Air Quality Research Center (AQRC) at the University of California, Davis (UCD).

2. SUMMARY OF THE METHOD

Analysis of IMPROVE aerosol filter samples is performed using energy dispersive X-ray fluorescence systems (EDXRF), specifically the E5 analyzers operating under vacuum. The basis of the method is the interaction of X-ray photons from the analyzer's excitation source with atoms of the elements present in the filter deposit.

The source of X-rays in the PANalytical E5 analyzer is a 100-kV side window X-ray tube with a dual Scandium (Sc)/Tungsten (W) anode. Generated X-rays are focused on one of six secondary targets in such geometry that polarized X-ray photons are used to excite a sample. These photons cause the ejection of inner shell electrons from the atoms in the sample. The vacancies are filled with outer shell electrons and the transitions result in the emission of X-rays, which are characteristic of each element present in the sample. These characteristic X-rays are detected in a solid-state Germanium (Ge) X-ray detector (Pan-32). Electrical charges generated by each entering photon are grouped into energy channels, counted, and displayed during analysis as a sample spectrum of X-ray counts versus energy. The characteristic peaks in the spectrum are superimposed on a background caused by the scatter of X-rays from the tube into the detector. The individual peak energies in the spectrum correspond to specific elements and peak areas are proportional to elemental mass loadings (although the relationships can become non-linear at high concentrations). Each spectrum is collected for the specified time and saved for further processing with the E5 software. Spectrum evaluation is done by non-linear least squares fitting based on the AXIL algorithm.²

The E5 is a fully integrated spectrometer exceling in high-throughput, high-sensitivity analysis for multiple elements. The high-power excitation source and polarizing optical

path provide low detection limits for many elements allowing analysis of small quantities of sample. The system's gain correction method assures high analyzer stability; the calibrations can be done less frequently. Because XRF is a non-destructive technique, the samples can be reanalyzed multiple times. However, exposure to the vacuum may result in the loss of some volatile species (e.g. ammonium, nitrate, chlorine, and bromine).

For the IMPROVE samples, six different analytical conditions are used during a single analysis run to balance sensitivity and exposure time for the 24 elements reported to IMPROVE. Each analytical condition is designed to optimize detection for a subset of the 24 elements and uses a different secondary target, X-ray tube voltage and current, energy detection range and resolution setting, and exposure time (see Table 1).

Table 1. Epsilon 5 setup for IMPROVE samples.

Secondary Target	Analysis Time, s	kV	mA	Detector Setting	Reported Elements
CaF ₂	600	40	15	High Resolution	Na, Mg, Al, Si, P, S, Cl, K
Fe	400	75	8	Standard	Ca, Ti, V, Cr
Ge	400	75	8	Standard	Mn, Fe, Ni, Cu, Zn
SrF ₂	400	100	6	Standard	As, Se, Br
Mo	400	100	6	Standard	Rb, Sr, Pb
Al ₂ O ₃	200	100	6	Standard	Zr

3. DEFINITIONS

- **Thin sample:** A sample with a deposit thin enough for enhancement and absorption phenomena to be negligible.
- **Energy Dispersive X-ray Fluorescence (EDXRF):** An analytical technique used to determine the elemental content of a sample.
- **Intensities:** The flux of emitted radiation at a particular wavelength. Intensities are quantified in units of counts per second per milliamp (cps/mA). Intensities are often referred to informally as counts.
- **Theoretical intensities:** The expected flux of emitted radiation by standard reference materials computed from the certified mass loadings and the library of fundamental parameters.
- **Raw intensities (referred to as “net intensities” in the PANalytical software):** The fluorescence intensities (cps/mA) measured and deconvoluted by the analyzer. These raw intensities construct a spectrum for each analyzed sample.
- **Net intensities (referred to as “corrected intensities” in the PANalytical software):** The deconvoluted and blank-corrected fluorescence intensities (cps/mA) calculated by the analyzer. The net intensities are per element and are used along with the calibration factors to calculate the mass loadings in the IMPROVE samples.
- **Deconvolution:** The mathematical processing to resolve the contributions of individual elements to the measured spectrum. An iterative least-squares method

is used to fit theoretical profiles to the measured spectrum, constrained by known theoretical ratios between different lines from the same element. Element raw intensities (cps/mA) are quantified by the deconvolution process.

- **XRF Application:** The collection of software and hardware settings used to analyze samples including the analytical operating parameters (secondary targets, times of analysis, X-ray tube operational parameters, detector settings, and reported elements), deconvolution parameters, and calibration factors for analyzing samples.
- **Reference material (RM):** Samples used to evaluate the performance of the XRF analyzers. These reference materials have assigned mass loadings, which are not necessarily assigned (or certified) by an authority. Reference materials can be samples obtained either from authoritative agencies such as the National Institute of Standards and Technology (NIST), or, produced by private companies, or, ambient air samples.
- **Standard Reference Material (Standards):** Reference materials with certified reference mass loadings and uncertainties. Standards are used to calibrate the XRF analyzers.
- **Re-analysis set:** consisting of selected IMPROVE samples and a NIST SRM2783 sample to check the stability of the analyzers and to verify calibration periodically (typically monthly).
- **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 of calibration function is estimated following an international method³.

$$C_{std,i} = E_i * I_{cor,i} \rightarrow U_{rel}(C_{std,i}) = k \frac{u(C_{std,i})}{C_{std,i}} = k \frac{\sqrt{\sum \left(\frac{\partial C_{std,i}}{\partial x} u(x) \right)^2}}{C_{std,i}}$$

$$= k \frac{\sqrt{(E_i * u(I_{cor,i}))^2 + (I_{cor,i} * u(E_i))^2 + (u(C_{std}))^2}}{C_{std}}$$

Where, $c_{std,i}$ is the re-constructed loading ($\mu\text{g}/\text{cm}^2$) of calibration standard i (c_{std}) using the calibration factor (E , in $[(\mu\text{g}/\text{cm}^2)/(\text{cps}/\text{mA})]$) and I_{cor} is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA). Although the uncertainty of c_{std} , $u(c_{std})$, is not a part of the $c_{std,i}$ calculation, it is added to the uncertainty equation for a conservative approach. The coverage factor, k , considers the distribution of uncertainties possible for a given measurement and, in this work, a coverage factor of 2 is used to give approximately the 95% confidence interval on the uncertainty value ($k = 1.96$ at 95% confidence level for a normal distribution).

- **Bias:** The ratio of difference between measured and certified loading of NIST SRM 2783 to certified loading (%).

$$\text{Bias} = 100 * \frac{C_{E5} - C_{cer}}{C_{cer}}$$

Where, c_{E5} and c_{cer} are the loadings by E5 and certified loadings of NIST SRM 2783, respectively.

- **Z-score:** The ratio of difference between each result from monthly reanalysis and reference value to accompanying uncertainty.

$$z = \frac{C_{E5} - C_{ref}}{\sqrt{U_{C_{E5}}^2 + U_{C_{ref}}^2}}$$

Where c_{E5} is the mass loading measured ($\mu\text{g}/\text{cm}^2$), c_{ref} is the reference mass loading; $U_{c_{E5}}$ and $U_{c_{ref}}$ are the expanded uncertainties of measured (c_{E5}) and reference (c_{ref}) mass loadings. The expanded uncertainties are estimated following an international method³.

- **Acceptance limits:**
 - **PTFE blanks:** analyzed daily; are determined as the mean plus three standard deviations of a set of lab blanks.
 - **UCD multi-elemental reference materials (ME-RMs):** analyzed daily and weekly; are determined as $\pm 10\%$ or ± 3 standard deviations, whichever is larger, of the reference loadings, depending on the concentration of the element on the ME-RM.
 - **SRM2783:** analyzed monthly; are element-specific and determined as root-mean-squared-relative-errors (RMSREs), plus three times standard deviations from a set of SRM measurements.

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

Where m refers to measurement month.

4. HEALTH AND SAFETY WARNINGS

The E5 is designed for safe operation. The XRF analysis is conducted in a radiation-sealed environment with interlocks that do not allow the operator to access the X-ray chamber while the X-ray tube is on. The analyzers are also inspected and certified by the Office of Environmental Health and Safety (EH&S) at UC Davis. However, the following cautions should be noted:

- **The Epsilon 5 analyzers produce X-rays**, which can be hazardous to health if precautions are not taken. Refer to the Epsilon 5 System User's Guide for more information (Chapter 3, page 7).
- **A Beryllium (Be) window is present in the analyzer** (X-ray tube and Ge detector). Fumes or the dust from beryllium and its compounds can be hazardous

if inhaled. The reader is referred to the Epsilon 5 System User's Guide (Chapter 3, pg. 8). The window is fragile and should not be touched or exposed to any pressure, which may cause a rupture. If a rupture occurs, extreme caution must be exercised during the cleanup (consult a service engineer and EH&S). The windows can be damaged by moisture condensation and they should be kept clean and dry at all times. The detector should not be stored or operated in a humid environment. If moisture condenses on the window during normal operation, either the humidity is too high or the detector has a vacuum problem. Moisture on the Beryllium window could result in Beryllium vapors which are toxic to breathe. Also fumes or the dust from Beryllium and its compounds can be hazardous if inhaled. During liquid nitrogen filling, condensation will occur. This is normal. It should go away as the unit warms up.

- ***Lead may be found as a shielding material in the Epsilon 5.*** Fumes or dust from lead can be hazardous if inhaled or ingested. For further information, please refer to the System User's Guide (Chapter 3, page 9).
- ***Liquid nitrogen is used to cool the Pan-32 Ge X-ray detector.*** It should be handled with care in well-ventilated rooms. Liquid nitrogen and nitrogen gas are not toxic. However, they may displace atmospheric oxygen when present in large quantities or when used in confined or poorly ventilated spaces resulting in a suffocation hazard. For further details on precautions when using liquid nitrogen and emergency actions in the event of a nitrogen leak, please read the Epsilon 5 System User's Guide (Chapter 3, pages 10-11). All staff handling liquid nitrogen should have proper training in cryogenic liquids according to UC Davis EH&S guidelines.
- ***Do not remove or open any panels that are not accessible by hand.*** Terminals may be live when the machine is connected to its power supply, and accessing these areas is likely to expose live parts. For further details, please refer to the Epsilon 5 System User's Guide (Chapter 3, page 7).

5. CAUTIONS

- The system user must be aware that changing any of the analyzer controls during a measurement (e.g., medium, high tension generator, target and filter selections, and/or sample handling) will influence the analysis results. Analyzer parameters and settings can also be changed in the software, which can influence the analysis results.
- No calculations or any other modifications to the running (active) application should be attempted.
- The analyzer's cover allowing access to the sample changing table can be opened only when the green light on the front panel is **ON**.
- The analyzer can be switched off only for a short period of time (< 2 hours) without a full restart. In this case the detector and generator high voltage should be kept ON. If the analyzer needs to be shut down for a longer period of time, the

shut down and start up procedures specified in the Epsilon 5 System User's Guide must be followed.

6. INTERFERENCES

All spectra from IMPROVE samples and field blanks are processed with the PANalytical E5 peak deconvolution software, and raw intensities are determined for each element and identified by the analyzer.

Some possible issues may come from the filter lot. Before being used in the network, contamination levels in a new lot of filters are evaluated through acceptance testing (see TI 251C). While small amounts of contaminants can be corrected with blank subtraction, large amounts of contaminant lead to concerns about the quality of the filter material. Also, variable amounts of contaminants will cause higher uncertainties in the measurements. New lots that fail acceptance testing are returned to the manufacturer for replacement.

The IMPROVE network routinely speciates only fine-particle samples, for which the attenuation of the fluorescent signal by within-particle absorption is minor for most elements. No attenuation correction for particle size or mass loading is performed at this time.

The X-ray beam is almost circular with a diameter of approximately 20 mm. The assumed area of the deposit on 25 mm polytetrafluorethylene (PTFE) filters for IMPROVE is 3.53 cm² (21 mm diameter), and the deposit is assumed to be homogeneous.

7. PERSONNEL QUALIFICATIONS

Only trained personnel listed in the RUA (Radiation Use Authorization) can operate the E5 analyzers. Any adjustments to the E5 analyzer settings can be performed only by the laboratory manager or by a delegated person with the laboratory manager's approval.

Sample handling, including loading and unloading of the E5 analyzers, can be performed by an employee who has been trained by an authorized user and has read this SOP and associated documents. All users must have previously completed the Radiation Safety for Users of Radiation Producing Machines course offered through EH&S.

In order to perform the liquid nitrogen fills, users should obtain relevant training and complete the Cryogenic Safety course available through EH&S.

The preparation of the filters for analysis and regular servicing of the analyzers, including weekly liquid nitrogen fills and detector calibration (automated), is the responsibility of lab technicians. Analyzer calibrations, quality control data evaluation (performed daily, weekly and monthly), and review of the data are the responsibility of the spectroscopist and laboratory manager. The duties of each of these positions are described below.

The Laboratory Manager will:

- oversee the XRF analysis

- approve schedules for routine analysis and special studies
- approve and oversee systems calibrations
- oversee maintenance and repair of the XRF analyzers
- resolve any inconsistencies in calibrations, re-analyses, or normal analyses
- approve the release of the final XRF data

The Spectroscopist will:

- review the results of all quality control tests
- review each data set in the context of historical data and of current system conditions
- identify abnormalities and provide recommendations for understanding and rectifying them
- perform systems calibrations as needed
- perform system troubleshooting and maintenance as needed

The Laboratory Technician will:

- load and unload filter samples to and from the XRF analyzers
- perform regular calibration checks and other Quality Control (QC) checks
- fill the analyzers' liquid nitrogen reservoirs weekly
- perform weekly energy calibrations (automated process)

8. EQUIPMENT AND SUPPLIES

The E5system consists of two main components: the XRF analyzer and the computer workstation (see Figure 1). The XRF analyzer includes an integrated robotic sample changer arm, a sample chamber where a single sample is inserted for analysis, and a sample table that can hold up to 52 samples. The sample table can be accessed only when the green light indicator is ON.

Figure 1. PANalytical Epsilon 5 analyzer and computer station in the XRF Laboratory at AQRC.



9. PROCEDURAL STEPS

The E5 System User's Guide provides complete detailed instructions for installing and operating the E5 analyzer. These instructions are followed whenever the E5 needs to be relocated or restarted.

9.1 XRF Application Setup

In order to start analyzing samples on the E5 analyzer, a specific application must be developed and set up. Setting up the application requires the following: selecting the elements to be reported, acquisition and reporting scheme conditions, a calibration standards file (along with measurement of standards), and deconvolution parameters. As long as no changes are made to the processing methods for a given application, the theoretical intensities of the standard reference materials remain valid. The basic application settings used for the routine IMPROVE sample analyses are shown in Table 1.

9.2 Calibration

The Epsilon 5 has been shown to be a stable analyzer that does not need frequent calibrations. Calibrations are performed upon first installation, approximately yearly or when the analyzer fails verification tests, and whenever an analysis-critical component (e.g., X-ray source or detector) of the analyzer receives maintenance or is replaced.

Calibration of the E5 analyzers is performed using the standards listed in the calibrations folder on the AQRC shared file server. Each year has a folder containing a workbook, YYYY_XRF_Calibration_Standards.xlsx, where the YYYY refers to the year of calibration. They consist of MicroMatter thin film foils on Nuclepore membranes (prepared by vacuum deposition), UCD-made standards on PTFE membranes⁵, and NIST Standard Reference Material (SRM) 2783 air particulate on polycarbonate filter

membranes. Each type of standard sample media has a corresponding blank membrane that must be analyzed and used for blank subtraction.

Calibration standards are selected in the E5 application, and the software calculates the theoretical relative intensities of the standards listed in the standards file using the operating and deconvolution parameters in the selected application; this calculation will be most accurate when the full composition of the standards is entered, including elements that are not of interest. Next, the standards are analyzed. The software then performs least-squares regression with the theoretical and measured intensities forcing the intercept to zero for each element. At least two standards for each element are required, preferably spanning the range of concentrations expected in the real-world samples. The calibration factors (slopes of linear regression) for the elements are stored within the application on the XRF computer.

The quality check of calibration is performed by a set of analyses summarized in Table 2. In addition, routine calibration verification and stability/performance of XRF analyzers are checked (see *UCD IMPROVE TI #301C: QAQC* for details).

Table 2. The calibration verification activities, criteria and corrective actions.

Analysis	Criterion	Corrective Action
Uncertainty of calibration	$U_{rel} \leq 10\%$ for stoichiometric standards and with loadings $\geq 3*MDL$	<ul style="list-style-type: none"> • 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	<ul style="list-style-type: none"> • Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards
PTFE Blank	\leq acceptance limits with exceedance of max two elements	<ul style="list-style-type: none"> • Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD Multi-element samples	Larger of $\pm 10\%$ 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	<ul style="list-style-type: none"> • Check sample for damage/contamination • Further cross-instrumental testing • Replace filter sample as necessary
Reanalysis samples	$z\text{-score} \leq 1$ for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn and Pb	
Analysis	Criterion	Corrective Action
Uncertainty of calibration	$U_{rel} \leq 10\%$ for stoichiometric standards and with loadings $\geq 3*MDL$	<ul style="list-style-type: none"> • 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	<ul style="list-style-type: none"> • Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards

Analysis	Criterion	Corrective Action
PTFE Blank	\leq acceptance limits with exceedance of max two elements	<ul style="list-style-type: none"> • Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD Multi-element samples	Larger of $\pm 10\%$ 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	<ul style="list-style-type: none"> • Check sample for damage/contamination • Further cross-instrumental testing • Replace filter sample as necessary
Reanalysis samples	z-score ≤ 1 for Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn and Pb	

9.3 Daily (or Weekly) Operation

Verify analyzer is set for the current IMPROVE application:

The current version of the IMPROVE application is used for analysis of all IMPROVE samples. The IMPROVE applications all use the same analytical settings. The processing parameters and calibration factors are analyzer and time specific. Therefore, the application version number changes on an analyzer each time an element calibration is performed. The application performs fully automated analyses of samples under the specified conditions, saves the measured spectra within the application database, and processes the spectra into raw intensities. Spectra can be accessed and viewed while analysis is in progress.

Liquid nitrogen (LN2) fills:

The Ge X-ray detector employed in the E5 must be cooled with liquid nitrogen (LN2) to provide stability. It is necessary to regularly fill the dewar completely (20 L capacity) with LN2. The LN2 is refilled once a week. An audible alarm will prompt the user to refill the LN2 if it is running low, but under normal operating conditions the LN2 should not run low if it is filled every week. Detector calibration is performed at least two hours after the LN2 fill to ensure detector temperature stability.

Users should refer to the System Users Guide and UCD IMPROVE TI 301A LN2 Fills and Detector Calibration for detailed safety information regarding the handling of LN2 and for specific instructions on performing the refill.

Detector calibration:

The detector calibration process consists of repeated measurements of the tungsten permanently installed in the E5. Tungsten has a characteristic fluorescence for $K\alpha$ at 58.856 keV and $L\alpha$ at 8.396 keV, which are used to calibrate the corresponding energy channels. During the process, the photon signals coming from the detector to the DSP (Digital Signal Processor) are positioned into the appropriate energy channels. The calibration is typically performed on a weekly basis, following the weekly LN2 fill. The analysis needs to be stopped to perform detector calibration. For more information on this process, please see UCD TI 301A.

9.4 Loading and Removing Filters

Filter Handling:

Sampled PTFE 1A and 5A filters previously received from the field are validated, post-weighed in the Sample Handling Laboratory, stored in Petri dishes, and organized according to a generated inventory list. For more information on these procedures, please see *UCD SOP #251: Sample Handling*.

Filter Preparation:

All IMPROVE A module samples and A module field blanks with valid status flags are organized into trays to be analyzed by XRF. More information on this process can be found in TI 251N.

The specific procedure used for loading samples requires generation of a sample list (XRF queue file) and loading it to each E5 utilized for IMPROVE analysis. The XRF queue file is used in conjunction with the E5 barcode scanner capabilities. Filters are scanned and transferred from labeled petri dishes into specially designed holders and placed into E5 trays (and positions) for analysis. Once a tray has been loaded and placed on the sample changer table in the E5 analyzer, the samples can be queued using the E5 software. Special attention must be given during loading and unloading to assure the proper identity of samples. In addition, physical changes to the sample before/after analysis (e.g. torn, dropped, etc.) must be reported in the IMPROVE web app. Detailed instructions for loading and unloading samples can be found in *UCD IMPROVE TI 301B: Sample Changes for 8 Position Trays*.

10. DATA AND RECORDS MANAGEMENT

10.1 Log Books

Each day the IDs (site and date) of the first and last samples loaded into each XRF analyzer are logged into the respective XRF Analyzer log book and the electronic log book.

10.2 Transferring Data to the IMPROVE Database

The E5 software calculates intensities and loadings, and stores them in a results database table within the E5 computer. The results are also transmitted automatically to the AQRC IMPROVE database.

10.3 Data Storage and Backups

Raw and processed spectra are saved and available for use at any time on the E5 computers. Copies of the net intensities and mass loadings are stored in the IMPROVE SQL Server database. Data safety and security are ensured by frequent backup of computerized raw data from the E5 PCs in the AQRC XRF Laboratory to two different locations, one in the Land, Air, Water Resources building on campus and to an external data backup vendor (cloud-based storage). Differential backups are performed daily and full backups are performed weekly.

10.4 Calculation of Mass Loadings, Method Detectable Limits (MDLs), and Uncertainties

Calculating Mass Loadings:

The E5 software reports intensities and mass loadings for each analyzed sample. The blank correction for each of the sample's mass loadings is performed after analysis on the XRF using field blanks, see *UCD IMPROVE SOP #351: Data Processing and Validation* for details.

Method Detection Limits:

XRF method detection limits (MDLs) for the network are calculated from the field blank results stored in the database. The MDL is calculated using a set of recently analyzed field blanks. The MDL is the greater of either the 95th percentile mass loading minus the median mass loading of these field blanks or an analytical MDL determined from lab blanks run on the XRF instruments. The analytical MDL values are determined from the analysis of approximately 50 to 100 lab blanks on each analyzer and calculated as the 95th percentile mass loading minus the median mass loading. Further details of the MDL calculation can be found in *UCD IMPROVE SOP #351: Data Processing and Validation*.

Uncertainty:

The reported network XRF uncertainties for each element, expressed as $\mu\text{g}/\text{m}^3$, are calculated by combining estimates of the additive and proportional uncertainties in the measurement. Additive uncertainties are derived from the MDLs described above and proportional uncertainties are estimated from paired collocated samples, see *UCD IMPROVE SOP #351: Data Processing and Validation* for details.

Analytical XRF uncertainties (i.e. those not related to network samples, like QC samples and standards) are calculated following an international method³. The mass loading of any element is calculated using the following equation:

$$C_{E5} = C_{\text{sample}} - C_{\text{blank}(\text{median})}$$

Where c_{sample} and $c_{\text{blank}(\text{median})}$ are the reported mass loading of any sample and median blank loading, respectively. The E5 software calculates any loadings using the net intensity and calibration factor (E). Thus, the equation can be re-written as:

$$C_{E5} = I_{\text{net},\text{sample}} \cdot E - I_{\text{net},\text{blank}} \cdot E = (I_{\text{net},\text{sample}} - I_{\text{net},\text{blank}})E$$

Applying the international method to this equation yields the expanded analytical uncertainty (u_{cE5}) given below (see ref 6 and 7 for details):

$$u(C_{E5}) = k \sqrt{\sum \left(\frac{\partial C_{E5}}{\partial x} u(x) \right)^2}$$

$$= k \sqrt{(E * I_{net, sample})^2 + (E * I_{net, blank})^2 + ((I_{net, sample} - I_{net, blank})u(E))^2}$$

The resultant values represent the uncertainties associated with the elemental mass loadings determined by XRF, expressed as $\mu\text{g}/\text{cm}^2$.

11. QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance/control for the XRF analyzers consists of the routine checks using analysis of several materials including blanks, ME-RMs, a re-analysis set, and NIST SRM2783. These checks serve to ensure the stability of analyzers, verification of calibration, and inter-analyzer comparison. The details of this testing can be found in TI 301C.

11.1 Performance Testing, Control Charts, Tolerances, and Actions to Be Taken

The stability of the analyzers is monitored routinely (daily, weekly and monthly) by analyzing blanks, RMs and re-analysis set (Table 3). The results (mass loadings in $\mu\text{g}/\text{cm}^2$ and net intensity in cps/mA from each check) are recorded in the database and displayed on a web application site. Graphs of the data are updated frequently and can be viewed at any time. Additionally, an overview of the daily QC results is accessible via <https://shiny.aqrc.ucdavis.edu/xrfDailyOps/>.

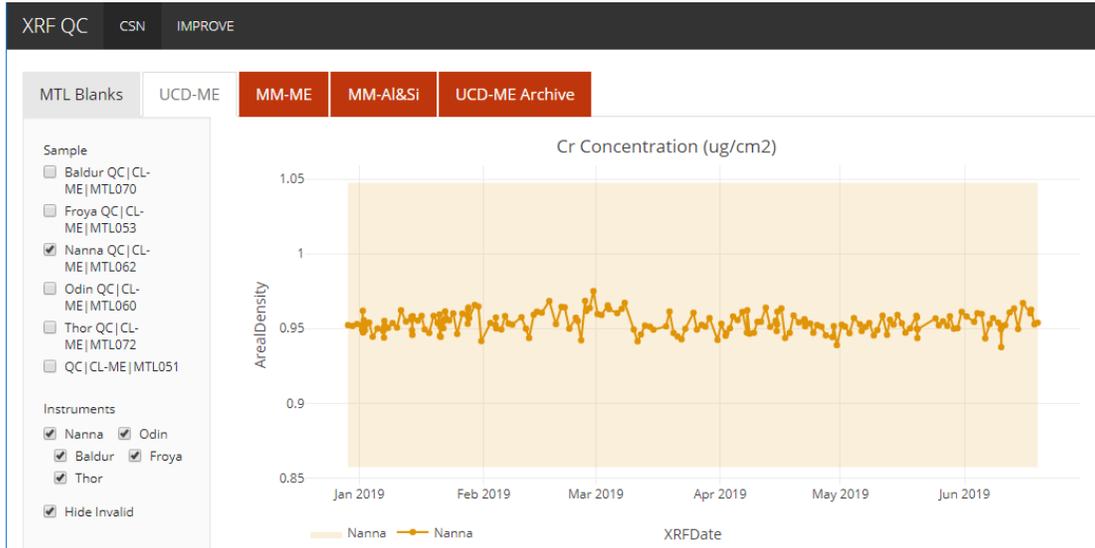
Table 3. The routine QA/QC activities, criteria and corrective actions.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"> • XRF software automatically adjust the energy channels
PTFE Blank	Daily	\leq acceptance limits with exceedance of any elements at least in two consecutive days	<ul style="list-style-type: none"> • Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing • Reanalyze network samples since last passing QC as needed.
UCD Multi-element sample	Daily [^]	Larger of $\pm 10\%$ 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	<ul style="list-style-type: none"> • 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 $\pm 10\%$ 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	
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	

[^]The difference between daily and weekly UCD Multi-Element sample analysis is the daily check uses a sample dedicated to each analyzer. They are not shared. The weekly check uses the same sample shared across all analyzers for an inter-instrument comparison.

A successful outcome of the above-listed tests grants further analysis of samples. If the values exceed acceptance limits, the XRF lab manager must be immediately notified and the problem must be fixed before analysis continues.

Figure 2. Performance testing with UCD-made ME sample analyzed daily. The upper and lower bounds of the shaded region are the acceptance limits.



11.2 Reproducibility Testing

Analyzing re-analysis sets on each analyzer every month serves long-term reproducibility and inter-analyzer comparability checks. The analyzers' reproducibility is monitored by z-score calculated using monthly results and the reference values. The mean of z-score for re-analysis set calculated for long-term reproducibility and inter-analyzer comparison must remain between -1 and 1 for the elements listed in Table 3. If continuous exceedances of the z-score limit are observed, the laboratory manager is notified and further tests are employed to determine the cause of instability.

11.3 Replicate Sample Analysis

Each XRF analysis takes approximately an hour; performing replicate analysis can be difficult to fit into the analytical schedules. To ease congestion, a full load of samples over the weekend will typically end before the following Monday morning, where one tray of samples is queued to repeat analysis over the weekend. Timing varies, but 8 samples per week per instrument can be expected. There are no laboratory level acceptance tests for the replicate measurements yet.

11.4 Data Validation

- All data entries (e.g., sample ID, sample status, etc.) in the sample changer are verified to match actual samples loaded. If there are any discrepancies, notes are made and the laboratory manager is notified.
- Data integrity, internal consistency and reasonableness of results are reviewed after analysis by the spectroscopist and/or laboratory manager.

The data integrity check consists of verifying that all valid samples were analyzed by XRF.

11.5 Approval of Data for Final Validation and Delivery

After the initial data review is complete, the elemental composition data are merged with data from other analyses and undergo final validation before delivery, see *UCD IMPROVE SOP #351: Data Processing and Validation* for details.

12. REFERENCES

1. Panalytical Manual for Epsilon 5
2. B. Vekemans et.al. "Analysis of X-ray Spectra by Iterative Least Squares (AXIL): New Developments". 1994, X-Ray Spectrometry, 23, 278-285.
3. Evaluation of measurement data-Guide to the expression of uncertainty in measurement, 2008. Joint Committee for Guides in Metrology, JCGM 100:2008. www.bipm.org.
4. *UCD SOP #251: Sample Handling*
5. *UCD TI #251: A-P*
6. *UCD SOP #351: Data Processing and Validation*
7. *UCD TI #301: A-C*