STANDARD OPERATING PROCEDURES

Determination of Trace Metals Deposited on Air Filters by XRF Analysis

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1.0 SCOPE AND APPLICATION

Once the post weighing of the PTFE® filters is completed and validated, a series of non-destructive analyses including X-ray fluorescence (XRF) are performed to determine contributions of different components of the samples. Looking at the trace metal content, determined through XRF, SPARTAN is currently able to quantify 26 elements. This SOP describes the steps to ensure quality XRF measurements are taken on the PTFE® filters.

2.0 SUMMARY OF METHOD

All filters are analyzed by XRF in the Epsilon 4 (E4) benchtop XRF analyzer from Malvern Panalytical, wherein they 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.

Accuracy and precision of these measurements is ensured by verifying results versus acceptance limits, periodic comparisons of measurements of blank filters for background use, and periodic recalibration of the instrument to account for any signal drift over time.

3.0 CONTAMINATION CONTROL

Filters are stored individually inside petri dishes and placed in a sealed plastic bag when not being analyzed. Once filters are ready to be analyzed, they are handled in a clean environment with PTFE®-coated tweezers. Tweezers are cleaned prior to 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. Carefully only touching the outer ring with the tweezers, filters are placed individually in the E4 sample holders. Filters are held in place by custom 3D-printed polylactic acid (PLA) 25mm filter holder rings which are periodically cleaned with methanol. The lid of the E4 is kept closed except during loading and unloading of samples to avoid contamination from dust or other foreign materials.

4.0 SAMPLE STORAGE AND RECORDKEEPING

Filters, placed in closed petri dishes and sealed inside a plastic bag, are stored at room temperature and labelled based on site and cartridge number. Following analysis, 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.

5.0 EQUIPMENT AND STANDARDS

5.1 Laboratory Equipment

- Epsilon 4 (E4) benchtop XRF analyzer - Malvern Panalytical
- Custom polylactic acid (PLA) 25mm filter holder rings (as well as 36mm and 47mm variants for appropriate standards)
- PTFE®-coated tweezers
- Methanol
- XRF calibration standards
- Sampled filters inside petri dishes
- Non-sampled filter blanks for background subtraction
- Helium (ultra-high purity)

A line of ultra-high purity (UHP) helium is connected to the E4. Helium is used during 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 tank opened prior to sampling.

5.2 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. Periodic analysis of standards should then be done to correct for instrument drift – particularly important for standards containing light elements (Al, Si) which are more prone to drift. One or more standards of Al and Si should be re-analyzed weekly when regular analysis is being undertaken. The NIST SRM 2783 standard should be re-analyzed at a minimum monthly, and ideally every two weeks when analysis is actively being undertaken.

Table 1. Elemental breakdown of the standards for XRF analysis. Concentrations are shown in µg/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	9	0.356	0.65	0.723	1.06	1.566	2.3303	2.42	5.06	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	6	1.1	3.39	4.5	12.57	23.4	28.69			
Cl	11	0.012	0.024	0.075	0.089	0.7	1.1	2.21	4	4.08
Cl (cont)		5.64	13.04							
Co	6	0.0008	0.024	0.048	0.104	0.5	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	2.66	4.26		
K	9	0.3	0.351	0.53	0.714	0.82	1.546	1.7	2.44	6.21
Mg	6	0.119	0.241	0.522	0.8	0.865	2.7			
Mn	6	0.032	0.059	0.121	0.261	1.7	7.5			
Na	7	0.1867	0.5	0.71	1.385	2.6	2.64	2.815	6.094	8.45
Ni	6	0.0024	0.024	0.048	0.104	1	6.4			
Pb	7	0.0318	0.119	0.241	0.43	0.522	0.93	2.63		
Rb	4	0.0024	0.024	0.048	0.104					
S	13	0.105	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	5.88	5.96
Sn	2	1.4	7.1							
Sr	3	0.024	0.048	0.104						
Ti	7	0.024	0.048	0.104	0.1495	1.67	5.05	8.54		
V	7	0.0049	0.024	0.048	0.104	0.9	1.32	2.86		
Zn	7	0.031	0.093	0.1797	0.365	0.56	1.99	3.6		

Included in the standards set are certified filter standards, blank filters of corresponding material. These are used as background subtraction for their corresponding standards (i.e. PALL blank filters for standards which are deposited on PALL filters, MTL blanks for standards on MTL filters, etc.).

6.0 ANALYSIS WITH X-RAY FLUORESCENCE

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.

6.1 Calibration of Epsilon 4

In order to proceed with initial analysis of standards for calibration, an application must be created in the Epsilon software in order to determine how analysis is undergone. The configuration of the application used for SPARTAN measurements (hereafter termed "SPARTAN XRF Analysis") is shown in **Error! Reference source not found.**. Once created, t his 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)
<Fe-Pb>	50	300	Ag	Air	Normal	540
<K-La>	12	1250	Al-50	Air	Normal	540
<Na-Cl>	9	1666	Ti	Helium	Normal	720
<Pd-Sb>	50	300	Cu-500	Air	Normal	540
<V-Mn,Ce>	20	750	Al-200	Air	Normal	540

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 E4 has been calibrated, the application created, and the condition sets implemented, analysis of samples can be performed.

6.2 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 in order to properly hold filters.
- Using the PTFE® coated tweezers, load filters individually deposit side down on to 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 the 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 "SPARTAN XRF Analysis" 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 analysis is complete, lift the lid of the XRF, and remove each filter with PTFE®-coated tweezers, replacing each filter into the corresponding petri dish, and resealing the plastic bag once all closed petri dishes have been replaced.

7.0 DATA VALIDATION

- The validation of data obtained through the XRF analysis is done by comparing to the acceptance limit for each element in the method. This acceptance limit is based on a method detection limit (MDL), determined as three times the standard deviation of the reported concentrations for a set of 9 lab blanks. Acceptance limits are calculated as the mean concentration of each element on those blanks plus the MDL. These lab blanks are stored in petri dishes and sealed in a plastic bag for future repetition of MDL testing. Any recorded concentration value below the elemental acceptance limit (listed in table 3) is determined to be below detection limits and value is set to zero.

Table 3. List of method detection limits used for elements measured by XRF

Element	Acceptance limit
Na	0.9963
Al	0.0078
Si	0.0257
S	0.0029
Cl	0.0486
K	0.1009
Ca	0.0410
Ti	0.0310
V	0.0012
Fe	0.0078
Zn	0.0027
Ce	0.0030
Pb	0.0060
As	0.0021
Co	0.0013
Cr	0.0018
Cu	0.0074
Mg	0.0765
Mn	0.0015

Ni	0.0017
Sb	0.0579
Rb	0.0056
Sr	0.0077
Cd	0.0147
Se	0.0006
Sn	0.0818

- 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.
- Periodic re-analysis of standards:
    - One or more standards each of Al and Si should be re-analyzed weekly.
    - NIST SRM 2783 standard should be re-analyzed at a minimum monthly, and ideally every two weeks when analysis is actively being undertaken.