

# **UCD IMPROVE Standard Operating Procedure #301**

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

*Interagency Monitoring of Protected Visual Environments*

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# **IMPROVE SOP #301: XRF ANALYSIS OF AEROSOL DEPOSITS ON PTFE FILTERS**

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## **1.0 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 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 is provided in the Technical Information (TI) documents that are referenced within this SOP. The PANalytical Epsilon 5 analyzer manual is referenced for more specific instructions on certain processes.<sup>1</sup>

Three PANalytical Epsilon 5 XRF analyzers are housed in Air Quality Research Center (AQRC, Jungerman Hall) at the University of California, Davis (UCD).

## **2.0 SUMMARY OF THE METHOD**

Analysis of IMPROVE aerosol filter samples is performed using energy dispersive X-ray fluorescence systems (EDXRF), specifically the Epsilon 5 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 Epsilon 5 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 seven 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 detector 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 Epsilon 5 software. Spectrum evaluation is done by non-linear least squares fitting based on the AXIL algorithm.<sup>2</sup>

The Epsilon 5 is a fully integrated spectrometer excelling 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; therefore 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 (i.e. ammonium, nitrate, chlorine, and bromine).

For the IMPROVE samples, seven 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 <sub>2</sub>	600	40	15	High Resolution	Na, Mg, Al, Si, P, S, Cl, K
Fe	400	75	8	Standard	Ca, Ti, V, Cr
Ge	300	75	8	Standard	Mn, Fe, Ni, Cu, Zn
KBr	300	100	6	Standard	As
SrF <sub>2</sub>	300	100	6	Standard	Se, Br
Mo	300	100	6	Standard	Rb, Sr, Pb
Al <sub>2</sub> O <sub>3</sub>	200	100	6	Standard	Zr

### 3.0 DEFINITIONS

- **Thin sample:** A sample with a deposit thin enough for enhancement and absorption phenomena to be negligible.
- **EDXRF – Energy Dispersive X-ray Fluorescence:** 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 milliamper (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 setting 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 (U<sub>rel</sub>):** The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%). U<sub>rel</sub> of calibration function is estimated following an international method<sup>3</sup>.

$$c_{std,ij} = \frac{I_{cor}}{b_j} \rightarrow U_{rel}(c_{std,ij}) = k \frac{u(c_{std,ij})}{c_{std,i}} = k \sqrt{\frac{\sum \left( \frac{\partial c_{std,ij}}{\partial x} \right)^2 u_x^2}{c_{std,i}}} \\ = k \sqrt{\frac{u^2(I_{cor,ij})}{b_j^2} + \left( \frac{I_{cor}}{b_j} \right)^2 u^2(b_j) + u^2(c_{std,i})} \\ c_{std,i}$$

Where,  $c_{std,ij}$  is the re-constructed loading ( $\mu\text{g}/\text{cm}^2$ ) of calibration standard i of element j using the calibration factor ( $b_j$ , in  $[(\text{cps}/\text{mA})/(\mu\text{g}/\text{cm}^2)]$ ),  $c_{std,i}$  is the certified loading standard i and  $I_{cor}$  is the blank subtracted intensity of X-rays emitted by the standard i ( $\text{cps}/\text{mA}$ ). Although uncertainty of  $c_{std,i}$ ,  $u(c_{std,i})$ , is not a part of  $c_{std,ij}$  calculation, it is added to uncertainty equation for a conservative approach. The coverage factor, k, takes into account 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).

- **Absolute bias:** The ratio of difference between measured and certified/reference loading of NIST SRM2783 to certified/reference loading (%).

$$\text{Absolute bias} = 100 * \frac{|c_{E5} - c_{cer}|}{c_{cer}}$$

Where,  $c_{E5}$  and  $c_{cer}$  is loadings by E5 and certified/reference loadings of NIST SRM2783, respectively.

- **z-score:** The ratio of absolute difference between each result from Re-analysis set analyzed monthly 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 method<sup>3</sup>. The reference loadings of IMPROVE samples were assigned as the mean of multiple analyses, and are fixed, which means they don't change by calibration. The certified/reference loadings of SRM2783 are used for z-score calculation.

- **Acceptance limits:**

- **PTFE blanks:** analyzed daily, are determined as three times Method Detection Limits (calculated as three times standard deviations of a set of lab blanks);
- **UCD multi-elemental reference materials (ME-RMs):** analyzed daily and weekly, are determined as  $\pm 10\%$  of the reference loadings (calculated as the mean of 5 measurements after calibration);
- **Micromatter made Al&Si reference materials:** analyzed weekly, are determined as  $\pm 10\%$  of the reference loadings (calculated as the mean of 5 measurements after calibration);
- **SRM2783:** analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations from 44 measurements between Jan 2013 and July 2016.

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

Where, m refers to measurement month.

## 4.0 HEALTH AND SAFETY WARNINGS

The Epsilon 5 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. Nevertheless, 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, pg. 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) and to Attachment 1. 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 has to be exercised during the cleanup (consult a service engineer and EH&S).
- ***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, the reader is referred to the System User's Guide (Chapter 3, pg. 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, the reader is referred to the Epsilon 5 System User's Guide (Chapter 3, page 10-11) and to Attachment 1.

- **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).

## 5.0 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 need to be followed.

## 6.0 INTERFERENCES AND POSSIBLE SOURCES OF ERROR

All spectra from IMPROVE samples and field blanks are processed with the PANalytical Epsilon 5 peak deconvolution software, and raw intensities are determined for each element identified by the analyzer. Raw intensities are then blank corrected to account for background contamination from the filter substrate and spectral noise. Sample or reference material intensities are corrected for any fluorescence resulting from the sample media itself by subtracting blank raw intensities from the sample raw intensities.

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 polytetrafluoroethylene (PTFE) filters for IMPROVE is  $3.53 \text{ cm}^2$  (21 mm diameter), and the deposit is assumed to be homogeneous.

Damaged filters are not analyzed because results can be affected by changes in distance between the sample and the X-ray tube and detector.

## **7.0 PERSONNEL QUALIFICATIONS, DUTIES, AND TRAINING**

Only trained personnel listed in the MUA (Machine Use Authorization) can operate the Epsilon 5 analyzers. Any adjustments to the Epsilon 5 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 Epsilon 5 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 taken the Analytical X-Ray Safety 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, reanalyses, 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

The Laboratory Technician will

- load and unload filter samples to and from the XRF analyzers
- transfer trayfiles to the analyzers and analysis data from the analyzers
- perform regular calibration checks and other QC checks
- fill the analyzers' liquid nitrogen reservoirs weekly

## **8.0 EQUIPMENT AND SUPPLIES**

The PANalytical Epsilon 5 EDXRF system 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 48 samples in an 8-position configuration. The sample table can be accessed only when the green light indicator is ON. Please see Attachment 2 of this SOP for a full list of equipment and supplies.

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



## 9.0 PROCEDURAL STEPS

The PANalytical Epsilon 5 System User's Guide provides complete detailed instructions for installing and operating the Epsilon 5 analyzer. These instructions are followed whenever the Epsilon 5 needs to be relocated or restarted.

### 9.1 XRF Application Setup

In order to start analyzing samples on the Epsilon 5 analyzer, a specific application needs to be developed and set up. Setting up the application requires 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 is maintained or replaced.

Table 2 below contains the list of standard reference materials used for calibrating the Epsilon 5 analyzers. They consist of 47 mm Micromatter thin film foils on Nuclepore membranes (prepared by vacuum deposition), PM<sub>2.5</sub> deposits on PTFE membranes, 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.

**Table 2.** Standard reference materials used for calibration of Epsilon 5.

a) Standards on Nuclepore from Micromatter

| Analyte/Code |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ag 32554     | CdSe 32556   | Cu 35143     | KCl 32509    | Pb 32571     | SiO 32504    | Ti 32516     |
| AgHg 32569   | CeF3 37492   | CuSx 32507   | KCl 32510_R  | Pb 32572     | SiO 33045    | V 32517      |
| AgHg 32570   | CeF3 37493   | CuSx 32508   | MgF2 32499   | Pb 35146     | SiO 33046    | V 32518      |
| Al 32501     | CeF3 37494   | Fe 32523     | MgF2 32500   | Pb 35163     | SiO 33053    | WO3 37730    |
| Al 32502     | CeF3 37495   | Fe 32524     | MgF2 33041   | RbI 32541    | SiO 33054    | WO3 37731    |
| Al 33044     | Co 32525     | Fe 35141     | MgF2 33042   | RbI 32542    | SiO 35139    | YF3 32545    |
| Al 35136     | Co 32526     | Fe 35142     | Mn 32521     | RbI 33051    | SiO 35140    | ZnTe 32532   |
| Al 35137     | Cr 32519     | GaAs 32535   | Mn 32522     | RbI 33052    | SiO 35160    | ZnTe 34875   |
| Al 35138     | Cr 32520     | GaAs 32536   | MoO3 32551   | Sb 32561     | Sn 32559     | ZnTe 34876   |
| Al 35164     | CsBr 32539   | GaP 32505    | MoO3 32552   | Sb 32562     | Sn 32560     | ZnTe 35162   |
| Al 35165     | CsBr 32540   | GaP 32506    | NaCl 32498_R | ScF3 32513   | SrF2 32543   | ZrF4 32547   |
| Al 35166     | CsBr 32565   | GaP 33059    | Nb2O3 32549  | ScF3 32514   | SrF2 32544   | ZrF4 32548   |
| BaF2 32567   | CsBr 32566   | GaP 33060    | Nb2O3 32550  | Se 32537     | SrF2 33055   |              |
| BaF2 32568   | Cu 32529     | Ge 32533     | Ni 32527     | Se 32538     | SrF2 33056   |              |
| CaF2 32511   | Cu 32530     | Ge 32534     | Ni 32528     | Se 33057     | Te 32563     |              |
| CaF2 32512   | Cu 33049     | In 32557     | Ni 33047     | Se 33058     | Te 32564     |              |
| CdSe 32555   | Cu 33050     | In 32558     | Ni 33048     | SiO 32503    | Ti 32515     |              |

b) Standards on PTFE filter produced by UCD and NIST, SRM2783 multi-element standard. The letters after “25” or “47” of UCD standards refer to certified element(s).

Code	Code	Code	Code	Code
UCD-47-Al&Ce-003	UCD-47-S-023	AWIM1 CRM NaCl 196	UCD-25-Al&Ce-003	UCD-25-V-006
UCD-47-Al&Ce-012	UCD-47-S-086	AWIM1 CRM NaCl 198	UCD-25-CaZr-002	UCD-25-ZnO-001
UCD-47-Cr-002	UCD-47-Si-001	AWIM1 CRM NaCl 204	UCD-25-CaZr-007	SRM2783 1617
UCD-47-Cr-006	UCD-47-Si-005	AWIM1 CRM NaCl 205	UCD-25-CaZr-009	SRM2783 1618
UCD-47-Cu&K-001	UCD-47-Si-043	AWIM1 CRM S 246	UCD-25-Cr-015	SRM2783 1719
UCD-47-Cu&S-002	UCD-47-Ti-003	AWIM1 CRM S 250	UCD-25-Fe-001	SRM2783 1720
UCD-47-CuO-005	UCD-47-ZnO-020	AWIM1 CRM S 253	UCD-25-Fe-002	
UCD-47-Fe-008	UCD-47-ZnO-010	AWIM1 CRM S 257	UCD-25-K&Cl-004	
UCD-47-K&Cl-014	UCD-47-ME-133	AWIM1 CRM S 263	UCD-25-S-001	
UCD-47-Na&Cl-007	UCD-47-ME-148	AWIM1 CRM S 265	UCD-25-S-002	
UCD-47-Na&Cl-008	UCD-47-ME-155	AWIM1 CRM S 268	UCD-25-S-003	
UCD-47-Na&Cl-011	UCD-47-ME-156	AWIM1 CRM S 280	UCD-25-S-004	
UCD-47-Pb-004	UCD-47-MTL-ME-007	AWIM1 CRM S 288	UCD-25-Ti-002	
UCD-47-Pb-058	UCD-47-MTL-ME-013	AWIM1 CRM S 291	UCD-25-Ti-004	
UCD-47-Pb-074	AWIM1 CRM NaCl 189	AWIM1 CRM S 293	UCD-25-V-002	
UCD-47-S-006	AWIM1 CRM NaCl 194	AWIM1 CRM S 299	UCD-25-V-003	

Calibration of the Epsilon 5 XRF analyzers is performed using the standards listed in Table 2. First, the standards are selected in the 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 IMPROVE samples. The calibration factors (slopes of linear regression) for the elements are stored within the application on the XRF computer. The calibration verification activities, criteria and corrective actions are performed by a set of analysis summarized in Table 3 (see TI 301E for details).

After each calibration is completed, the element calibration factors must be copied and provided to the Database Manager for ingestion into the IMPROVE SQL Server database.

**Table 3.** The calibration verification activities, criteria and corrective actions.

Analysis	Criterion	Corrective Action
Uncertainty of calibration	$U_{rel} \leq 10\%$ for stoichiometric standards	<ul style="list-style-type: none"> <li>Check calibration line and spectra</li> <li>Check standard(s) for damage/contamination</li> <li>Exclude standard(s) from calibration line</li> <li>Further cross-instrumental testing</li> <li>Recalibration with current or new standards</li> </ul>
NIST SRM2783	Absolute bias $\leq$ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	<ul style="list-style-type: none"> <li>Check sample and blank for damage/contamination</li> <li>Further cross-instrumental testing</li> <li>Recalibration with current or new standards</li> </ul>
PTFE Blank	$\leq$ acceptance limits with exceedance of two elements at least in two consecutive days	<ul style="list-style-type: none"> <li>Change/clean blank if contaminated/damaged</li> <li>Clean the diaphragm, if necessary</li> <li>Further cross-instrumental testing</li> </ul>
Micromatter Al&Si RMs	within acceptance limits	<ul style="list-style-type: none"> <li>Check sample(s) for damage/contamination</li> <li>Further cross-instrumental testing</li> <li>Replace sample(s) as necessary</li> </ul>
UCD-made ME-RMs	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Reanalysis set	$z\text{-score} \leq 1$ for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	

### 9.3 Daily (or weekly) operation

*Verify that analyzer is set for the current IMPROVE application (7 targets)*

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 Epsilon 5 needs to be cooled with liquid nitrogen (LN2) to provide stability. It is necessary to regularly fill the dewar of about 20 L capacity with LN2. The LN2 is refilled every Wednesday. The software will prompt the user to refill the LN2 if it is running low, but under normal operating conditions, the LN2 should never run low if it is filled every week. The LN2 level calibration is performed automatically immediately following the refill, and the detector calibration is performed minimum two hours later.

Users should refer to the System Users Guide and TI 301A 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 Epsilon 5. 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 liquid nitrogen fill on Wednesdays. The analysis needs to be stopped to perform detector calibration. For more information on this process, please see TI 301A.

### *Creating and loading tray files*

Tray files are a set of procedures written in .XML format that are used to queue samples. Tray files uniquely identify each sample by site and date. Thus, they record and track the sample associated with each collected spectrum. They also guide the laboratory technician in loading samples into the analyzer so that each sample is placed in its assigned position in the analysis queue. The procedures for creating, transferring, and using tray files are described in detail in TI 301B.

## **9.4 Loading and removing filters**

### *Filter Handling*

Sampled PTFE “A” 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 SOP 251, “Sample Handling.”

### *Filter Preparation*

All IMPROVE “A” filters and “A” 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 251M, “AD Tray Check.”

Sets of filters (8 traysx50 filters=400 filters per set) are assigned to the Epsilon 5 analyzers in a way that allows an equal distribution of field blanks among the analyzers. Epsilon 5 specific XRF tray files are created to organize and control distribution of the samples to each Epsilon 5 analyzer.

In general, tray files are transferred to the PANalytical sample changer software using a program called LIMS. Filters are transferred from labeled Petri dishes to the tray and position designated by the tray file. Once a tray has been loaded and placed in the analyzer, the samples are queued

using the software. Detailed instructions for loading and unloading the trays can be found in TI 301C.

At this time, filters are only identified by the position of the cup they have been placed in once the filters have been removed from their labeled Petri dishes. Special attention must be given during loading and unloading to assure the proper identity of samples. In addition, any physical changes to the sample after analysis (torn, dropped, etc.) must be reported and noted in the database.

## **10.0 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. The detailed list of all samples analyzed is included in that day's trayfiles, which serve as an electronic version of the log book.

### **10.2 Transferring data to the IMPROVE database**

The Epsilon 5 software calculates raw intensities and stores them in a results database table within the application in which the samples were analyzed. At a designated time interval (usually nightly) a program referred to as the XRF Migration Service uploads any new raw intensities data to a table in the IMPROVE database.

### **10.3 Data storage and backups**

Raw and processed spectra are saved and available for use at any time on the Epsilon 5 computers. Copies of the intensity data are stored in the IMPROVE SQL Server database. Small changes or corrections are sometimes made to the sample metadata (e.g., sample dates may be swapped) during the data validation process. The details of data validation process can be found in TI 301D. These changes are recorded in a “Table of Changes” in the IMPROVE SQL Server database.

A backup service copies the files from each Epsilon 5 PC and places them in analyzer-specific compressed folders on AQRC’s backup server. Differential backups are performed daily, while full backups are performed weekly.

### **10.4 Calculation of mass loadings, Method Detectable Limits (MDLs), and uncertainties**

Several different stored procedures in the IMPROVE SQL Server database are executed to calculate median field blank (FB) intensities, blank-correct the raw sample intensities, calculate mass loadings for each of the elements detected in the sample, and calculate uncertainties and method detection limits. The stored procedures are described in detail in TI 301D.

Blank correction is applied to each set of XRF data during data processing. Blank correction is specific to an analyzer, an analyzer application, and a month. The blank correction procedure consists of the following steps:

- For each element, determine the median FB raw intensities for the sample month and each analyzer-configuration used with that month. The median FB raw intensities will be used to subtract from raw intensities of samples.
  - For each analyzer select the last 25 FB results.
  - The 25 selected FBs for each analyzer that were used to calculate the blank subtraction will be recorded in another table along with a new field to identify which month they were used to process, BlankSetID.

- Determine the median FB intensity (cps/mA) by element by sorting the intensities from high to low and select the 13<sup>th</sup> record.
  - Save the median FB intensity (cps/mA) to another table along with the month for which they were calculated, the date on which they were calculated, and the BlankSetID parameter (described above).
- Subtract the median FB intensity (cps/mA) from the sample intensity (cps/mA) to determine the blank-corrected intensity for each element in the selected month by analyzer and analyzer configuration.
- Multiply the blank-corrected intensity for each element by the analyzer-configuration-specific calibration factor for that element. This converts the blank-corrected intensities to blank-corrected mass/area ( $\mu\text{g}/\text{cm}^2$ ) loadings that will be exported into a .dbf file for subsequent processing and final delivery.

Method detection limits (MDLs) for XRF have been determined separately for each of the three Epsilon 5 analyzers used for IMPROVE. The MDLs were determined from the analysis of approximately 50 to 100 field blanks on each analyzer, performed in 2012. For each element on each analyzer the MDL was calculated as the 95<sup>th</sup> percentile value of the intensity measured on these field blanks. The analyzer calibration factors in effect at that time were used to convert the intensities (cps/mA) to elemental mass loadings ( $\mu\text{g}/\text{cm}^2$ ). These MDLs are static, with the same value being used for all samples analyzed subsequently on each analyzer.

Uncertainties for each element are calculated by combining estimates of the additive and proportional uncertainties in the measurement. Additive uncertainties are derived from the MDLs described above. One-sigma additive uncertainty is estimated as  $\text{MDL}/1.6449$ , 1.6449 being the 90% critical value for a normal distribution. Coefficients for proportional uncertainties were based on the XRF analysis of paired samples from sites with collocated modules. For each pair in which both values A1 and A2 are above three times the MDL, the signed scaled relative difference was calculated as:

$$RD = \sqrt{2} \frac{(A - B)}{(A + B)}$$

The one-sigma proportional uncertainty coefficient was then estimated as one-half the difference between the 84<sup>th</sup> and 16<sup>th</sup> percentiles of these RD values, equivalent to one standard deviation for a normal distribution. Data from collocated pairs analyzed on two of CNL's Epsilon 5 analyzers were used together without distinction. Data for the third analyzer were treated separately. These proportional uncertainty coefficients are static, with the same value being used for all samples analyzed subsequently.

The one-sigma uncertainty,  $U_i$ , associated with each XRF measurement of element i ( $\mu\text{g}/\text{cm}^2$ ) is then determined as:

$$U_i = \sqrt{(\text{Additive uncertainty}_i)^2 + (\text{proportional uncertainty coefficient}_i * \text{mass loading}_i)^2}$$

where the mass loading is distinct for each field sample.

The resultant values represent the MDLs and uncertainties associated with the elemental mass loadings determined by XRF, expressed as  $\mu\text{g}/\text{cm}^2$ . SOP 351 (Data Processing and Validation), Section 5.3.5, describes how these XRF-specific values are used in the calculation of MDLs and uncertainties associated with ambient concentrations, expressed as  $\mu\text{g}/\text{m}^3$ .

## 11.0 QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Quality assurance/control for the XRF analyzers consists of the routine checks using analysis of several materials including blanks, RMs and Re-analysis set. These checks serve to check the stability of analyzers, verification of calibration, and inter-analyzers comparison. The details of this testing can be found in TI 301E.

### 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 4). The results (mass loadings in  $\mu\text{g}/\text{cm}^2$  and net intensity in cps/mA from each check) are recorded into a web application site. Graphs of the data are updated frequently and can be viewed at any time.

**Table 4.** The routine QA/QC activities, criteria and corrective actions.

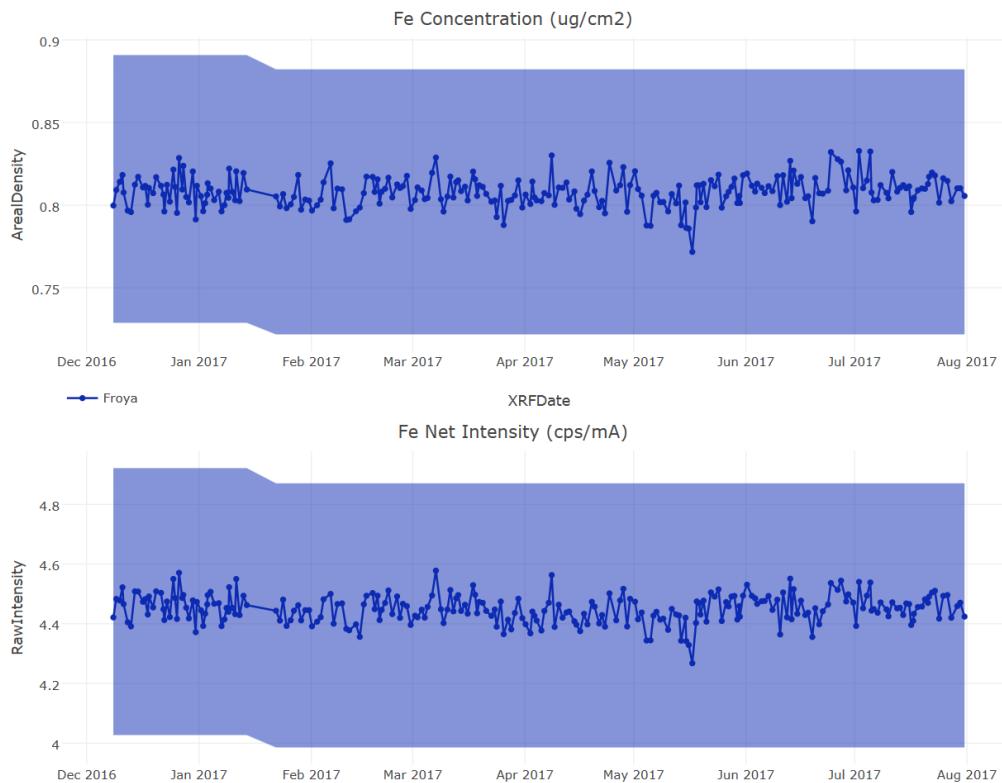
Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	<ul style="list-style-type: none"><li>• XRF software automatically adjust the energy channels</li></ul>
PTFE Blank	Daily	$\leq$ acceptance limits with exceedance of two elements at least in two consecutive days	<ul style="list-style-type: none"><li>• Change/clean blank if contaminated/damaged</li><li>• Clean the diaphragm, if necessary</li><li>• Further cross-instrumental testing</li></ul>
UCD-made ME-RMs	Daily	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	
Micromatter Al&Si RMs	Weekly	within acceptance limits	<ul style="list-style-type: none"><li>• Check sample for damage/contamination</li></ul>
UCD-made ME-RMs	Weekly	within acceptance limits for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	<ul style="list-style-type: none"><li>• Further cross-instrumental testing</li></ul>
Re-analysis set	Monthly	$z\text{-score} \leq 1$ for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	<ul style="list-style-type: none"><li>• Replace sample if necessary</li></ul>
SRM 2783	Monthly	Absolute bias $\leq$ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	

- The mass loadings of PTFE blanks analyzed daily must remain within the acceptance limits. If prolonged exceedance of the limits is observed for at least two elements, checks are made to determine possible causes (i.e., atmospheric deposition). PTFE blanks are air brushed to remove any possible contaminants. If exceedance of limit continues, blank is replaced with a new one.
- The upper and lower acceptance limits of daily analyzed UCD-made ME-RMs are listed and clearly marked on the charts (Fig.2). If the values of each daily check are within limits for the elements listed in Table 4, no action is necessary. In case of exceedance of acceptance limits of those elements at least for two consecutive days, the actions listed in Table 4 must be taken.
- Results of Micromatter Al&Si RM and UCD-made ME-RM analyzed weekly must remain with acceptance limits for elements listed in Table 4. In case of exceedance of acceptance limits of those elements at least for two consecutive measurements, the actions listed in Table 4 must be taken.
- Mean z-score for Re-analysis set must remain equal to or less than 1 for elements listed in Table 4. The absolute biases from SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni,

Cu, Zn and Pb must remain equal to or less than the acceptance limits. If the results exceed the acceptance limits, several tests are performed to determine the cause and solve the problem.

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.



## 11.2 Reproducibility testing

Analyzing of Reanalysis set 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 analyzer-specific reference values. The inter-analyzer comparison is monitored by z-score calculated using monthly results and the average of the reference values from other two analyzers. The mean of z-score for Re-analysis set calculated for long-term reproducibility and inter-analyzer comparison must remain equal to or less than 1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr. 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 Data Validation

- All data entries (e.g., sample ID, sample status, etc.) in the sample changer (from tray files) 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.

Initial data validation to detect outliers/anomalies in the XRF data (so called Level I Validation of XRF data, see TI 301F for details) includes checking correlations between elements, ratios of sums of quantified elements to PM masses, ratios of crustal elements, and reconstructed elemental ratios provided from previous years' measurements. The detected outliers/anomalies and basic statistics (e.g., mean, median and 90<sup>th</sup> percentile) for the examination of year to-year observed trends are reported for final validation. Any changes made to the original data are reflected in the "Table of Changes" and saved in the IMPROVE database. The details of this testing can be found in TI 301D.

#### **11.4 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.

### **12.0 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](http://www.bipm.org).