UCD CSN Standard Operating Procedure #302

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

Chemical Speciation Network
Air Quality Research Center
University of California, Davis

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications

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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 CSN 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 CSN 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 E5 analyzer manual is referenced for more specific instructions on certain processes. [1]

Two out of four E5 XRF analyzers dedicated to analyses of CSN samples are housed in Air Quality Research Center (AQRC, Jungerman Hall) at the University of California, Davis (UC Davis).

2. SUMMARY OF THE METHOD

Analysis of CSN aerosol filter samples is performed using energy dispersive X-ray fluorescence systems, specifically the E5 XRF 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 eight 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. 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 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; 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 (e.g. ammonia, nitrate, chlorine, bromine).

For CSN samples, eight different analytical conditions are used during a single analysis run to balance sensitivity and exposure time for the 33 elements reported to CSN. Each analytical condition is designed to optimize detection for a subset of the 33 elements and uses a different secondary target, X-ray tube voltage and current, resolution setting, and exposure time (Table 1).

Table 1. Epsilon 5 setup for CSN 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	300	75	8	Standard	Mn, Fe, Co, Ni, Cu, Zn
KBr	300	100	6	Standard	As
SrF_2	300	100	6	Standard	Se, Br
Mo	300	100	6	Standard	Rb, Sr, Pb
Al_2O_3	200	100	6	Standard	Zr, Sn, Sb, Cs, Ba, Ce
CsI	200	100	6	Standard	Ag, Cd, In

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.
- **Reanalysis:** Periodic analysis of selected ambient air samples to check the long term reproducibility
- **Reference Materials (RMs):** Samples used to evaluate the performance of the XRF analyzers. The mass loadings of reference materials have been assigned, although are not necessarily assigned (or certified) by an authority. Reference materials can be samples obtained from authoritative agencies such as the National Institute of Standards and Technology (NIST), samples produced by private companies or ambient air quality samples that are assigned as reference materials and analyzed multiple times.
- **Standard Reference Materials (Standards):** Reference materials with certified reference mass loadings and uncertainties. Standards are used to calibrate the XRF analyzers.
- **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.
- **Net intensities:** The fluorescence intensities (cps/mA) measured and deconvoluted by the analyzer. These net intensities construct a spectrum for each analyzed sample per element and are used along with the calibration factors to calculate the mass loadings in the CSN 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 net 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.
- **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 method[3].

$$c_{std,i} = \frac{I_{cor}}{b} \rightarrow U_{rel}\Big|_{c_{std}} = k\frac{u(c_{std,i})}{c_{std}} = k\frac{\sqrt{\Sigma\left(\frac{\partial c_{std,i}}{\partial x}\right)^2 u_x^2}}{c_{std}}$$

$$= k\frac{\sqrt{\frac{u^2(I_{cor})}{b^2} + \left(\frac{I_{cor}}{b^2}\right)^2 u^2(b) + u^2(c_{std})}}{c_{std}}$$

Where, $c_{std,i}$ is the re-constructed loading ($\mu g/cm^2$) of calibration standard i (c_{std}) using the calibration factor (b, in [(cps/mA)/($\mu g/cm^2$)]) and I_{cor} is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA). Although uncertainty of c_{std}, $u(c_{std})$, is not a part of $c_{std,i}$ 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 loading of NIST SRM2783 to certified loading (%).

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

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

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

$$z = \frac{\left| c_{E5} - c_{ref} \right|}{\sqrt{U_{c_{E5}}^{2} + U_{c_{ref}}^{2}}}$$

Where c_{E5} is the mass loading measured ($\mu g/cm^2$), c_{ref} is the reference mass loading; U_{cE5} and U_{cref} are the expanded uncertainties of measured (c_{E5}) and reference (c_{ref}) mass loadings. The expanded uncertainties are estimated following an international method[3].

- **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-element samples:** analyzed daily and weekly, are determined as ±10% of the reference loadings (calculated as the mean of 5 measurements after calibration);
  - **Micromatter made multi-element samples:** analyzed weekly, are determined as ±10% of the reference loadings (calculated as the mean of 5 measurements after calibration).
  - **SRM:** analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations (STDs) 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. 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. 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.   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 E5 System User's Guide need to be followed.

6.   INTERFERENCES AND POSSIBLE SOURCES OF ERROR

All spectra from CSN samples and laboratory blanks are processed with the PANalytical E5 peak deconvolution software, and the net intensities are determined for each element identified by the analyzer. Using the net intensities and calibration factors, the software calculates the elemental mass loadings in $\mu g/cm^2$.

A subset of laboratory blanks received with each batch of samples will be analyzed to determine the median loadings of filter material to be subtracted from loadings of CSN samples collected on the same filter batch/lot. The CSN 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 47 mm polytetrafluorethylene (PTFE) filters for CSN is 11.86 cm^2 (46.2 mm diameter), and the deposit is assumed to be homogeneous. Any effects of inhomogeneity are minimized by utilizing the sample spinner, which spins the sample during the analysis at a rate of approximately 3 rpm.

User has to be aware of the fact that analysis of damaged filters can alter the results, because the geometry of source-sample-detector will be affected.

7.   PERSONNEL QUALIFICATIONS, DUTIES, AND TRAINING

Only trained personnel listed in the MUA (Machine 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 taken the Analytical X-Ray Safety Course offered through EH&S. E5 users/operators do not have to wear any dosimetry during loading and unloading of the samples.

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

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 analyzers' 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 and energy calibrations
- review each data set in the context of historical data and current analyzer conditions
- identify abnormalities and provide recommendations for understanding and rectifying them
- perform analyzers' calibrations as needed

The Laboratory Technician will:

- receive samples and prepare for XRF analysis
- load and unload filter samples to and from the XRF analyzers
- perform regular calibration checks and other QC checks
- fill the analyzers' liquid nitrogen reservoirs weekly
- perform weekly energy calibration (automated process)
- archive the XRF analyzed samples

8.   EQUIPMENT AND SUPPLIES

The E5 system consists of two main components: the XRF Epsilon 5 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.

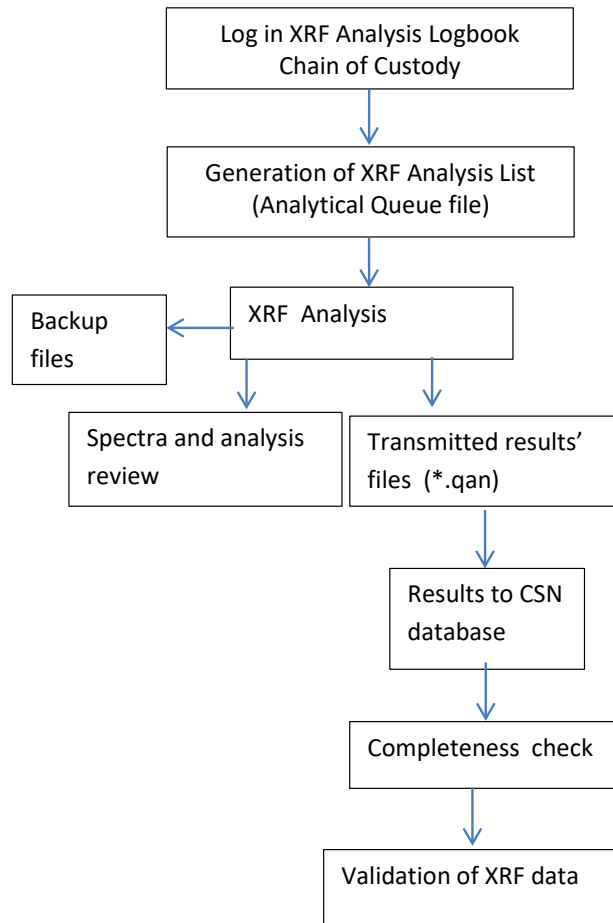Figure 1. PANalytical Epsilon 5 analyzer and computer station in the XRF Laboratory at AQRC.

9.   PROCEDURAL STEPS

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

The typical flowchart of XRF analysis is presented in Figure 2.

Figure 2. The flowchart of XRF analysis of CSN samples

```
┌─────────────────────────────┐
│  Log in XRF Analysis Logbook│
│      Chain of Custody       │
└─────────────────────────────┘
              │
              ▼
┌─────────────────────────────┐
│  Generation of XRF Analysis │
│  List (Analytical Queue     │
│  file)                      │
└─────────────────────────────┘
              │
              ▼
┌──────────┐     ┌─────────────────────────────┐
│ Backup   │◄────│      XRF  Analysis          │
│ files    │     └─────────────────────────────┘
└──────────┘          │                │
                      ▼                ▼
        ┌─────────────────────┐  ┌─────────────────────┐
        │ Spectra and analysis│  │ Transmitted results'│
        │ review              │  │ files  (*.qan)      │
        └─────────────────────┘  └─────────────────────┘
                                          │
                                          ▼
                                 ┌─────────────────────┐
                                 │ Results to CSN      │
                                 │ database            │
                                 └─────────────────────┘
                                          │
                                          ▼
                                 ┌─────────────────────┐
                                 │ Completeness  check │
                                 └─────────────────────┘
                                          │
                                          ▼
                                 ┌─────────────────────┐
                                 │ Validation of XRF   │
                                 │ data                │
                                 └─────────────────────┘
```

9.1 Sample Receiving and Preparation for XRF Analysis

The received samples are inventoried and prepared for XRF analysis. The details of this procedure can be seen in TI 302B.

9.2 XRF Application Setup

In order to start analyzing samples on the E5 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, 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 CSN sample analyses are shown in Table 1.

9.3   **Calibration**

The E5 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.

Table 2 below contains the list of standard reference materials used for calibrating the E5 analyzers. They consist of 47 mm Micromatter thin film foils on Nuclepore membranes (prepared by vacuum deposition), UCD-made standards on PTFE membranes[4], 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 of the E5 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 CSN samples. The calibration factors (slopes of linear regression) for the elements are stored within the application on the XRF computer.

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

a)   Standards on Nuclepore from Micromatter

Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code	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	

The quality check of calibration is performed by a set of analysis summarized in Table 3. In addition, routine calibration verification and stability/performance of XRF analyzers are checked (see TI 302D for details).

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

Analysis	Criterion	Corrective Action
Uncertainty of calibration	Urel≤10% for stoichiometric standards and with loadings≥3*MDL	• Check calibration line and spectra • Check standard(s) for damage/contamination • Exclude standard(s) from calibration line • Further cross-instrumental testing • Recalibration with current or new standards
NIST SRM2783	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti , Cr, Mn, Fe, Ni, Cu, Zn and Pb	• Check sample and blank for damage/contamination • Further cross-instrumental testing • Recalibration with current or new standards
Teflon Blank	≤ acceptance limits with exceedance of max two elements	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD Multi-element samples	±10% of reference mass loadings for Al, Si, S, K, Ca, Ti , Cr, Mn, Fe, Ni, Cu, Zn and Pb	
Micromatter Al & Si sample	±10% of reference mass loadings	• 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, Ti, Mn, Fe, Zn, Se and Sr	

9.4   Daily (or weekly) operation

Verify that analyzer is set for the current CSN application (8 targets)

The current version of the CSN applications are used for analysis of all CSN samples. The processing parameters and calibration factors are analyzer and time specific. Therefore, the application version number changes on each analyzer after the new calibration is performed. The application performs fully automated analyses of samples under the specified conditions defined in application, saves the measured spectra within the application database, and processes the spectra into net 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 needs to 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. 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 two hours later.

Users should refer to the System Users Guide and TI 302A for detailed safety information regarding the handling of liquid nitrogen 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_α at 58.856 keV and L_α 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 TI 302A.

9.5   Loading and removing filters

Filter Inventory

Sampled PTFE filters will be shipped to AQRC from AMEC via UPS overnight in a cooler at 4° C with a Chain of Custody (COC) forms, see Fig.3 for an example of this form. An electronic inventory list of all shipped samples will be emailed or received by Sharepoint.

A laboratory technician will sign and date the COC and enter the information in the CSN database. Filter inventory is done upon receipt of samples by counting the samples and

verifying barcodes with COC and electronic records. For more information on these procedures refer to TI 302B.

Figure 3. The example of Chain of Custody (COC) forms

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Filter Handling

Samples previously received from AMEC will be stored in Petri slides, the samples are identified by Lab Analysis ID Barcode. AMEC will organize the Petri trays to match the

order on the COC. Each Petri tray holds 50 samples and is identified by Batch number and tray number. For more information on these procedures refer to TI 302B.

Filter Preparation

All CSN samples, field blanks and trip blanks are analyzed by XRF regardless of their reported status.

The specific procedure used for loading samples requires generation of a sample list (XRF queue file) and loading it to each E5 utilized for CSN analysis. The XRF queue file is used in conjunction with the E5 scanner capabilities. Filters are scanned and transferred from labeled Petri slides into the specially designed holders and placed into the E5 trays (and positions) for the 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, any physical changes to the sample before/after analysis (torn, dropped, etc.) must be reported and noted in the CSN database as an AQS code FX with appropriate comment. Detailed instructions for loading and unloading the trays can be found in TI 302C.

10.   DATA AND RECORDS MANAGEMENT

10.1   Log books

Each day, the IDs of the first and last samples loaded into each XRF analyzer are logged into the both the XRF Analyzer log book and the electronic log book.

10.2   Transferring data to the CSN database

The E5 software calculates intensities and loadings, and stores them in a results database table within the application in which the samples were analyzed. At the same time, the file (*.qan) with the result is transmitted to the designated location on E5 computer and the result is uploaded into the CSN 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 derived mass loadings are stored in the CSN SQL Server database. Data safety and security are ensured by frequent transfer of computerized raw data from the 5 PCs in AQRC XRF Laboratory (Jungerman Hall) to 2 different servers located in AQRC and LAWR buildings on campus. Differential backups are performed daily and full backups are performed weekly.

10.4   Calculation of mass loadings, Method Detection Limits (MDLs), and uncertainties

The E5 software reports intensities and mass loadings for each analyzed sample. The blank correction for each of the sample's mass loadings is done by subtraction of the median value of mass loadings from the set of lot-specific laboratory blanks. A lot-specific set of

blanks (currently 32) are analyzed on each E5 using active CSN application to determine the median values. When the filter lot changes, a subset of the new lot is analyzed with current CSN applications. A new CSN application with the current lot also requires re-analysis of the blank subset. Thus, the blank subset to be used for subtraction is the filter lot, E5 and the active CSN application specific.

The Method Detection Limits (MDLs) of XRF analysis depend on a number of factors, including type of filter media, manufacturer of filter media, consistency of filters with respect to thickness and background contaminations, analysis counting time, analysis conditions, and element. For each element, the MDL is calculated as three times the standard deviation of at least 32 laboratory blanks in $\mu g/cm^2$. These MDLs are static, with the same value being used for all samples analyzed subsequently on each analyzer. Typical MDLs for PTFE membrane filters from MTL are presented in Table 4 below.

Table 4. The typical MDLs based on analysis of PTFE laboratory blanks from MTL

Element	MDL (ng/cm^2)
Na	54.4
Mg	41.9
Al	28.8
Si	11.9
P	1.7
S	6.0
Cl	2.8
K	9.7
Ca	7.0
Ti	2.7
V	1.7
Cr	3.2
Mn	5.5
Fe	18.8
Co	2.5
Ni	1.8
Cu	7.2
Zn	3.2
As	2.2
Se	4.5
Br	3.7
Rb	6.3
Sr	5.4
Zr	30.9
Ag	15.4
Cd	19.7
In	25.3
Sn	35.0
Sb	37.0
Cs	61.4

Ba	67.7
Ce	94.7
Pb	12.4

Reported 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 MDL/1.6449, with 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 84th and 16th percentiles of these RD values, equivalent to one standard deviation for a normal distribution. Data from collocated pairs analyzed on two of AQRC's E5 analyzers were used together without distinction. 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 ($\mu g/cm^2$) is then determined as:

$$U_i = \sqrt{\begin{array}{c}(Additive\ uncertainty_i)^2\ + \\ (proportional\_uncertainty\_coefficient_i * mass\_loading_i)^2\end{array}}$$

Where the mass loading is distinct for each field sample.

XRF analytical uncertainties: Calculated following an international method[3]. The mass loading of any element is calculated using the following equation:

$$c_{E5} = c_{sample} - c_{blank(median)}$$

Where c_{sample} and $c_{blank(median)}$ 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 (b). Thus, the equation can be re-written as:

$$c_{E5} = \frac{I_{net,sample}}{b} - \frac{I_{net,blank}}{b} = \frac{(I_{net,sample} - I_{net,blank})}{b}$$

Applying the international method to this equation yields expanded analytical uncertainty (u_{cE5}) given below (see ref 5 and 6 for details):

$$u_{c_{E5}} = k \sqrt{\sum \left(\frac{\partial c_{E5}}{\partial x}\right)^2 u_x^2} =$$

$$k \sqrt{\frac{u^2(I_{net,sample})}{(b)^2} + \frac{u^2(I_{net,blank})}{(b)^2} + \left(\frac{(I_{net,sample} - I_{net,blank})}{(b)^2}\right)^2 u^2(b)}$$

The resultant values represent the MDLs and uncertainties associated with the elemental mass loadings determined by XRF, expressed as μg/cm^2.

11. QUALITY ASSURANCE AND QUALITY CONTROL

The QA/QC of analyzer performance is summarized in Table 5. The QC for the XRF analyzers consists of the following checks (see the details in TI 302D):

- checking the performance of each analyzer against UCD-made multi-elemental samples, which are analyzed daily and weekly,
- checking the performance of each analyzer with selected PTFE blanks which are analyzed daily,
- re-analyzing selected ambient air samples (16) and one NIST SRM 2783 on each analyzer on a monthly basis to evaluate long-term reproducibility and inter-analyzer performance,
- checking SRM 2783 absolute bias for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb

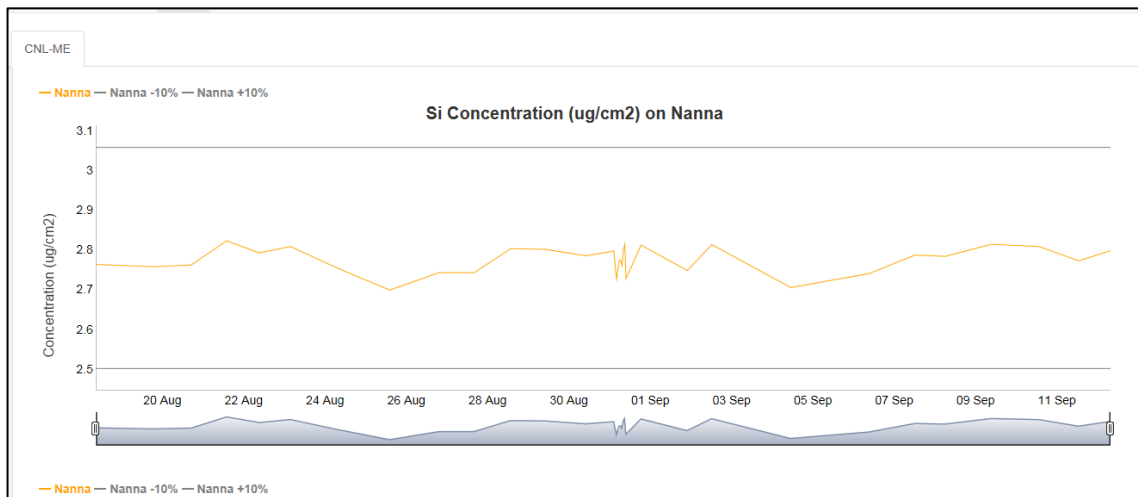Table 5. The routine QC activities, criteria and corrective actions.

Analysis	Frequency	Criterion	Corrective Action
Detector Calibration	Weekly	None (An automated process done by XRF software)	• XRF software automatically adjust the energy channels
Teflon Blank	Daily	≤ acceptance limits with exceedance of any elements at least in two consecutive days	• Change/clean blank if contaminated/damaged • Clean the diaphragm, if necessary • Further cross-instrumental testing
UCD Multi-element sample	Daily	±10% of reference mass loadings for Al, Si, S, K, Ca, Ti , Cr, Mn, Fe, Ni, Cu, Zn and Pb	
Micromatter Al & Si sample	Weekly	±10% of reference mass loadings	• Check sample for damage/contamination • Further cross-instrumental testing • Replace sample if necessary
UCD Multi-element sample	Weekly	±10% of reference mass loadings for Al, Si, S, K, Ca, Ti , Cr, Mn, Fe, Ni, Cu, Zn and Pb	
Reanalysis samples	Monthly	z-score≤1 for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se and Sr	

SRM 2783	Monthly	Absolute bias ≤ acceptance for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb

12.   PERFORMANCE TESTING

The stability of the analyzer is monitored daily by analyzing E5 specific UCD-made multi-element samples containing the majority of CSN elements. The analyzer can process the analysis queue while the data from the QC materials is displayed and evaluated. The results (mass loadings in $\mu g/cm^2$ and/or net intensities in cps/mA for each element on each of the multi-element material) from each daily check are recorded and the visual representation of the data can be viewed at any time on a dedicated web page (Figure 4 below as an example).

Figure 4. Performance testing with UCD-made ME sample.

The upper and lower acceptance limits (± 10%) are listed and clearly marked on the charts. If the values of each daily check are within limits no action is necessary. In case of permanent damage to the sample, the sample is replaced. If the values exceed acceptance limits at least for two consecutive days, the XRF laboratory manager must be immediately notified and the problem must be fixed before analysis continues. Detailed procedures are described in TI 302D.

12.1   Long-term reproducibility testing

Long-term reproducibility is monitored by analyzing Re-analysis set. The individual result of each monthly analysis is compared to its reference loading. The average of z-score for Re-analysis set must remain within their accompanying uncertainties. The absolute bias from SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb will also be checked for ongoing verification of calibration.

If continuous exceedances of the limit are observed in the reproducibility, the laboratory manager is notified and further tests are employed to determine the cause of the instability. The details of this testing can be found in TI 302D.

12.2   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 samples were analyzed by XRF.

12.3   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 by UCD before delivery to DART for state level 2 validation and final reporting to AQS by UCD.

13.   ARCHIVE OF THE FILTERS

Refer to UCD SOP: *UCD CSN SOP #901: Long-term Archiving of Filters*.

14.   REFERENCES

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