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Evaluation of MTL Filters:

X-Ray Fluorescence Data Report

By

Teri L. Conner
US EPA, Office of Research and Development, National Exposure Research Laboratory, Human Exposure and Atmospheric Sciences Division, Research Triangle Park, NC 27711

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC, 27711

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Introduction

Three different types of PTFE blank filters were analyzed on the Kevex energy dispersive x-ray spectrometer. Filters analyzed comprised the following: 1) 10 MTL filters with the filter ID marked on the filter itself, near the outer edge, 2) 10 Whatman filters with the filter ID marked on the support ring, and 3) 8 MTL filters with no ID markings. The purpose of these analyses was to determine if markings on the filter itself interfere with the XRF analyses. The procedures followed for the analysis and data processing and the science behind those procedures are described in the listed references, unless otherwise noted in this report. This report gives an assessment of the issues impacting data quality and an overall impression of the data set.

Data Quality Control and Assessment

At the beginning and end of a run of samples a set of quality control filters is measured to monitor the operational status of the spectrometer. The QC parameters checked are peak areas (monitors change in sensitivity); background areaș (monitors contamination or background changes); CHAN or centroid (monitors gain and baseline adjustment to insure that spectra are assigned the correct centroid); and FWHM (monitors degradation of the detector resolution). These parameters are measured for elements ranging from sodium to lead and include atmospheric argon. The target and tolerance values are based on the average and standard deviation of at least 10 analyses of the quality control filters. The allowable range includes the target value plus or minus three standard deviations. Any deviation from these established limits is automatically flagged at run-time for quick review. This process results in a total of 68 measurements to assure proper operating condition of the XRF spectrometer. These tolerances were applied to the QC standards for the blank filter analyses (XRFID 3205). Table 1 gives a summary of the QC failures for XRFID 3205. There were only two failures – one peak area, one blank peak area - not exceeding 5-sigma. This met the target of 5 or less deviations greater than 3-sigma for the Kevex spectrometer.

Table 1. Number and Type of QC Failures for Each Sample Run

		Beginning QC				End QC			
XRFID	Analysis Start Date	Bkgd Area	Peak Area	Centroid	FWHM	Bkgd Area	Peak Area	Centroid	FWHM
3205	9/30/10	0	1	0	0	1	0	0	0

To monitor the accuracy of the spectrometer, reference materials of known concentrations are analyzed and the beginning and end of each sample run. NIST certified reference standard, Standard Reference Material SRM1833-1425 and SRM 1832-1365, were analyzed at the beginning and end respectively of each analysis. The acceptance criterion for accuracy is that the XRF concentration ± 3 times the uncertainty must overlap the NIST certified concentration ± 1 times its reported uncertainty.

Table 2 shows the percent difference between the SRM element concentrations from each analysis and the NIST certified concentrations. XRF results not meeting the acceptance criterion are in bold font.

Table 2. Percent Difference Between the SRM Element Concentrations from Each Analysis and the NIST Certified Concentrations

	SRM 1833 - % Difference from NIST concentrations						SRM 1832 - % Difference from NIST concentrations							
XRFID	Si	K	Ti	Fe	Zn	Pb	Na	Al	Si	Ca	V	Mn	Co	Cu
3205	0.0	-8.1	-0.6	-3.8	-0.9	3.6	4.2	5.6	-2.3	0.4	7.4	4.6	4.8	**-10.3**

The reported Cu concentration for SRM 1832-1356 had been previously determined to be higher than the true value (R. Kellogg, personal communication). A concentration reported incorrectly high would lead to measured concentrations low compared to the reported value and possibly to failures in the acceptance criteria. For XRF ID's 2894 – 2903, XRF results for Cu did not meet the acceptance criterion for accuracy. Based on information previously reported, this result was expected and can be disregarded in the accuracy evaluation. All other elements in the newer SRM filters met the acceptance criterion for accuracy.

Results

The first step in computing elemental concentrations is to subtract that background spectrum arising from the filter medium and the spectrometer system. The spectra from 8 unmarked MTL laboratory blank filters were summed together to produce composite spectra for spectral background corrections. These spectral background corrections were applied during the least squares computation of the concentrations for the marked MTL blanks and the Whatman blanks. Data processing also includes attenuation and interference corrections and converts raw data into volumetric concentrations. Uncertainties associated with each variable are propagated through the calculation and reported as the 1-sigma uncertainty.

The limit of detection is typically defined as three times the standard deviation of a set of blanks (such as the laboratory blanks associated with a set of ambient filters). This is the concentration level that can be distinguished from noise or background. The EPA XRF lab takes a similar approach and considers an element to be detected when its concentration is equal to or greater than three times its propagated uncertainty. The minimum concentration level at which one concentration can be distinguished from another, also known as the limit of quantification (LOQ), is typically defined as ten times the standard deviation of a set of blanks. The propagated uncertainties of the 8 unmarked blanks were used to calculate the LOD and LOQ for these analyses.

In the data tables presented in this report, detection parameters presented include frequency of detection and average signal-to-noise. Frequency of detection is defined as the percent of concentrations measured above the 3-sigma detection limit, and signal-to-noise is defined as the ratio of concentration to the propagated 1-sigma uncertainty. In addition, average concentrations for each element are compared to their limit of quantification, determined from the variability of the laboratory blanks (the unmarked MTL filters in this case).

Table 3 shows the average, standard deviation, and detection parameters for the marked MTL filters and Whatman filters, along with a summary for the unmarked MTL blank filters and the LOQ computed from those filters. Average concentrations of all elements on all filters were lower than the limit of quantification. All elements on all filters had an average signal-to-noise of greater than 3.0, with most being below 1.0. Nearly all elements on all filters were detected at a frequency of 20% or less – most were always below detection.

Table 3. Average, Standard Deviation, and Detection Parameters for the Unmarked and Marked MTL filters and the Ring-Marked Whatman Filters.

		Unmarked MTL Blank Filters (8 filters)				Marked MTL Blank Filters (10 filters)				Marked Whatman Blank Filters (10 filters)			
Element	LOQ ng/cm^2	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %
Na	313	9.6	31.3	0.2	0	3.0	40.9	0.0	0	0.6	58.5	0.1	0
Mg	172	5.2	17.2	0.2	0	-6.7	17.4	0.6	0	12.0	18.9	-0.3	0
Al	224	-7.5	22.4	-0.3	0	-45.0	38.6	-0.3	10	-5.3	36.9	-1.7	0
Si	236	0.5	23.6	0.0	0	-8.5	24.3	0.4	20	7.1	40.7	-0.5	0
P	38	-2.7	3.8	-0.5	0	-1.6	7.1	0.0	0	0.1	5.4	-0.3	0
S	35	-2.4	3.5	-0.6	0	-4.9	4.9	-0.9	0	-3.7	7.6	-1.1	0
Cl	32	-1.1	3.2	-0.4	0	-4.0	4.0	0.1	0	0.5	3.8	-1.2	0
K	28	-0.1	2.8	0.0	0	-2.0	2.3	0.3	0	0.8	2.8	-0.7	0
Ca	11	-0.2	1.1	0.1	0	-0.4	2.5	-0.6	0	-0.8	2.2	-0.3	0
Sc	6	0.1	0.6	0.1	0	1.1	1.5	1.5	20	1.5	1.2	1.0	10
Ti	16	0.3	1.6	0.2	0	2.3	1.7	-0.1	0	-0.2	1.5	1.1	0
V	16	0.0	1.6	0.0	0	-0.7	0.9	-0.1	0	-0.1	1.5	-0.6	0
Cr	9	-0.1	0.9	-0.1	0	1.0	0.8	1.0	10	0.7	0.8	1.3	10
Mn	19	-0.1	1.9	-0.1	0	-0.2	1.8	0.7	0	1.3	1.8	-0.1	0
Fe	17	-0.2	1.7	-0.2	0	0.8	1.4	0.3	10	0.5	2.6	0.6	0
Co	10	-0.2	1.0	-0.2	0	0.4	1.6	0.2	0	0.2	1.1	0.4	0
Ni	16	0.1	1.6	1.0	0	0.0	1.7	0.1	0	0.2	1.4	0.0	0
Cu	6	-0.1	0.6	-0.1	0	0.7	1.2	0.9	0	0.7	0.8	0.7	0
Zn	4	0.1	0.4	0.1	0	1.0	0.7	1.9	10	1.3	0.6	1.4	10
Ga	14	-0.6	1.4	-0.3	0	-2.3	2.5	-0.5	0	-1.0	2.8	-1.0	0
Ge	8	0.0	0.8	0.0	0	-1.0	3.1	-0.9	0	-1.6	1.4	-0.5	0
As	20	-0.9	2.0	-0.5	0	-5.8	3.1	-1.3	0	-2.3	2.3	-2.9	0
Se	11	-0.1	1.1	-0.1	0	-0.4	1.1	-0.4	0	-0.5	1.4	-0.3	0
Br	17	0.3	1.7	0.3	0	0.4	1.9	-0.1	0	0.0	1.5	0.3	0
Rb	14	0.0	1.4	0.0	0	1.6	1.5	1.6	10	1.9	1.1	1.2	10
Sr	21	-0.6	2.1	-0.3	0	0.4	3.6	0.8	0	2.1	3.0	0.1	0
Y	39	-0.2	3.9	-0.1	0	2.6	2.8	0.1	0	0.4	3.6	1.0	10
Zr	33	0.3	3.3	0.1	0	0.1	2.4	0.6	0	1.7	2.9	0.0	0
Nb	23	0.3	2.3	0.1	0	6.0	4.8	1.6	10	5.0	3.3	1.8	20
Mo	27	1.6	2.7	-0.5	0	3.2	2.9	1.2	10	-3.8	3.5	1.0	0
Rh	38	2.5	3.8	0.3	0	7.6	9.5	0.9	0	6.5	5.3	1.0	0
Pd	41	-1.6	4.1	-0.3	0	-7.0	9.3	-0.7	0	-4.7	8.0	-1.1	0
Ag	115	1.0	11.5	0.1	0	-6.7	18.4	-0.2	0	-2.1	10.1	-0.5	0
Cd	63	-1.3	6.3	-0.2	0	4.5	9.4	0.6	0	3.8	5.0	0.7	0
In	75	0.2	7.5	0.0	0	2.4	6.5	-0.2	0	-1.0	5.9	0.4	0
Sn	38	-0.9	3.8	-0.3	0	-3.5	1.7	0.0	10	-0.1	4.7	-1.0	0
Sb	35	-0.1	3.5	0.0	0	3.0	3.9	1.1	0	3.2	4.0	0.9	0
Te	23	0.1	2.3	0.0	0	-0.3	3.2	0.5	0	1.6	3.5	-0.1	0
I	42	-0.5	4.2	-0.2	0	-1.8	2.9	-0.1	0	-0.4	4.6	-0.5	0
Cs	31	-0.6	3.1	-0.3	0	-0.4	3.0	0.8	10	2.0	3.9	-0.2	0
Ba	43	-1.0	4.3	-0.2	0	0.0	3.9	-0.2	0	-0.7	3.8	0.0	0
La	23	-0.1	2.3	-0.1	0	2.5	1.8	0.6	0	1.6	2.7	0.9	0
Ce	25	-0.1	2.5	0.0	0	-0.1	3.1	0.2	0	0.6	2.6	0.0	0
Pr	32	-0.6	3.2	-0.2	0	-0.3	4.3	0.1	0	0.4	2.3	-0.1	0
Nd	22	-0.3	2.2	-0.2	0	0.5	1.7	0.5	10	0.9	3.2	0.2	0

Table 3. *Continued.*

		Unmarked MTL Blank Filters (8 filters)				Marked MTL Blank Filters (10 filters)				Marked Whatman Blank Filters (10 filters)			
Element	LOQ ng/cm^2	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %	Avg. ng/cm^2	Std Dev ng/cm^2	S/N[a]	Freq Det %
Sm	14	-0.1	1.4	0.0	0	1.5	3.4	0.9	0	2.2	2.2	0.5	0
Eu	71	-0.5	7.1	-0.1	0	-0.4	5.5	-0.5	0	-2.1	4.9	-0.1	0
Gd	17	-0.2	1.7	-0.6	0	-1.7	2.9	-0.3	0	-0.5	1.3	-0.8	0
Tb	17	-0.5	1.7	-0.2	0	-5.4	3.6	-0.7	0	-1.6	2.1	-2.3	0
Dy	17	0.2	1.7	0.1	0	-2.7	2.8	0.1	10	0.2	3.6	-1.1	0
Ho	22	0.0	2.2	0.0	0	-0.9	2.7	0.0	0	0.0	2.5	-0.5	0
Er	14	-0.3	1.4	-0.1	0	0.7	3.7	0.4	0	1.0	2.0	0.3	10
Tm	15	-0.6	1.5	-0.4	0	1.3	1.5	0.6	10	1.2	2.8	0.7	0
Yb	31	-0.9	3.1	-0.3	0	4.0	5.7	1.1	0	3.6	3.5	1.1	20
Lu	10	-0.8	1.0	-0.6	0	0.1	1.7	0.5	0	0.8	2.0	0.1	0
Ta	11	0.4	1.1	0.2	0	0.5	2.0	1.3	10	1.9	1.8	0.3	0
W	72	0.9	7.2	0.1	0	-1.3	12.4	-0.3	0	-1.8	6.0	-0.2	0
Pt	27	-1.5	2.7	-0.4	0	2.9	6.9	0.5	0	1.9	4.0	0.6	0
Au	29	-1.4	2.9	-0.5	0	3.3	4.2	1.0	0	3.3	2.6	0.9	0
Hg	20	-1.6	2.0	-0.5	0	0.9	7.3	0.5	0	1.4	2.9	0.2	10
Tl	23	-0.9	2.3	-0.6	0	1.9	3.4	0.7	0	1.4	2.4	0.8	10
Pb	29	0.1	2.9	0.0	0	9.3	6.5	1.1	10	4.0	4.6	2.4	30
Bi	20	-0.3	2.0	-0.2	0	0.5	2.6	-0.1	0	-0.2	2.6	0.2	0
Th	59	-1.6	5.9	-0.3	0	-0.2	6.6	0.3	0	1.6	5.4	-0.1	0
U	43	-0.4	4.3	-0.1	0	2.6	5.1	-0.3	0	-0.6	7.4	0.5	0

[a]S/N = signal-to-noise (Avg./Stdv)
[b]LOQ = limit of quantification

Summary

Three different types of PTFE blank filters were analyzed on the Kevex energy dispersive x-ray spectrometer. Filters analyzed comprised the following: 1) 10 MTL filters with the filter ID marked on the filter itself, near the outer edge, 2) 10 Whatman filters with the filter ID marked on the support ring, and 3) 8 MTL filters with no ID markings. The purpose of these analyses was to determine if markings on the filter itself interfere with the XRF analyses.

Quality control measurements were conducted at the beginning and end of the analysis (XRFID 3205) to assure proper operating condition of the XRF spectrometer. There were only two failures – one peak area, one blank peak area - not exceeding 5-sigma. This met the target of 5 or less deviations greater than 3-sigma for the Kevex spectrometer.

NIST certified reference standard, Standard Reference Material SRM1833-1425 and SRM 1832-1356, were analyzed at the beginning and end respectively of the analysis to monitor the accuracy of the spectrometer. The acceptance criterion for accuracy is that the XRF concentration ± 3 times the uncertainty must overlap the NIST certified concentration ± 1 times its reported uncertainty. Spectrometer accuracy was confirmed based on acceptance criteria.

In the data tables presented in this report, detection parameters presented include frequency of detection and average signal-to-noise. Average concentrations of all elements on all blank filter types were lower than the limit of quantification. All elements on all blank filter types had an average signal-to-noise of greater than 3.0, with most being below 1.0. Nearly all elements on all filters were detected at a frequency of 20% or less – most were always below detection.

These results indicate that the on-filter markings do not have a significant influence on the XRF analytical results. However, the markings were located on the edge of the filter, so it could be that the markings simply were not impacted by the fluorescer radiation. Thus, it could not be determined from this experiment whether the markings have sufficiently low elemental composition to influence the XRF results or if the markings simply were not in the active XRF analysis area of the filter.

References

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"Spectral Analysis of Energy-Dispersive X-Ray Spectra of Ambient Aerosols, Guidance Document," Alion Science and Technology, February 2007.