



## **STANDARD OPERATING PROCEDURES**

### **Determination of Trace Metals Deposited on PTFE Filters by X-Ray Fluorescence Analysis**

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## 1.0 SCOPE AND APPLICATION

After the post weighing of PTFE filters is completed and validated, a series of non-destructive analyses, including X-ray fluorescence (XRF), are performed to determine the chemical composition of the samples. The SPARTAN network is currently capable of quantifying 26 elements using XRF. This standard operating procedure (SOP) describes the steps to ensure quality XRF measurements are taken on the polytetrafluorethylene (PTFE) filters.

REVISION HISTORY			
Revision No.	Change Description	Date	Authorization
2.0	Additional processed for calibration and data validation	July 7 2021	Xuan Liu

## 2.0 SUMMARY OF METHOD

All filters are analyzed using the Epsilon 4 (E4) benchtop energy dispersive X-ray fluorescence (EDXRF) analyzer from Malvern PANalytical. The source of X-rays in the E4 analyzer is a 15-Watt X-ray tube with a silver anode. Samples are excited by an x-ray beam, and the resulting fluorescence is measured by the instrument's detector. The counts measured at various intensities are then deconvoluted by the E4 software to assign them to characteristic elemental excitation energies. The number of counts per second (cps) for each element is used to calculate the concentration of the element in question per unit area on the filter, based on previously measured calibration standards with known concentrations. A variety of elements can be quantified based on availability of standards – currently 26 elements are measured in the SPARTAN protocol.

## 3.0 CONTAMINATION CONTROL

Filters are stored individually inside Petri dishes and placed in a sealed plastic bag at room temperature when not in use. Before loading filters, the surface next to the instrument used for filter prep is cleaned using a methanol-soaked Kimwipe®. The PTFE-coated tweezers are also cleaned before handling filters with a methanol-soaked Kimwipe®. Extreme care should be taken when lifting filters to avoid sample contamination or loss during handling, which is particularly relevant for this analysis, as trace metals have inherently low concentrations. Filters are placed individually in the E4 sample holders with the deposit side facing down, carefully touching only the outer ring with the tweezers. Filters are held in place by custom 3D-printed polylactic acid (PLA) 25mm filter holder rings which are wiped before each use with methanol. The lid of the E4

is kept closed except during the loading and unloading of samples to avoid contamination from dust or other foreign materials.

## **4.0 EQUIPMENT AND STANDARDS**

### **4.1 Equipment**

- Epsilon 4 benchtop XRF analyzer - Malvern Panalytical
- Custom polylactic acid 25mm filter holder rings (as well as 36mm and 47mm variants for appropriate standards)
- PTFE-coated tweezers
- ACS-grade methanol
- XRF calibration standards
- Sampled filters stored in Petri dishes
- Lab blanks for spectrum background subtraction
- Helium (ultra-high purity)

A line of ultra-high purity (UHP) helium is connected to the E4. Helium is used during the analysis of light elements, as it enhances the signal-to-noise ratio. Prior to analysis, presence of helium in the tank should be verified and valve opened. The valve can be kept open during the regular operation of the XRF.

### **4.2 Standards**

The calibration of the E4 relies on standards with known values of reference elements. This allows for the instrument to assign concentrations of elements in unknown samples based on cps values of various concentrations. An elemental breakdown of the standards used is found in Table 1. During initial calibration, all standards must be analyzed.

**Table 1.** Elemental breakdown of the standards for XRF analysis. Concentrations are shown in  $\mu\text{g}/\text{cm}^2$  and reported in ascending order of concentration. Certain standards are certified for multiple elements.

Element	# of Stds	[Std 1]	[Std 2]	[Std 3]	[Std 4]	[Std 5]	[Std 6]	[Std 7]	[Std 8]	[Std 9]
Al	8	0.356	0.65	0.723	1.06	1.566	2.3303	2.42	5.52	
As	4	0.0012	0.119	0.241	0.522					
Ca	7	0.356	0.723	1.3253	1.4	1.566	2.44	5.79		
Cd	3	0.024	0.048	0.104						
Ce	7	0.0023	1.1	3.39	4.5	12.57	23.4	28.69		
Cl	8	0.73	0.75	1.1	2.21	4.0	4.08	5.64	13.04	
Co	6	0.0008	0.024	0.048	0.104	0.50	5.4			
Cr	6	0.0136	0.119	0.241	0.522	1.02	5.3			
Cu	6	0.035	0.0406	0.109	0.484	1.35	6.7			
Fe	7	0.356	0.723	0.94	1.566	1.82	2.6606	4.26		
K	9	0.28	0.351	0.5301	0.714	0.82	1.546	1.7	2.44	6.21
Mg	3	0.80	0.8655	2.7						
Mn	6	0.0321	0.059	0.121	0.261	1.7	7.5			
Na	9	0.1867	0.47	0.71	1.385	2.6	2.64	2.815	6.094	8.45
Ni	6	0.0068	0.024	0.048	0.104	1.00	6.4			
Pb	6	0.0318	0.119	0.241	0.43	0.522	0.93			
Rb	4	0.0024	0.024	0.048	0.104					
S	13	0.1054	0.57	0.83	1.12	1.18	1.8	1.95	2.373	4.63
S (cont.)		4.823	7.19	10.442	10.55					
Sb	3	0.0072	0.95	6.8						
Se	5	0.059	0.76	0.121	0.261	5.3				
Si	9	0.65	0.703	0.98	1.428	2.71	3.092	4.5	5.8835	5.96
Sn	2	1.4	7.1							
Sr	3	0.024	0.048	0.104						
Ti	7	0.024	0.048	0.104	0.1496	1.67	5.05	8.54		
V	7	0.0049	0.024	0.048	0.104	0.90	1.32	2.86		
Zn	7	0.031	0.093	0.1797	0.365	0.56	1.99	3.6		

## 5.0 PROCEDURAL STEPS

Ensure Epsilon 4 instrument is powered on – instrument should remain on except in times of prolonged absence of sampling. Power on connected computer and open Epsilon software application.

### 5.1 XRF Application set up

To start analyzing samples on the E4, a specific application must be developed and set up. Setting up the application requires the following: selecting the elements to be reported and

conditions used for each element, calibration standards file (along with measurement of standards), and deconvolution parameters.

The configuration of the application used for SPARTAN measurements (hereafter termed “SPARTAN XRF Analysis”) is shown in **Error! Reference source not found. 2**. Once created, this application is used for all SPARTAN analysis, as it is constructed to optimize results from filter XRF analysis.

**Table 2.** Configuration of “SPARTAN XRF Analysis” application in E4 software

Condition name	kV	uA	Filter name	Medium	Detector mode	Analysis time (s)	Reported Elements
<Fe-Pb>	50	300	Ag	Air	Normal	540	Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Pb
<K-La>	12	1250	Al-50	Air	Normal	540	K, Ca, Ti
<Na-Cl>	9	1666	Ti	Helium	Normal	720	Na, Mg, Al, Si, S, Cl
<Pd-Sb>	50	300	Cu-500	Air	Normal	540	Cd, Sn, Sb
<V-Mn,Ce>	20	750	Al-200	Air	Normal	540	V, Cr, Mn, Ce

## 5.2 Interference and possible sources of error

To account for background contamination from the filter substrate and spectral noise, spectrum background subtraction is conducted in the software for every filter measured. This is done by subtracting the raw intensity of the corresponding blank from the sample raw intensity, which gives the net intensity of the sample. The blanks used as background for different samples are listed below:

- For different types of standards, the corresponding blank membrane should be measured along with the standards and used for spectrum background subtraction.
- For field samples and field blanks (travelling blank, one of which is found in each cartridge), the latest lab blank (blank that has never been in loaded in a cartridge or sent to the field) measurement that passes the daily quality check is used for spectrum background subtraction.
- For the lab blank, because it is used to monitor the long-term stability of XRF, the initial lab blank measurement after a new calibration has been performed is used for spectrum background subtraction in the regular lab blank measurements.

Before being used in the network, contamination levels in a new box of filters are evaluated through acceptance testing (see *SPARTAN Acceptance Testing 1.0*). Boxes that fail acceptance testing are not used for sampling.

To account for contamination from the sampling and shipping process, further blank subtraction is performed for field samples in post-processing by using the median concentration of at least 35 recently analyzed field blanks.

The X-ray beam is almost circular with a diameter of approximately 20 mm. The assumed area of the deposit on 25 mm PTFE filters for SPARTAN is 3.53 cm<sup>2</sup> (21 mm diameter). The E4 instrument has a spinner designed to reduce the influence of inhomogeneity of the deposit on air filters.

No attenuation correction for particle size or mass loading is performed at this time.

### 5.3 Calibration

Calibration of the E4 occurs through measurements of the standards listed above, which are given the above known concentrations in the software. Once analysis of the standards is complete, the cps values of those standards with varying elemental concentration can be used to create individual calibration curves for each element of interest. Once the condition sets are implemented, the application created, and the E4 has been calibrated, analysis of samples can be performed.

Calibrations are performed upon the first installation, whenever the analyzer fails verification tests, and whenever an analysis-critical component (e.g., X-ray tube or detector) of the analyzer undergoes maintenance or is replaced.

Calibration standards consist of MicroMatter thin films on Nucleopore membranes (prepared by vacuum deposition), standards at UC Davis on PTFE membranes from PALL Corporation and MTL Corporation, 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 spectrum background subtraction (i.e., PALL blank filters for standards that are deposited on PALL filters).

Calibration standards are selected in the E4 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. Next, the standards are analyzed. The software performs least-squares regression 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.

Before analysis, a quality check (verification) of the calibration is performed using the set of analyses summarized in Table 3.

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

Analysis	Criterion	Correction Action
Uncertainty calibration of	$U_{rel} \leq 10\%$ 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>• Recalibration with current or new standards</li> </ul>
NIST SRM2783	Bias between acceptance limits 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>• Recalibration with current or new standards</li> </ul>
PTFE Blank	$\leq$ acceptance limits of an element not to exceed two consecutive days	<ul style="list-style-type: none"> <li>• Change/clean blank if contaminated/damaged</li> <li>• Clean the diaphragm, if necessary</li> </ul>
UCD-made ME-RMs	$\pm 10\%$ or $20\%$ of reference loadings for Al, Si, S, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, and Pb	<ul style="list-style-type: none"> <li>• Check sample(s) for damage/contamination</li> <li>• Replace sample(s) as necessary</li> </ul>
Re-analysis set	$-1 \leq z\text{-score} \leq 1$ for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr	

#### 5.4 X-ray fluorescence measurements of PTFE filters

- Ensure that 3D printed holders are placed in stainless steel sampling cups. Holders should only be removed when being cleaned. Holders should be placed with the small, raised ring facing upwards to properly hold filters.
- Using the PTFE-coated tweezers, load filters individually, with deposit side down, onto the filter holders in the E4 sample changer.
- Once all samples are loaded, ensure the spinner arm is in the active position (closer to the sample changer) so that samples are properly rotated during analysis.
- Close the lid of the E4, as the X-ray beam cannot be turned on if the cover is not in the closed position.
- Initiate sampling using the current version of the SPARTAN application in the Epsilon 4 software. Sampling is initiated by specifying the name and slot of each filter in the sample changer, using the unique filter name on the petri dish for consistency.
- When the analysis is completed, lift the lid of the E4, remove each filter with PTFE-coated tweezers, replace each filter into the corresponding petri dish, and reseal the plastic bag once all closed Petri dishes have been replaced.



## 5.5 Data storage and backups

After each measurement, the elemental concentrations on the filter are recorded in the E4 software along with the date and time of analysis. After analysis is complete, filters are returned to their petri dishes and resealed in a plastic bag. An XRF E-Log is filled out to record the date of analysis. Any physical changes to the filters that occur during XRF analysis (i.e., filters dropped or ripped) are recorded in the XRF E-Log, as well as other relevant observations. Monthly backups of the E4 user data to a cloud-based storage system are conducted to prevent accidental loss of data due to hardware or media failure.

## 6. DATA VALIDATION

### 6.1 Calculation of areal density, method detection limits (MDLs) and uncertainties

Each analyzed field sample is blank corrected using the median concentration of at least 35 recently analyzed field blanks as shown the following equation.

$$C_{E4} = C_{sample} - C_{blank(median)}$$

The MDL and uncertainty are reported with each elemental concentration. The MDL is the greater of either the 95th percentile mass loading minus the median mass loading of at least 35 recently analyzed field blanks or an analytical MDL determined from lab blanks run on the XRF instrument as shown in the equation below. The analytical MDL values are determined from the analysis of approximately 50 to 100 lab blanks and calculated as the 95th percentile mass loading minus the median mass loading.

$$MDL = \max ((P95 - median), MDL_{analytical})$$

The reported uncertainties for each element are currently analytical uncertainties which are derived from the MDLs as shown in the following equation where 1.645 is the critical value of z score in a one-tailed test for 5% significance level.

$$\sigma_a = MDL/1.645$$

## 6.2 Data validation

All measured XRF values are reported publicly, alongside its MDL value and measurement uncertainty. The reported MDL is the greater of the MDL calculated from at least 35 most recent field blanks or the analytical MDL, and the MDL value and associated measurement uncertainty should be taken into account when using corresponding XRF values. Any measurement which falls below the reported MDL is flagged for user's discretion.

Data validation also involves manual inspection of the XRF results for outliers, concentrations outside of the range of calibration, and to ensure field blanks show notably less deposition of trace metals than sampled filters.

## 6.3 Routine Quality Control Checks

The stability of the E4 is monitored routinely (daily, weekly, and monthly) by analyzing blanks, UCD-made multi-element reference materials (ME-RMs), Micromatter Al&Si RMs, re-analysis set, and NIST SRM2783 shown in Table 4.

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

Analysis	Frequency	Criterion	Correction Action
PTFE Blank	Daily	$\leq$ acceptance limits with exceedance of an element not to exceed two consecutive days	<ul style="list-style-type: none"> <li>Change blank if contaminated/damaged</li> <li>Clean the diaphragm, if necessary</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 with exceedance of these elements not to exceed two consecutive days	<ul style="list-style-type: none"> <li>Check sample for damage/contamination</li> <li>Replace sample if necessary</li> </ul>
Micromatter Al&Si RMs	Weekly		
NIST SRM 2783	Monthly	Absolute relative bias $\leq$ acceptance limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb	
Re-analysis set	Monthly	$-1 \leq$ mean z-score $\leq 1$ for Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, and Sr	

The acceptance limits for different materials are defined as follows:

- **PTFE blanks:** mean plus three standard deviations of 50 to 100 lab blanks.
- **UCD-made ME-RMs:**  $\pm 10\%$  or  $\pm 20\%$  of the reference loadings (10% for certified loadings, 20% for reference loadings).
- **Micromatter Al&Si RMs:**  $\pm 5\%$  of the reference loadings.

- **SRM2783:** root-mean-squared-relative-errors (RMSREs) plus three times standard deviations of the absolute relative bias from previous measurements.

$$RMSREs = \sqrt{\frac{1}{m} \sum_1^m \left( \frac{C_{E4} - C_{ref}}{C_{ref}} \right)^2}$$

Where  $m$  refers to measurement month.

The re-analysis set consists of selected SPARTAN samples that are representative of samples with low, medium, and high loadings in the SPARTAN network.

The z-score is defined as the ratio of the difference between each result from monthly reanalysis and reference value to accompanying uncertainty as shown in the following equation. The reference value is assigned as the mean results of multiple measurements which are fixed and not updated every calibration.

$$z = \frac{C_{E4} - C_{ref}}{\sqrt{U_{C_{E4}}^2 + U_{C_{ref}}^2}}$$

## 6.4 Reproducibility testing in data validation

The long-term reproducibility of E4 is monitored by z-score calculated using monthly analysis results and the reference values of the re-analysis set. The mean of z-score for the re-analysis set must remain between -1 and 1 for the elements listed in Table 4. If continuous exceedances of the z-score limit are observed, further tests are employed to determine the cause of instability.

Data integrity, internal consistency, and reasonableness of results are reviewed after analysis. After the initial data review is complete, the elemental composition data are merged with data from other analyses and undergo final validation before delivery.

## 7.0 REFERENCES

1. *UCD IMPROVE Standard Operating Procedure #301 X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*
2. *UCD IMPROVE SOP #301 Technical Instruction*
3. *UCD IMPROVE Standard Operating Procedure #351 Data Processing and Validation*