CALIFORNIA
AIR RESOURCES BOARD

Standard Operating Procedure for the Determination of Elemental Concentrations in Ambient Air by Energy-Dispersive X-Ray Fluorescence (EDXRF) Spectroscopy

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Approval Signatures	Approval Date
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Standard Operating Procedure for the Determination of Elemental Concentrations in Ambient Air by Energy-Dispersive X-Ray Fluorescence (EDXRF) Spectroscopy

1. Introduction

This document describes a non-destructive analytical method for determining aerometric concentrations in nanogram per cubic meter (ng/m^3) for 28 elements that are captured on thin Teflon® membrane filters used in fine particulate matter (PM2.5) or on coarse particulate matter (PM10) sampling devices. This method employs Energy Dispersive X-ray Fluorescence (EDXRF) system, which is applicable to the analysis of a broad range of non-volatile elements from atomic numbers (Z) 11 to 92. The EDXRF method does not distinguish oxidation states, and only total elemental concentrations are measured.

2. Summary of Method

The particles collected on the Teflon filters are placed under vacuum in the EDXRF spectrometer and irradiated with X-rays of various energies. Samples excited by these primary X-rays emits X-ray fluorescence, which have characteristic energies for each element in the sample.

The method uses four optimal acquisition conditions that address the subset groups of the elements of interest. The particulate matter is assumed to be distributed uniformly on the filter. With the sample as a thin layer of particles, matrix effects are nullified.

3. Acronyms

°C	Degrees Celsius
CFR	Code of Federal Regulations
cm^2	Centimeter squared
cps	Counts per second
DAC	Digital to analog converter
DT	Deadtime
e-	Electron
eV	Electron volt
FWHM	Full Width Half Maximum - measure of resolution
KeV	Kilo electron volt
kV	Kilovolt

LIMS	Laboratory Information Management System, a database used to record and store sample information and analytical results as well as perform workflow and data tracking and reporting.
LIMSLink	Software allowing review and transfer of data to LIMS.
mA	Milli amperes units for tube current
MDL	Method Detection Limit
mg	Milligram
MLD	Monitoring and Laboratory Division
mm	Millimeter
mm Hg	Millimeters in mercury
ng	Nanogram
ng/cm^2	Nanogram per centimeter squared – raw EDXRF data
ng/m^3	Nanogram per cubic meter – aerometric concentration
NIST	National Institute of Standards and Technology
NLB	Northern Laboratory Branch
PHA	Pulse Height Analyzer - addresses the status of Silicon Drift Detector (SDD) detector
PM10	Particulate matter with an aerodynamic diameter less than or equal to 10 micrometers
PM2.5	Particulate matter with an aerodynamic diameter less than or equal to 2.5 micrometers
PTFE	Polytetrafluoroethylene
QC	Quality Control
RL	Reporting limit
ROI	Region of Interest used to calculate peak counts
RPD	Relative percent difference
RSD	Relative Standard Deviation
SDD	Silicon Drift Detector - high purity silicon with very low leakage current
sec	Second
SOP	Standard Operating Procedure
t	Time
U.S. EPA	United States Environmental Protection Agency
Z	Notation for Atomic Number of an atom
μg	Microgram
μs	Microsecond

4. Definitions

4.1 Beryllium (Be): an alkaline earth metal (very rare), that has low density, thermally stable and conductive, and is transparent to X-rays and other ionizing radiation. Be is used as windows (thin foils) in X-ray tubes and X-ray detectors. These foils are very thin and brittle and Be dust is extremely toxic and corrosive to tissues.

4.2 Characteristic (Emission) Lines: Emission spectral lines produced by the target element. For Rhodium (Rh) tube: Rh L-lines 2.69 kilo electron volt (keV) and Rh K-lines $K\alpha$ = 20.16 keV, $K\beta$ = 22.71 keV.

4.3 Centroid: The weighted center of the peak, calculated as the energy at which the side of the peak to the left has the same number of counts as the side of the peak to the right of this point (used in interpretation of the stability results).

4.4 Convolution: Convolution is an operation performed on two signals which involves multiplying one signal by a delayed version of another signal (usually in Fourier domain), integrating or averaging the product, and repeating the process for different delays.

4.5 Deadtime (DT): Measure of the period of time in which the system is unable to accept another signal for processing. DT is influenced by incoming count rate and pulse processor rate

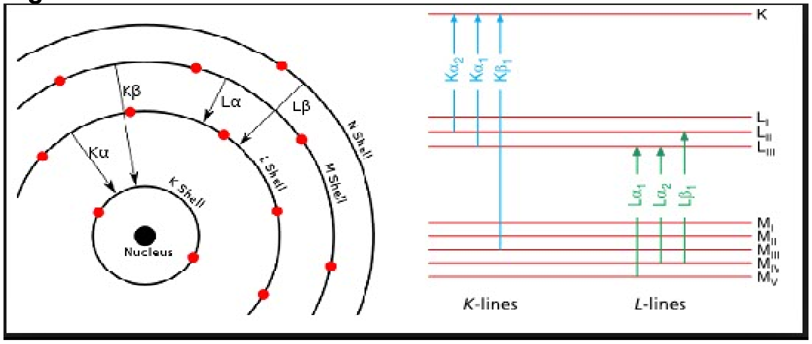
4.6 Deconvolution: The process of mathematically filtering a spectrum to compensate for undesired electronic noise or distortion in the spectrum. It is used to minimize the contribution of the signal distortion on a spectrum in order to improve resolution.

4.7 Digital to Analog Converter (DAC): A multi-channel electronic device that converts a digital (usually binary) code to an analog signal (current, voltage, or electric charge).

4.8 Full Width Half Max of the Peak (FWHM): Calculated as the distance between the left and right sides of the peak at half of its maximum height. Defines the detector resolution (in electron volt; eV).

4.9 K, L, M Lines: Intra-atom electron transitions responsible for principal X-ray spectral lines. The numeral following each orbital symbol (K, L1, L2, M, etc.) is the number of electrons in that orbital when full. Shells have specific names and only hold a certain number of electrons: K-shell (2 e-), L-shell (8 e-), Mshell (18 e-), and N-shell (32 e-). Characteristic K -and L-emission lines for all elements are given in Table A-1, Appendix A.

Figure 1: Intra-Atom Electron Transition Lines



4.10 Poisson Distribution: Discrete probability distribution that expresses the probability of a given number of events occurring in a fixed interval of time and/or space if these events occur with a known average rate and independently of the time since the last event. For large number of events (>1000 counts), then the counting error in the intensity can be no greater than the width of the Poisson distribution, 3 σ, where σ is the standard deviation or [# counts]$^{1/2}$.

4.11 Rhodium (Rh, Z=45): The anode material of the X-ray tube plated on a copper block. The tungsten filament is heated by a pulse width modulated AC current from Voltage/Current control board. The heated filament cathode emits electrons, which accelerate to anode (Rh), where they lose energy by producing X-rays (1%) and heat (99%).

4.12 Region of Interest (ROI): used to calculate the peak counts. The ROI depends on the element and detector type used to conduct the test.

4.13 Tube Current: Automatically set by the software and governs the intensity of the signal. Tube current can be manually adjusted to achieve 50% DT.

4.14 X-ray: Form of electromagnetic radiation. X-rays have a wavelength in the range of 0.01 to 10 nanometers and in energies in the range 100 eV to 100 keV. The wavelengths are shorter than those of ultraviolet rays and longer than those of gamma rays. X-ray travels at the speed of light, behaves as both a quantum of energy and a wave and is not deflected by electric or magnetic fields. X-ray may be collimated, transmitted, reflected, refracted, diffracted, polarized, scattered, or absorbed.

4.15 X-ray Tube (Source): The X-ray source consists of an evacuated chamber with a heated cathode, which is usually a tungsten wire, and an anode, which is held at a potential difference of several tens of kilovolts relative to the cathode. Thermal electrons are released from the cathode and accelerated toward the anode. When the electron beam impinges upon the anode, bremsstrahlung radiation as well as X-ray lines characteristic of the anode material are emitted. These photons escape through a beryllium window built into the side of the tube.

5. Interferences

5.1 Sum Peaks – Arise when 2 or more X-rays enter the detector crystal at exactly the same time. Made up of integer multiples of the parent peak. These are reduced by keeping count rates low.

5.2 Rayleigh Scatter – Elastic scatter (coherent), favored in scatter from high Z materials. There is no energy lost. This is the reason that the tube anode lines appear in the spectrum. The Rayleigh scatter lines are from tube Rh characteristic lines and are modeled and accounted for in the software.

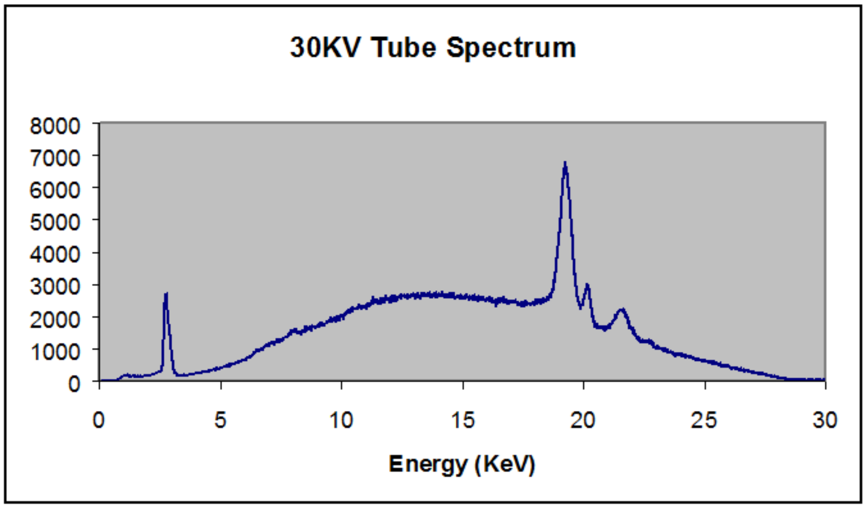
5.3 Compton Scatter - Inelastic scatter (incoherent) where there is a photon energy loss to a loosely bound electron. The emission peak is evident below the energy of the incident photon. The Compton scatter produces large intensity Rh $K\alpha$ 20.167 KeV and Rh $K\beta$ 22.759 KeV emission lines. The Compton scatter is favored from low Z elements. The Compton scatter lines are from tube Rh characteristic lines and are modeled and accounted for in the software.

5.4 Attenuation Corrections – Attenuation occurs when incoming (excitation) or outgoing (fluorescent) photons are absorbed by sample. The net effect is that the instrument detects less signal from the element that would be expected. The software determines the attenuations and their uncertainties for each element and automatically corrects it.

5.5 Escape Peaks - Occurs when the lithium-drifted silicon [Si (Li)] detector crystal emits a Si X-ray that results in a loss of energy equal to the Si photon energy. Escape peaks (ghost peaks) are 1.74 KeV below parent peak and are modeled and accounted for in software.

5.6 Bremsstrahlung Radiation – Continuous radiation or background radiation due to deceleration of electrons as they strike the anode of the X-ray tube. It is characterized by a continuous distribution of radiation which becomes more intense and shifts toward higher frequencies when the energy of the bombarding electrons is increased as shown in the spectrum below.

Figure 2: Bremsstrahlung Radiation



5.7 Atmosphere – Air absorbs low energy X-rays (elements below Ti (Z = 22)), and Argon (1% of the composition of air) has an absorption edge below K (Z = 19) and Ca (Z = 20). All analysis conditions are done in vacuum to remove these interferences.

5.8 Peak Overlaps - Spectral interferences that occur when the EDXRF detector is unable to resolve peaks that are very close to each other. Some of the peak overlaps are given below (the Mα transitions lines are not measured by the EDXRF method).

Table 1: Peak Overlaps

Element	Overlap
Al Kα	Br Lα, Tm Mα, Yb Mα
Si Kα	Rb Lα, Sr Mα, W Mα
P Kα	Zr Lα, Ir Mα
S Kα	Mo Lα, Pb Mα
Cl Kα	Rh Lα, Ru Mα
Ca Kα	Te Lα, Sb Mα
Ti Kβ	Ba Kα, La Mα
V Kβ	Cr Kα
Cr Kβ	Mn Kα
Mn Kβ	Fe Kα
Fe Kβ	Co Kα
Pb Mα	S Kα, Mo Lα
Pb Lα	As Kα
Ba Lα	Ti Kα
Br Lα	Al Kα

To correct for peak overlaps and obtain accurate peak intensities, a specialized peak-fitting method is employed. In this method, a library of pure reference spectra is generated for all elements determined by the method. Then sample spectrum deconvolution is performed by multiple, linear least squares fitting of the reference spectra to the sample spectrum. Additionally, digital filtering of spectra is used to correct for background interferences before the peak fitting treatment is performed.

6. Personnel Qualifications

Prior to performing this method, new personnel must be trained by staff with detailed knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and/or guidance, and this Standard Operating Procedure (SOP). Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, the quality assurance components, and Laboratory Information Management System (LIMS) functionality pertaining to the program.

Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record).

7. Safety Requirements

7.1 The EDXRF analytical system is registered with California Department of Public Health Radiologic Health Branch.

7.2 All personnel must follow the general health and safety requirements found in NLB's Chemical Hygiene Plan, including the Radiation Protection Program. See Reference 19.12.

8. Analytical Equipment, Standards, and Supplies

8.1 Thermo Quant'X-EDXRF Spectrometer (Thermo Scientific) or equivalent, bench top, laboratory grade:

8.1.1 X-ray Source

X-ray Tube: 50-Watt, Rhodium target (Rh), end window emission with 76 μm beryllium (Be) window, air cooled.

X-ray Power Supply: Voltage range, 4-50 kV in 1 kV increments; current range 0.0 to 1.98 mA (0.02 mA increments).

Primary Beam Filters: Automated 8-position beam filter wheel with an open position for direct excitation and 7 transmission filters as indicated in the following table:

Table 2: Primary Beam Filters

Filter Material (Primary Beam Filters)	**Thickness** (mm)
Cellulose	n/a
Aluminum	0.13
Palladium (Pd thin)	0.025
Palladium (Pd med)	0.05
Palladium (Pd thick)	0.125
Copper (Cu thin)	0.377
Copper (Cu thick)	0.63

n/a = Not Applicable

8.1.2 X-ray Detector

Silicon Drift Detector (Si(Li)): Si 30 mm^2 surface area, Peltier air cooled, < 12.5 μm Be window, which provides a resolution of <175 FWHM for Cu $K\alpha 1$ at 8.041 keV.

Field Effect Transistor: collect charges and integrate to derive voltage pulse.

8.1.3 Instrument Controller

Computer system (Intel Core i5 or better), 64-bit operating system (Windows 7 or better).

Applications software:

Spectrometer Manager; monitor the system status.

Method Explorer; data analysis program used in developing methods (e.g., filter selection, excitation parameters, and sample chamber environment), analysis and generating reports.

Acquisition Manager; acquire spectra and operate automated analysis using tray lists.

8.1.4 Auto-sampler

10-position auto-sampler tray.

Sample adapters with spinning capability and ability to accommodate either 37 mm or 47 mm diameter Teflon filters.

Retaining rings, 31 mm inner diameter and 47 mm outer diameter, for holding Teflon filters in sample holders.

8.1.5 Vacuum pump

Edwards Model- RV 8 vacuum pump (or equivalent) with Ultra grade Oil (no silicates) for evacuating the spectrometer sample chamber.

8.2 Standards

8.2.1 Pure Copper disk (Cu Kα 8.041 Kev), for energy calibration of detector.

8.2.2 Calibration standards: thin vapor-deposited films of elements and compounds, National Institute of Standards and Technology (NIST) traceable. These standards are available for all 28 elements analyzed by the EDXRF method and with deposit masses gravimetrically determined to ± 5%. These reference standards are pure elements, oxides or salts, with no peak overlaps.

8.2.3 Quality Control standards: thin vapor-deposited films of elements and compounds, NIST traceable, from a source independent from the calibration standards. These standards are pure elements, oxides or salts, with no peak overlaps. The standards represent each of the four acquisition conditions for the method.

8.3 Antistatic and powder free gloves

8.4 Polytetrafluoroethylene (PTFE Teflon) filter with a support ring: circular, 46.2 mm diameter ±0.25 mm

8.5 LIMS and LIMSLink

9. Method Analytical Conditions

Optimal analytical conditions for EDXRF are governed by two principles: (1) there must be a significant source energy above absorption edge energy (the upper limit of the K or L radiation) of the element of interest. The closer the source energy is to the absorption edge, the higher the intensity (counts per second (cps)) and sensitivity will be for the element of interest (2) the background X-rays (Bremsstrahlung radiation) within the region of the elements of interest should be reduced as much as it is practical.

9.1 Adjustable Excitation parameters

9.1.1 X-ray Tube Voltage (in kV) – tube voltage must be set higher than highest absorption edge energy (1.5–2.0 times the absorption edge energy of the highest energy element in the acquisition group). Tube voltage/ radiation filter combinations provides the range for energy emission spectra. The intensity is proportional to the current (mA), which is adjusted to 50% DT. The power setting (kV and mA) is optimized for each acquisition group.

9.1.2 Primary radiation filters - filter lies between the X-ray tube and the sample.

The purpose of a filter is to (1) reduce background (Bremsstrahlung scatter) in energy region being analyzed, (2) to eliminate X-ray tube characteristic lines which overlap with an element of interest, and (3) to transmit X-rays of sufficient energy to excite the elements of interest.

9.1.3 Atmosphere – Vacuum - all analysis conditions are done in vacuum. See Section 5.7.

9.1.4 Acquisition Rate – it is the time interval between pulses that are counted. Current time (t) setting for all acquisitions is 2 μs.

9.1.5 Time (t) - improves the statistical precision. For each acquisition condition the time is fixed, long enough to permit accumulation of enough counts (achieve >1,000,000 counts with 50% DT) for the required statistical precision. The set preset time (t) for each acquisition condition is the same for samples and standards.

9.1.6 Spinner – rotates the filter sample about its center during the acquisition to ensure homogeneity in the analysis.

9.2 Acquisitions Parameters

Four acquisition conditions are used for this method to optimize the measurement of each subset group of elements. “Low", "Mid", and "High" refers to the voltage range for each acquisition parameter, while "Za/b/c” refers to the particular elemental group of interest.

9.2.1 Low Zb Acquisition Parameters

Table 3-1: Low Zb Acquisition Condition

Condition 1 - Low Zb	**Acquisition Settings**
Primary Beam Filter	Cellulose [a)]
Voltage	10 kV [b)]
Current	Auto
Atmosphere	Vacuum
Energy Range	0 – 10 keV
Acquisition Rate	2 μs
Live Time Limit	800 sec
Warm Up Time	60 sec
Spinner	On
Elements of Interest	***Al*** *[c)], Si, P, S, Cl, K, Ca*

a) Cellulose filter is used for the analysis of the K-lines of the Na (Z=11) through Ti (Z=22). This filter effectively removes the Rh Lα1 line 2.7 keV. This permits unobstructed evaluation of the Cl and S K-emission lines. The cellulose filter also eliminates most of the low energy <4 keV Bremsstrahlung radiation. This provides low scattered background in the spectrum beneath the Cl (Z=17) through Sc (Z=21) K-lines and the L-lines of Tc (Z=43) through Cs (Z=55).
b) Typical tube voltages range between 10 to 15 kV for optimum analysis of emission lines in the 1 to 8 keV range.

c) Aluminum (**Al**) is the representative quality control (QC) standard for low Zb.

9.2.2 Mid Za Acquisition Parameters

Table 3-2: Mid Za Acquisition Condition

Condition 2 - Mid Za	**Acquisition Settings**
Primary Beam Filter	Pd thin (0.025 mm) [a)]
Voltage	30 kV [b)]
Current	Auto
Atmosphere	Vacuum
Energy Range	0 – 20 keV
Acquisition Rate	2 μs
Live Time Limit	400 sec
Warm Up Time	0 sec
Spinner	On
Elements of Interest	*Ti, V, Cr, Mn, **Fe** [c)], Co, Ni, Ba (L-lines)*

a) The Pd thin filter is useful for the analysis of K emission lines from Fe (Z=26) to Ge (Z=32) and the L-lines of Eu (Z=63) through Au (Z=79). Ba (Z=56) has emission line Lα1 4.467 keV. Selectively passes only high energy Bremsstrahlung from the Rh X-ray tube and the K characteristic lines.
b) Useful range is 4 to 20 KeV with tube voltages selected in the range of 20 to 35 kV.
c) Iron (**Fe**) is the representative QC control standard for mid Za acquisition.

9.2.3 Mid Zc Acquisition Parameters

Table 3-3: Mid Zc Acquisition Condition

Condition 3 - Mid Zc	**Acquisition Settings**
Primary Beam Filter	Pd thick (0.125 mm) [a)]
Voltage	50 kV [b)]
Current	Auto
Atmosphere	Vacuum
Energy Range	0 – 40 keV
Acquisition Rate	2 μs
Live Time Limit	400 sec
Warm Up Time	0 sec
Spinner	on
Elements of Interest	*Cu, Zn, As, Se, Br, Rb, Sr, Y, Mo, Hg and **Pb** [c)] (L-lines)*

a) Effective excitation for mid Zc acquisition is achieved for emission lines in the 8 to 19 keV range which include the K- lines of Ga (Z=31) through Mo (Z=42) and the L-lines of Hg (Z=80) through U (Z=92). Both Hg and Pb are analyzed for their L-emission lines (Hg Lα1 9.987 keV and Pb Lα1 10.549 keV). Pd thick eliminates the Bremsstrahlung scatter in the spectrum < 12 keV, but still transmitting the intense Rh K-lines (Kα1 20.214 keV and Kα2 20.072 keV).
b) Tube voltages of 45 to 50 kV are typical.
c) Lead (**Pb**) is the representative QC control standard for mid Zc acquisition.

9.2.4 High Za Acquisition Parameters

Table 3-4: High Za Acquisition Condition

Condition 4 - High Za	**Acquisition Settings**
Primary Beam Filter	Cu thin (0.377 mm) a)
Voltage	50 kV b)
Current	Auto
Atmosphere	Vacuum
Energy Range	0 – 40 keV
Acquisition Rate	2 μs
Live Time Limit	800 sec
Warm Up Time	0 sec
Spinner	on
Elements of Interest	***Sn*** c), *Sb*

a) The Cu thin filter removes the K-lines of Rh from the radiation striking the sample and permits the elemental analysis of Rh (characteristic lines). Excitations by Bremsstrahlung are > 25 keV. The useful analytical range is 12 and 34 keV for analysis of the K-lines of Tc (Z=43) through La (Z=57).

b) Tube voltage required is 45 to 50 kV.

c) Tin (**Sn**) is the representative QC control standard for high Za acquisition.

10. Analytical Tests for Spectrometer

The following are conditions that must be met before operating the EDXRF system. If any of the required conditions are not met, call the service contractor and follow their instruction in resolving the issue.

10.1 Analytical Spectrometer

10.1.1 Confirm that the power indicator on the front panel is ON. If not, check system power is ON and that the X-ray source key switch is on the standby position on the back panel.

10.1.2 Make sure that vacuum pump accessories and power jumper cords are properly attached to the instrument.

10.1.3 Turn ON the vacuum pump to set ready for operation.

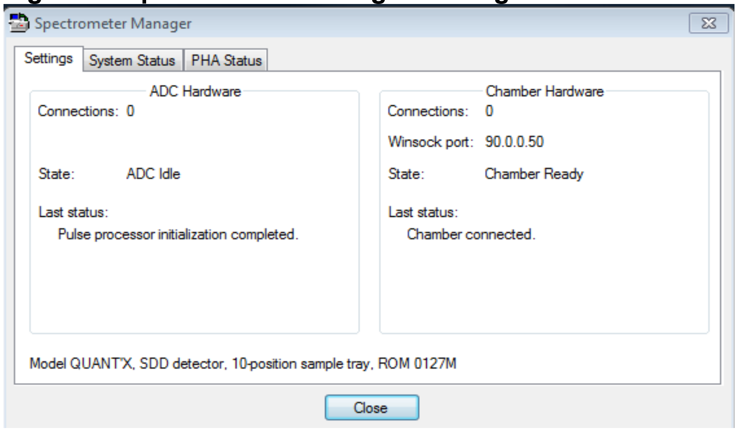
10.1.4 Verify that the Ethernet dedicated port is connected from the spectrometer to the instrument controller.

10.2 Instrument Controller

10.2.1 Open *QuantX* folder and select *Spectrometer Manager*.

10.2.2 In the *Settings* tab verify the *Chamber Hardware State* is *Chamber Ready* and is *Chamber connected*. This assures that the software is communicating with the system. If the connection fails, verify that all steps in the adapter installation were correctly done.

Figure 3: Spectrometer Manager Settings



ADC Hardware

Connections: 0

State: ADC Idle

Last status:
Pulse processor initialization completed.

Chamber Hardware

Connections: 0

Winsock port: 90.0.0.50

State: Chamber Ready

Last status:
Chamber connected.

Model QUANT'X, SDD detector, 10-position sample tray, ROM 0127M

10.2.3 In the *System Status* tab check the *Temperature and Power Supplies Status* (left side of the slide) are within the normal set values. If any value is out of range, it will be highlighted yellow, the system is not ready for operation. Call the service contractor and follow their instruction in resolving the issue.

10.2.4 Confirm that the Pulse Height Analyzer (PHA) Status is within the acceptable conditions:

Detector Temperature	“OK” is displayed, indicating that the detector is at normal operating temperature
% Dead Time	less than 5.0%
Preamp Resets	less than 5 /sec
Zero width	less than 200 eV

10.2.5 Close the *Spectrometer Manager* application.

10.3 Energy adjustment

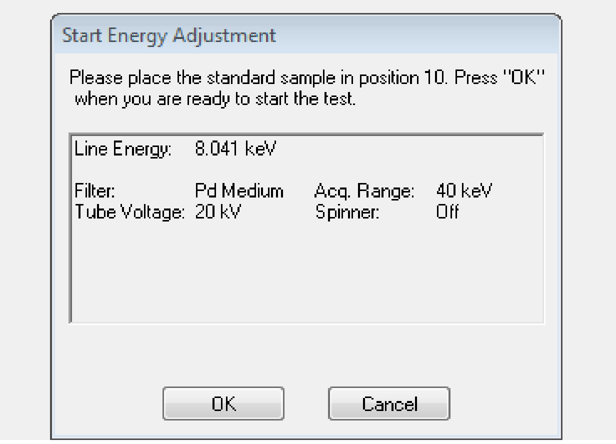
Energy calibration is performed to adjust the DAC gain so that detected X-rays appear at the correct energy. Using pure copper (Cu) at 8.041 keV in position 10, calibrate the instrument before any sample analysis or at least once a week, to achieve optimal quantitative performance.

10.3.1 Open *QuantX* folder and select *Energy Adjustment.qtl >Analyze>Tests>Energy Adjustment*.

10.3.2 Place the Cu Kα 8.041 keV standard in position 10 and close the lid.

10.3.3 Confirm the set conditions of the test and start *Energy Adjustment*. It should complete in less than one minute.

Figure 4: Energy Adjustment



Please place the standard sample in position 10. Press "OK" when you are ready to start the test.

Line Energy: 8.041 keV

Filter: Pd Medium
Acq. Range: 40 keV
Tube Voltage: 20 kV
Spinner: Off

10.3.4 When the energy adjustment report is generated, check if the following parameters meet their acceptable values:

Initial and Final gain DAC settings	The weekly fluctuation between the initial (old) and final (new) gain DAC settings must be no more than 100. If the change exceeds 100, perform a ‘Complete Energy Adjustment’ followed by ‘Stability Test’ as described in Quant’X Technical Manual (Reference.1).
Error (eV)	< 4.0 eV
FWHM (eV)	< 175 eV
Zero Width (eV)	< 100
Peak Count Rate (cps/mA)	The peak count rate output is compared with the previous values. A reduction in counts of greater than 25% might be a sign of X-ray tube aging or stability problems. Contact the service contractor for more comprehensive diagnostics.

10.4 Resolution Test

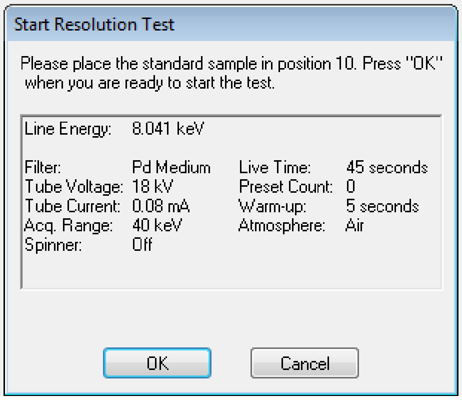
This test verifies the operation of the detector and related circuitry. Copper (Cu) at 8.041 keV is used. Energy Adjustment must be completed prior to this test.

10.4.1 Open up *QuantX* folder and select *Energy Adjustment.qtl >Analyze>Tests>Resolution.*

10.4.2 Place the Cu standard in position 10 and close the lid.

10.4.3 Confirm the set conditions of the test and start the test.

Figure 5: Resolution Test



Start Resolution Test

Please place the standard sample in position 10. Press "OK" when you are ready to start the test.

Line Energy:	8.041 keV		
Filter:	Pd Medium	Live Time:	45 seconds
Tube Voltage:	18 kV	Preset Count:	0
Tube Current:	0.08 mA	Warm-up:	5 seconds
Acq. Range:	40 keV	Atmosphere:	Air
Spinner:	Off		

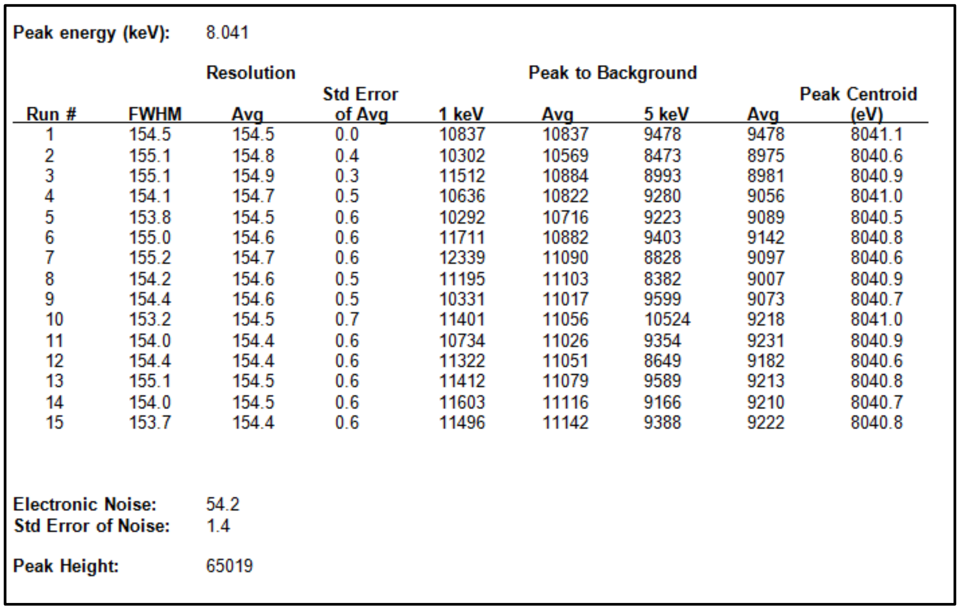
10.4.4 When Resolution Test Results are generated, confirm that:

The average Resolution (eV) for the silicon drift detector (SDD) does not exceed 175.

The average peak-to-background (p/b) values are equal to or greater than: (p/b) at 1 Kev ≥1200
(p/b) at 5 Kev ≥ 400

Note: The resolution (FWHM) is indicative of the detector and its electronics. The peak-to-background ratio is indicative of the detector alone.

Figure 6: Resolution Test Results Example



Peak energy (keV): 8.041

	Resolution			**Peak to Background**				
Run #	**FWHM**	**Avg**	**Std Error of Avg**	**1 keV**	**Avg**	**5 keV**	**Avg**	**Peak Centroid (eV)**
1	154.5	154.5	0.0	10837	10837	9478	9478	8041.1
2	155.1	154.8	0.4	10302	10569	8473	8975	8040.6
3	155.1	154.9	0.3	11512	10884	8993	8981	8040.9
4	154.1	154.7	0.5	10636	10822	9280	9056	8041.0
5	153.8	154.5	0.6	10292	10716	9223	9089	8040.5
6	155.0	154.6	0.6	11711	10882	9403	9142	8040.8
7	155.2	154.7	0.6	12339	11090	8828	9097	8040.6
8	154.2	154.6	0.5	11195	11103	8382	9007	8040.9
9	154.4	154.6	0.5	10331	11017	9599	9073	8040.7
10	153.2	154.5	0.7	11401	11056	10524	9218	8041.0
11	154.0	154.4	0.6	10734	11026	9354	9231	8040.9
12	154.4	154.4	0.6	11322	11051	8649	9182	8040.6
13	155.1	154.5	0.6	11412	11079	9589	9213	8040.8
14	154.0	154.5	0.6	11603	11116	9166	9210	8040.7
15	153.7	154.4	0.6	11496	11142	9388	9222	8040.8

Electronic Noise: 54.2
Std Error of Noise: 1.4

Peak Height: 65019

10.5 Stability Test

Stability test is run semiannually or whenever the system is suspected or known to be unstable. For example, QC standards exceeding limits, anomalous energy calibration results, or failed resolution test. This test is to verify that the X-ray generation and detection subsystems are functioning correctly. This test is usually run overnight and can also be used to monitor system performance as part of a preventive maintenance program.

10.5.1 Place the Cu Kα 8.041 keV disk in tray Position10 in the sample tray.

10.5.2 Open *QuantX* folder and select *Energy Adjustment.qtl >Analyze>Tests>Stability.*

10.5.3 Confirm the set conditions of the stability test and start the test.

Table 4: Stability Test Report Example

Stability Test Report	
Voltage:	20 kV
Current:	0.16 mA
Livetime:	300 sec
Filter:	Pd Medium
Peak Energy	8.041

	Peak		**Peak**	**Peak**	**Total**	**Total**
Run #	**FWHM**	**Centroid**	**Counts**	**RSD**	**Counts**	**RSD**
1	155.9	8042	8913294	0.00%	17324458	0.00%
2	156.1	8042	8916406	0.02%	17335633	0.05%
3	156	8042	8919586	0.04%	17336246	0.04%
24	156.3	8042	8909310	0.05%	17334238	0.03%
25	156	8042	8912523	0.05%	17334597	0.03%
26	156.1	8042	8911821	0.05%	17332579	0.03%
27	156	8042	8914940	0.05%	17323356	0.03%
			Peak RSD	0.04%	**Total RSD**	0.02%

10.5.4 Results

Instability due to changes in the X-ray tube output or peak shift will be detected. Verify that the following criteria are met:

PEAK counts RSD	< 0.23%
TOTAL counts RSD	< 0.20%
FWHM	Maximum value: < 175 eV Deviation: +5 eV
Peak Centroid	Maximum value: 8.041 (if calibrated) Deviation: +3 eV

10.5.5 *SAVE Report* as the *Stability Test.rtf* in *Reports\Stability & Resolution* folder on the hard drive.

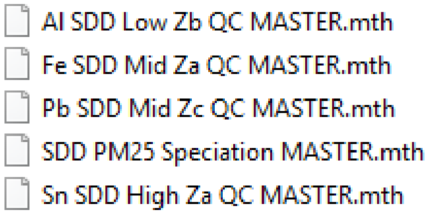
11. Method Calibration

Method calibration is performed annually, followed by a Method Detection Limit (MDL) verification (Section 12). Calibration is also performed when a change in fluorescence, X-ray tube, or detector is made; a serious malfunction occurs requiring significant repairs; or if a control standard result falls outside control limits. See Section 16, QC criteria for Method Calibration.

The peak intensities of the analyte are measured on certified NIST traceable reference materials (Section 8.2.2). All available standards and a blank are used for calibration. Perform linear regression analysis on normalized intensity (cps/mA) verses elemental loading (μg/cm^2) and calculate correlation coefficients. Correlation coefficients must be 0.980 or better for all elements. Calibrate the instrument using the standards that are listed in Appendix A, Table A-2.

11.1 SDD PM2.5 Speciation Method Calibration

11.1.1 There are total of five *MASTER.mth* methods in the *Master Method* folder. These are the templates for all of the working methods. They must not be edited or tampered with. Always make a copy and rename it before making any changes.

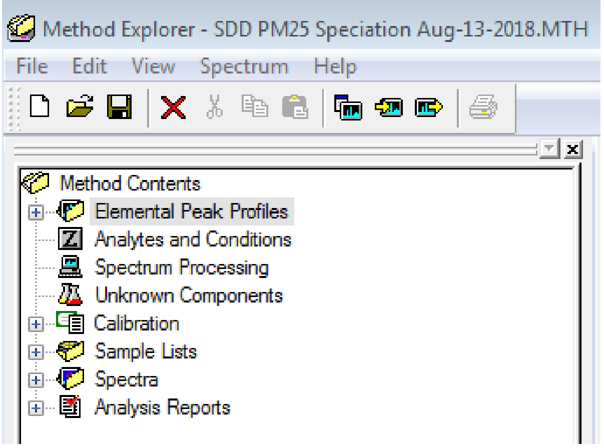


Al SDD Low Zb QC MASTER.mth
Fe SDD Mid Za QC MASTER.mth
Pb SDD Mid Zc QC MASTER.mth
SDD PM25 Speciation MASTER.mth
Sn SDD High Za QC MASTER.mth

11.1.2 The Current *SDD Current Methods* folder will contain all the working/calibrated methods. Rename the copied master method to reflect the date of your calibration process e.g., SDD PM25 Speciation Aug-13-2018.MTH.

11.1.3 Open *Analytes and Condition* under the *Method Explorer* content. Review the list of elements, their grouping and corresponding to acquisition conditions, filter, voltage, and live time settings defined for method calibration. See Section 9.2.1-9.2.4 for the list of analytes and conditions.

Figure 7. Method Explorer



11.1.4 Browse to *Calibration* directory of the *Method Explorer* content and review the list of NIST traceable calibration elements, their concentration units, and their corresponding running conditions to be used during calibration. See table below for full description of method calibration.

Table 5: Calibration Elements

Element	Atomic # Z	Running Condition	Primary E Line Kev	Filter	Voltage kV	Energy Range KeV	Life Time Limit sec
Al	13	Low Zb	Kα 1.487	Cellulose	10	0 – 10	800
Si	14	Low Zb	Kα 1.740	Cellulose	10	0 – 10	800
P	15	Low Zb	Kα 2.015	Cellulose	10	0 – 10	800
S	16	Low Zb	Kα 2.307	Cellulose	10	0 – 10	800
Cl	17	Low Zb	Kα 2.622	Cellulose	10	0 – 10	800
K	19	Low Zb	Kα 3.312	Cellulose	10	0 – 10	800
Ca	20	Low Zb	Kα 3.610	Cellulose	10	0 – 10	800
Ti	22	Mid Za	Kα 4.508	Pd thin	30	0 – 20	400
V	23	Mid Za	Kα 4.949	Pd thin	30	0 – 20	400
Cr	24	Mid Za	Kα 5.411	Pd thin	30	0 – 20	400
Mn	25	Mid Za	Kα 5.895	Pd thin	30	0 – 20	400
Fe	26	Mid Za	Kα 6.400	Pd thin	30	0 – 20	400
Co	27	Mid Za	Kα 6.925	Pd thin	30	0 – 20	400
Ni	28	Mid Za	Kα 7.472	Pd thin	30	0 – 20	400
Cu	29	Mid Zc	Kα 8.041	Pd thick	50	0 – 40	400
Zn	30	Mid Zc	Kα 8.631	Pd thick	50	0 – 40	400
As	33	Mid Zc	Kα 10.532	Pd thick	50	0 – 40	400
Se	34	Mid Zc	Kα 11.210	Pd thick	50	0 – 40	400
Br	35	Mid Zc	Kα 11.907	Pd thick	50	0 – 40	400
Rb	37	Mid Zc	Kα 13.375	Pd thick	50	0 – 40	400
Sr	38	Mid Zc	Kα 14.142	Pd thick	50	0 – 40	400
Y	39	Mid Zc	Kα 14.933	Pd thick	50	0 – 40	400
Mo	42	Mid Zc	Kα 17.443	Pd thick	50	0 – 40	400
Sn	50	High Za	Kα 25.193	Cu thin	50	0 – 40	800
Sb	51	High Za	Kα 26.274	Cu thin	50	0 – 40	800
Ba	56	Mid Za	Lα 4.467	Pd thin	30	0 – 20	400
Hg	80	Mid Zc	Lα 9.987	Pd thick	50	0 – 40	400
Pb	82	Mid Zc	Lα 10.549	Pd thick	50	0 – 40	400

11.1.5 Start the calibration process. Click *Collect* (NOT *Collect All*) to finish calibration spectra.

11.1.6 Load the first tray with 10 calibration standards to their corresponding position as directed in the *Automated Tray* list. Close the lid of the sample chamber and start the acquisition.

11.1.7 When the first tray of samples is finished with acquisition, the *Acquisition Manager* will prompt for the next tray to be loaded and analyzed. Remove the first set of standard materials, load with the second set of calibration standard samples, and proceed with the analysis.

11.1.8 This is repeated for all five trays. When the analysis of the standards is completed, select *Continue* to reprocess the method and to complete the calibration.

11.2 Quality Control (QC) Methods Calibration

11.2.1 There are four copied *QC MASTER.mth* in the *SDD Current Methods* folder that need to be calibrated. These QC methods address one representative element (Al, Fe, Pb and Sn) for each acquisition condition (Low Zb, Mid Za, Mid Zc and High Za).

11.2.2 For each QC Master method, corresponding spectra for each element needs to be exported from the calibrated *SDD PM25 Speciation method* file and then imported into their designated QC master method.

QC Master method	Acquisition Condition	Representative Element	Spectra to be imported from SDD PM25 Speciation method
Al SDD Low Zb QC MASTER.mth	Low Zb	Al	Blank (Low Zb) Al 39.8 14372 Al 43.2 12891
Fe SDD Mid Za QC Master.mth	Mid Za	Fe	Blank (Mid Za) Fe 38.4 4457 Fe 51.7 10613
Pb SDD Mid Zc QC Master.mth	Mid Zc	Pb	Blank (Mid Zc) Pb 18.8 83317 Pb 49.2 11315
Sn SDD High Za QC Master.mth	High Za	Sn	Blank (High Za) Sn 41.8 9813 Sn 47.4 9814

Export: open the most recent *SDD PM25 Speciation method* file and go to the *Spectra* folder under *Method Contents*. On the left side of spectra content, select all 12 spectra and export (*Export Spectrum*) to *the SDD Current Methods* folder.

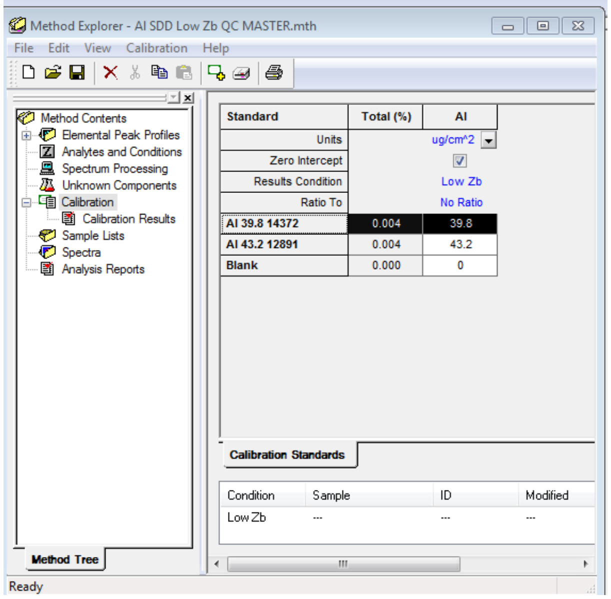
Import: open *Al SDD Low Zb QC MASTER.mth*. Under *Spectra* directory, select Blank (Low Zb) and Al spectra and import into *Al SDD Low Zb QC MASTER.mth*.

11.2.3 Calibration of QC Master.mth:

Go to *Calibration* in the Method tree, highlight Al 39.8 14372 standard on the right pane in the *Calibration Standards* tab. On the bottom, select Low Zb condition, right click mouse, select *Set Spectrum*, and proceed to identify the imported Al standard spectrum. Repeat for each standard.

When all three imported spectra are associated with the appropriate method, press *Calibrate* in the method tool bar and *Continue*. When the calibration results are displayed, save and exit the method.

Figure 8: Method Calibration



Standard	Total (%)	Al
Units		ug/cm^2
Zero Intercept		☑
Results Condition		Low Zb
Ratio To		No Ratio
Al 39.8 14372	0.004	39.8
Al 43.2 12891	0.004	43.2
Blank	0.000	0

Condition	Sample	ID	Modified
Low Zb	---	---	---

11.2.4 Go to the *SDD Current Methods* folder, select *Al SDD Low Zb QC MASTER.mth,* and rename it. Use the same date as in *SDD PM25 Speciation MMM-DD-YYYY.MTH* calibration.

11.2.5 Repeat Section 11.2.2 – 11.2.4 to complete the calibration for all four QC Master methods.

12. MDL Analysis

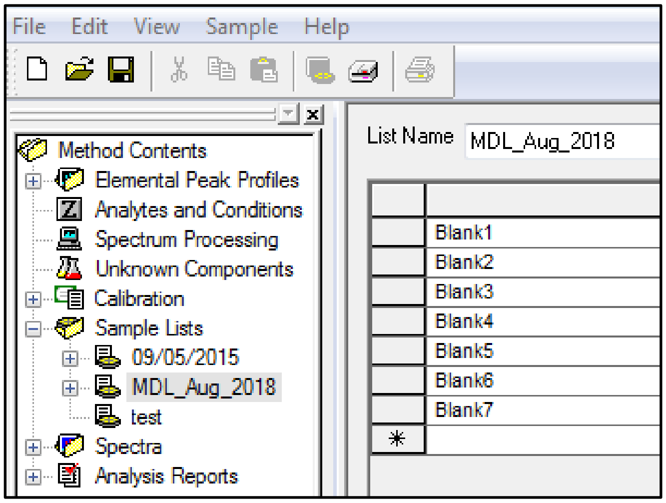
12.1 MDL Analysis of Calibrated SDD PM25 Speciation Method

12.1.1 Open the most recently calibrated *SDD PM25 Speciation method* file.

12.1.2 Select *Sample Lists* and *Add Sample List*. A *New Sample List* will appear with a time stamp. Rename the *New Sample List* to *MDL_YYYY* or equivalent.

12.1.3 List the names of the blank sample filters (Blank1, Blank2 …Blank7) in the sample list and save.

Figure 9: MDL Sample List



List Name MDL_Aug_2018

	Blank1
	Blank2
	Blank3
	Blank4
	Blank5
	Blank6
	Blank7
✳	

12.1.4 Notice that each blank sample is analyzed for all four acquiring conditions as described in the method. Press *Analyze* and *Continue* to start spectrum acquisition manager.

12.1.5 Select minimum of seven Teflon filters (preferably from different lot #s) and load the filters into the sample tray according to the position number listed in the automated tray list (usually position 1 through 7). Close the sample chamber lid cover.

12.1.6 Start *Acquisition*. The analysis will take several hours. All *MDL_YYYY* spectra is automatically acquired and saved in the most recent *SDD PM25 Speciation method* file.

12.1.7 When MDL analysis is complete, the *Acquisition Manager* will prompt to *Continue* to save the acquired spectra and to generate Analysis Report.

12.1.8 Close *Acquisition Manager* and transfer the Blank samples back to original sample containers.

The EDXRF analytical method supports several programs. To distinguish the samples between programs and provide separate records in LIMS, the fully calibrated and MDL verified *SDD PM25 Speciation method* file is copied, and the copy is renamed in a manner that properly denotes the additional program.

12.2 MDL Calculation of Calibrated SDD Speciation Method

The MDL is defined as the minimum net peak intensity expressed in concentration unit (ng/cm^2) equal to 3 times the square root of the background intensity for a specified counting time. This minimum net peak intensity is 3 standard counting errors (σ) of a set of measurements of the background intensity under the trace element peak giving the 99.7% confidence that an analyte can be detected and its concentration is above zero.

Calculation of detection limits follows the EDXRF industry and scientific community standard for MDL determination and is also referenced in Section 19.1.

The calculation uses Poisson probability distribution which expresses the probability of a given number of events (counts) occurring in a fixed interval of time (livetime ts) and space (defined Region of Interest-ROI) if these events occur with a known average rate and independently of the time since the last event:

$$MDL = \left[3 \times Cstd \times \sqrt{B}\right] \div Istd$$

Where,

$Cstd$ - Concentration of standard (ng/cm^2)

$Istd$ - Net peak counts from element standard calibration:

$$Istd = \left[\frac{cps}{mA}\right] x\ ts$$

$\left[\frac{cps}{mA}\right]$= normalized intensity of calibration standard

ts = livetime in *seconds* of the analysis for a given condition

$\sqrt{B}$ - Total counts from blank filter = $[Ipeak + Ibkg] \times ts$

$Ipeak$ + $Ibkg$ are peak and background intensities for the corresponding element obtained from MDL analysis

Sample calculation for Aluminum (Al) MDL from Blank 1:

$Cstd$	43200 $ng/cm2$
ts	800 sec

$Istd$	$1097.64\frac{cps}{mA} \times 800\ sec$
$Ipeak$	$1.0\,\frac{cps}{mA}$
$Ibkg$	$2.0\,\frac{cps}{mA}$
B	$[Ipeak + Ibkg] \times 800\ sec$

$$MDL_{Al} = 3 \times 43200 \times [(1.0 + 2.0) \times 800]^{1/2} / (1097.64 \times 800) = 7.23$$

The MDLs are represented as 3σ of the background and peak counting statistic uncertainties and do not include uncertainties contributed by the instrument, calibration and systematic errors. They are defined as the statistical limits for this method.

Obtain seven MDL values for each element using seven Blank filters. The average of the seven MDL values must not exceed the Reporting Limit (RL) for that element.

13. Sample Analysis

PM2.5 samples are stored in a 4°C refrigerator after gravimetric analysis has been completed and mass loading recorded in LIMS. There is no holding time requirement for these samples and are left in cold storage until scheduled for EDXRF analysis. PM2.5 samples scheduled for EDXRF analysis are removed from cold storage and are allowed to come to room temperature.

With a 10-tray auto sampler, batches of 10 or less are organized for EDXRF analysis.

13.1 A typical analytical run is performed as follows:

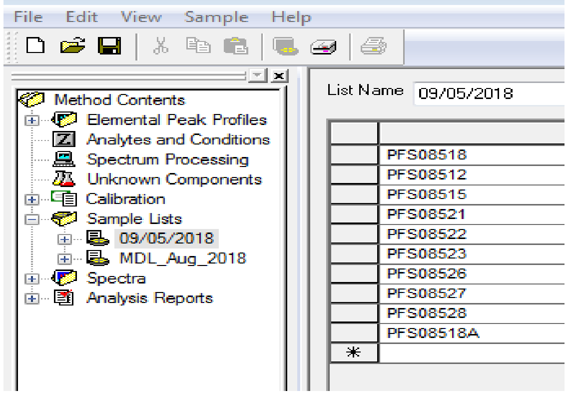
Four QC Standards (Al, Fe, Pb, Sn)
Set of sample filters (no more than 10)
Sample Replicate, on first sample analyzed
Filter Blank (at least monthly, for each program)
Four Closing QC Standards (Al, Fe, Pb, Sn)

13.2 Generate a Method Tray List for a sample batch. Open the most recently calibrated *SDD PM25 Speciation method* file.

13.3 Under *Method Content* > *Sample Lists,* create a new sample list. Click on *Add Sample List* icon in the method tool bar, a *New Sample List* will appear with a time stamp. Rename the *New Sample List* to MM/DD/YYYY notation (current analysis date).

13.4 Double click on the new sample list and fill the list with samples to be analyzed. Enter sample IDs including a replicate analysis of a sample in batch by using suffix A to the barcode.

Figure 10: Sample Analysis List



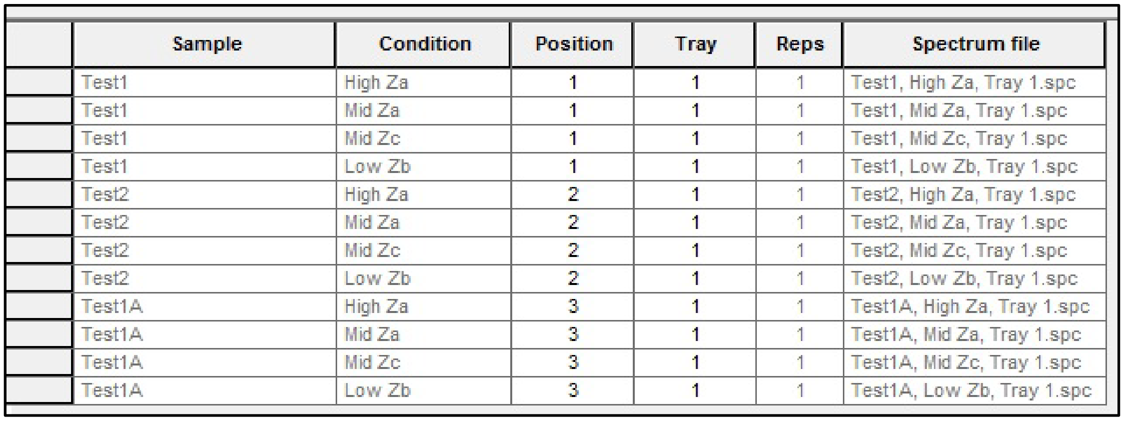
List Name 09/05/2018

PFS08518
PFS08512
PFS08515
PFS08521
PFS08522
PFS08523
PFS08526
PFS08527
PFS08528
PFS08518A

13.5 Click *Analyze* and *Collect All* to start the spectrum acquisition and to acquire missing spectra > generates automated tray list.

13.6 Following the entry for the last sample as replicate in the tray list, enter Position ‘1’ and edit number ‘2’ in the Tray list column. See the table below for the method tray list information.

Figure 11: Method Tray List



	Sample	Condition	Position	Tray	Reps	Spectrum file
	Test1	High Za	1	1	1	Test1, High Za, Tray 1.spc
	Test1	Mid Za	1	1	1	Test1, Mid Za, Tray 1.spc
	Test1	Mid Zc	1	1	1	Test1, Mid Zc, Tray 1.spc
	Test1	Low Zb	1	1	1	Test1, Low Zb, Tray 1.spc
	Test2	High Za	2	1	1	Test2, High Za, Tray 1.spc
	Test2	Mid Za	2	1	1	Test2, Mid Za, Tray 1.spc
	Test2	Mid Zc	2	1	1	Test2, Mid Zc, Tray 1.spc
	Test2	Low Zb	2	1	1	Test2, Low Zb, Tray 1.spc
	Test1A	High Za	3	1	1	Test1A, High Za, Tray 1.spc
	Test1A	Mid Za	3	1	1	Test1A, Mid Za, Tray 1.spc
	Test1A	Mid Zc	3	1	1	Test1A, Mid Zc, Tray 1.spc
	Test1A	Low Zb	3	1	1	Test1A, Low Zb, Tray 1.spc

13.7 Load filters into the sample tray according to the Position number listed in the method tray list.

13.7.1 Slowly and carefully raise the sample chamber cover.

13.7.2 Before any filters are loaded into the sample tray, inspect the sample rings for proper alignment and seating in the sample tray.

13.7.3 Place filters in their respective sample holders face-side down. If a filter is stuck in the Petri container, gently tap the sides of the Petri dish to gently let the filter drop into the sample ring face down. If necessary, forceps can be used to carefully remove the filter.

13.7.4 Carefully place retainer ring onto the filter.

13.7.5 Continue to load samples until entire batch is loaded.

13.7.6 Slowly and carefully lower and close the sample chamber cover.

13.8 Record the samples, replicates, and filter Position numbers in EDXRF logbook.

13.9 *Start Acquisition* to begin analysis. Spectra is automatically acquired and saved in the method file associated with the filter type.

13.10 After acquisition is complete for Tray 1, a dialog box prompts to ensure that Tray 2 is in place. Click OK and acquisition continues for a replicate sample.

13.11 After acquisition for the replicate sample is complete, an analysis report is displayed in the *Acquisition Manager* window.

13.12 Close *Acquisition Manager* and transfer the samples back to original Petri dish containers.

14. Data Management

Data management involves samples logged into LIMS, create summary *.csv files, transfer and review of PM EDXRF quantitative elemental analysis to LIMS, documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, and archiving of PM filters. Records of sample analysis and maintenance are to be documented in a logbook and kept with the instrumentation at all times.

14.1 Data analysis is automatically performed and results are imported into the method file associated with the type of filter analyzed. Further processing of the result file is necessary for LIMSLink to transfer the data into LIMS.

14.1.1 Generate a comma separated value (csv) file for each batch of samples analyzed, as well as the associated QC standards.

14.1.2 Save the Excel file as a *.csv file with the correct LIMS format prefix, such that the method file will be recognized properly by LIMS.

14.1.3 Copy the *.csv file generated the *C:\QUANT'X\Reports\CSV* Files.

14.1.4 Review the results; add QC samples (replicate and controls) to LIMS, then send results to LIMS (successful transfer to LIMS is when the LIMS status is “Complete”).

14.2 Generate a Report on the completed EDXRF data analysis including the following components:

14.2.1 Data Report Cover Sheet – includes the analytical method, sampling period, and peer review and Management signatures.

14.2.2 Summary Results report from LIMS on speciation of elemental concentration (ng/m^3) for all the PM filter samples analyzed by EDXRF during a given time period (report generated from LIMS).

14.2.3 XRF Data transfers (LIMSLink) – record of PM samples that have been analyzed by EDXRF (including all the QC standards and replicate samples analysis) and have been transferred into LIMS (*.csv transfers) for a specified time period.

14.2.4 QC summary reports from LIMS.

14.2.5 QC Standard Tables for all representative QC standards that were run during the specified time period.

14.2.6 EDXRF Calibration Verification – last calibration date of the method and the calibration results for each element.

14.2.7 Control chart, bracketing the time period during which the samples were analyzed.

14.2.8 IC sulfur (as sulfate) versus EDXRF Sulfur (sulfur) report – generated from LIMS. Specific to the PM2.5 Speciation program. This is optional, though it is a useful comparison of comparable data between two different analyses.

14.2.9 The complete Monthly Report package is submitted for peer review, and management review and approval.

15. Calculations

15.1 Conversion of Area Metric Units to Aerometric Units

The following calculations are used to determine the elemental concentrations in various formats, as determined by the data user. Raw concentration values are given as ng/cm^2.

Elemental values are converted to nanogram per filter by:

$$\frac{\text{ng}}{\text{filter}} = \left(\frac{\text{ng}}{\text{area in cm}^2}\right) \text{x (filter exposure area in cm}^2\text{)}$$

To determine ng/m^3:

$$\frac{\text{ng}}{\text{m}^3} = \frac{\frac{\text{ng}}{\text{filter}}}{\text{total air volume in m}^3}$$

Or

$$\frac{\text{ng}}{\text{m}^3} = \frac{\text{ng}}{(\text{area in cm}^2)} \text{ x} \frac{(\text{filter exposure area in cm}^2)}{(\text{total air volume in m}^3)}$$

15.2 Replicates Relative Percent Difference (RPD)

$$RPD = \frac{|\,(Y - X)\,|}{((Y + X)/2)} \times 100$$

Where: *X* = sample result and *Y*= replicate result

16. Quality Control

Table 6: Quality Control Criteria

	QC	Acceptance Criteria	Corrective Action
1	Method Calibration		
	Method calibration is performed annually. For each element, use one or two NIST standards (if available) and a blank.	Perform linear regression analysis on intensity (cps/mA) verses elemental loading (µg/cm^2) and calculate correlation coefficients. Correlation coefficients r must be $\geq$ 0.980 or better for all elements.	Re-run the calibration analysis. No sample analysis is performed until the issue is resolved. Evaluate ‘Energy Adjustment’ and do the overnight ‘Stability Test’. Contact the service representative of the XRF instrument to diagnose the problem.
2	Filter Blanks		

	QC	Acceptance Criteria	Corrective Action
	Filter Blank QC is run at least monthly for each program.	QC limit is less than 2x RL for each element.	Reanalyze sample if a blank result is outside acceptance criteria. Refer to the NLB Laboratory Quality Control Manual for blank corrective action criteria.
3	Field Blanks		
		QC limit for field blank is less than 2x RL of each element.	Field blank results are valid and reported. Notify the site operator or program liaison if more than half of reported analytes exceed 2x RL.
4	QC Standards		
	Analyze control NIST standards before and after every sample batch.	QC NIST Standards: Al5327: 38.8 µg/cm^2 (low Zb) Fe11312: 42.2 µg/cm^2 (mid Za) Pb4475: 43.0 µg/cm^2 (mid Zc) Sn5345: 44.0 µg/cm^2 (high Za) The allowable criteria are ±5.0% for the warning limits and ±7.5% for control limits from the established mean value.	If the results exceed the criteria, the samples in the associated batch must be reanalyzed. Control results outside the control limits require instrument re-calibration and re-evaluation of the system until the controls are acceptable. Control results outside the warning limits and within the control limits require system investigation and correction of any identified problems with instrument performance.
5	Replicates		
	Replicates are run in every sample batch or at the frequency of > 10% of all the samples analyzed.	The RPD between the elemental concentrations must meet the criteria as follows: [Samples] ≤ 20x RL with RPD < 25% [Samples] > 20x RL with RPD < 10%. [Samples] < 5x RL are not reported	If an analyte is outside criteria, then re-analyze samples in the associated batch. If RPD is outside criteria, then affected analytes are invalid.
6	Annual MDL Verification		
	The MDLs are represented as 3σ of the background	The average of the seven MDL values must not exceed the RL for that element.	Perform DAC calibration to address the detector, X-ray tube or DAC electronic module malfunction. Notify

	QC	Acceptance Criteria	Corrective Action
	and peak counting statistic.		Unity Lab Services for assistance.
7	Filter Sample		
	Inspect every PM sample before analysis	Samples must have uniform loading across the sample area. Refer to SOP MLD055 for further filter inspection criteria such as signs of damage, pinholes, scuffs, scratches, or other imperfections, or any obvious discoloration that may indicate contamination.	Damaged samples are invalidated for EDXRF analysis. Document in LIMS and the laboratory notebook.

17. Periodic Maintenance

The maintenance procedures prescribed are preventative in nature and minimizes operational down-time.

17.1 Before Sample Batch Analysis:

17.1.1 Spectrometer Manager Status (Section 10.2.2).

17.1.2 Energy Adjustment (Section 10.3).

17.2 Quarterly:

17.2.1 Resolution Test (Section 10.4).

17.2.2 Check the vacuum pump oil level (middle level of sight glass).

17.2.3 Check/clean the air filters on the right side panel.

17.3 Semiannually:

17.3.1 Stability test (Section 10.5).

17.4 Annually:

17.4.1 Annual Preventative Maintenance Service. This is performed by an outside vendor and includes vacuum pump maintenance, safety feature checks, cleaning, and analysis of instrument resolution and stability.

17.4.2 Method Calibration (Section 11).

17.4.3 MDL Verification (Section 12).

18. Revision History

Table 7: Revision History

	Date	Updated Revision	Original Procedure
1	**Description**: **SOP MLD034 Revision Number unknown**		
	Approved on June 17, 1991	Note: Revisions were not recorded.	
2	**Description**: **SOP MLD034 1.1**		
	Approved on June 9, 1992	Note: Revisions were not recorded.	
3	**Description**: **SOP MLD034 2.0**		
	Approved on January 31, 2006	Note: Revisions were not recorded.	
4	**Description**: **SOP MLD034 3.0**		
	November 15, 2022	Updates based on new instrumentation, conformance to QC Manual (Reference 19.11), and SOP format requirements (Reference 19.16). Thermo Quant'X-EDXRF Spectrometer, which no longer requires liquid nitrogen. Added Filter Blanks as part of QC. Added Sections: Acronyms, Definitions, Personnel Qualifications, Methods Analytical Conditions, Analytical Tests for Spectrometer, Method Calibration, MDL Analysis, Calculations, and Revision History.	Thermo QuanX-EC XRF Spectrometer.

19. References

19.1 Thermo Scientific, *Quant'X Technical Manual*, Revision A (March 2015).

19.2 Thermo Scientific, WinTrace Software User Guide, Revision A (April 2015).

19.3 Thermo Scientific, *Quant'X Technical Manual*, AA83826 Revision 3 (March 2018).

19.4 Thermo Scientific, WinTrace Software User Guide, AA83806 Revision 1 (July 2017).

19.5 U.S. Environmental Protection Agency, June 1999. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Compendium Method IO-3.3, *Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy,* EPA/625/R-96/010a, Office of Research and Development.

19.6 Standard Operating Procedure for Preparation of Northern Laboratory Branch's Standard Operating Procedures. MLD076 Revision 1.0. December 30, 2021 (or current).

19.7 Bertin, E.P., *Principles and Practice of X-Ray Spectrometric Analysis*, New York: Plenum Press, 1975.

19.8 Birks, L.S., *X-Ray Spectrochemical Analysis*, New York: Interscience Publishers, 1969.

19.9 40 CFR, Part 50, Appendix L; Reference Method for the Determination of Fine Particulate Matter as PM2.5 in the Atmosphere; U.S. Environmental Protection Agency, September 2013.

19.10 40 CFR, Part 50, Appendix J; Reference Method for the Determination of Particulate Matter as PM10 in the Atmosphere; U.S. Environmental Protection Agency, September 2013.

19.11 CARB NLB Laboratory Quality Control Manual, Revision 5.0, December 7, 2021 (or current).

19.12 CARB, "NLB Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street," November 2021 (or, current version)

19.13 CARB, "Radiation Protection Program, AP# BMB-21-005," July 16, 2021

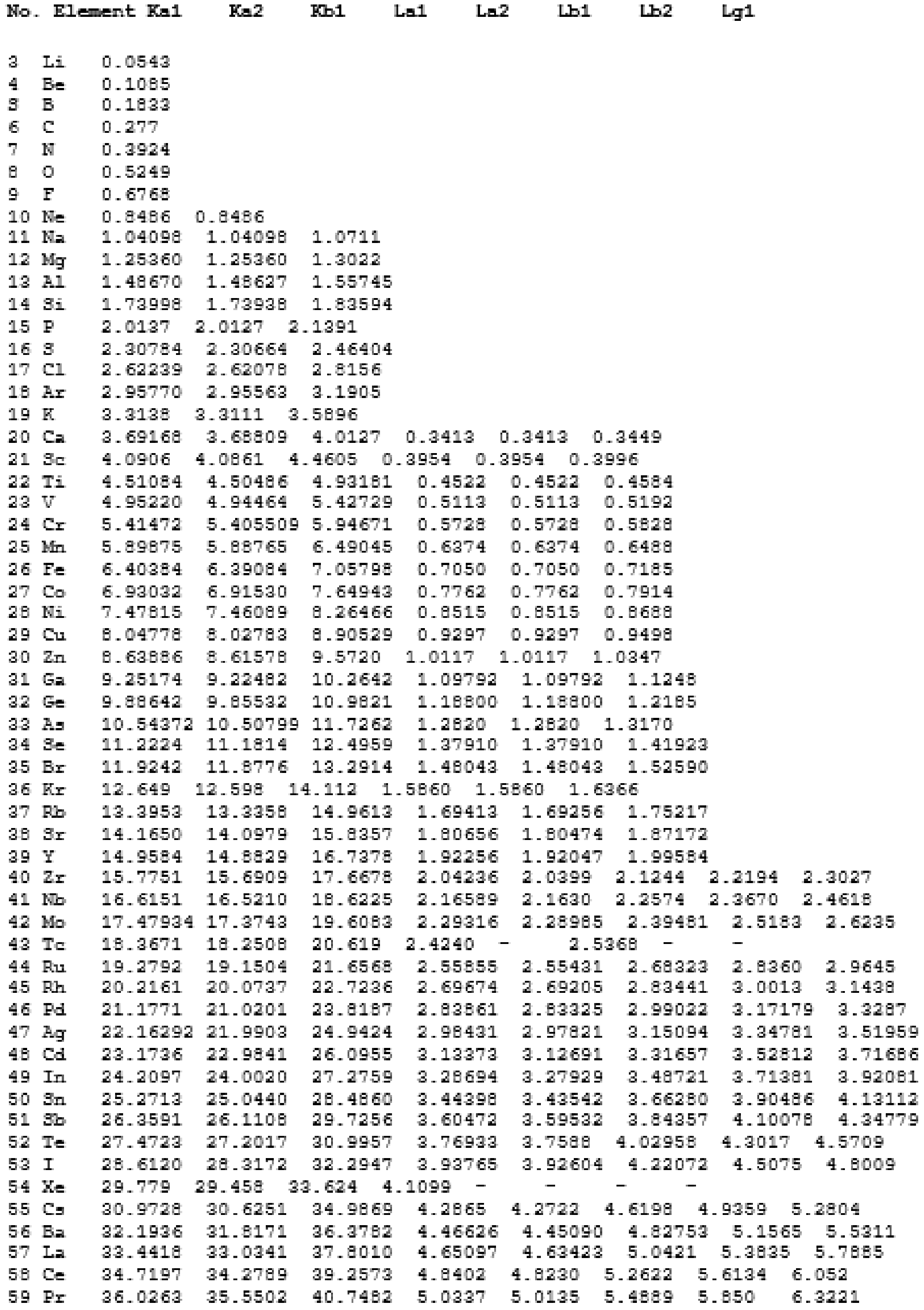
19.14 Title 40, Chapter 1, Subchapter C, Part 58, Subpart B, Code of Federal Regulations, "Monitoring Network." U.S. Environmental Protection Agency, March 28, 2016.

19.15 U.S. EPA PM Sampling Schedule, https://www.epa.gov/amtic/sampling-schedule-calendar

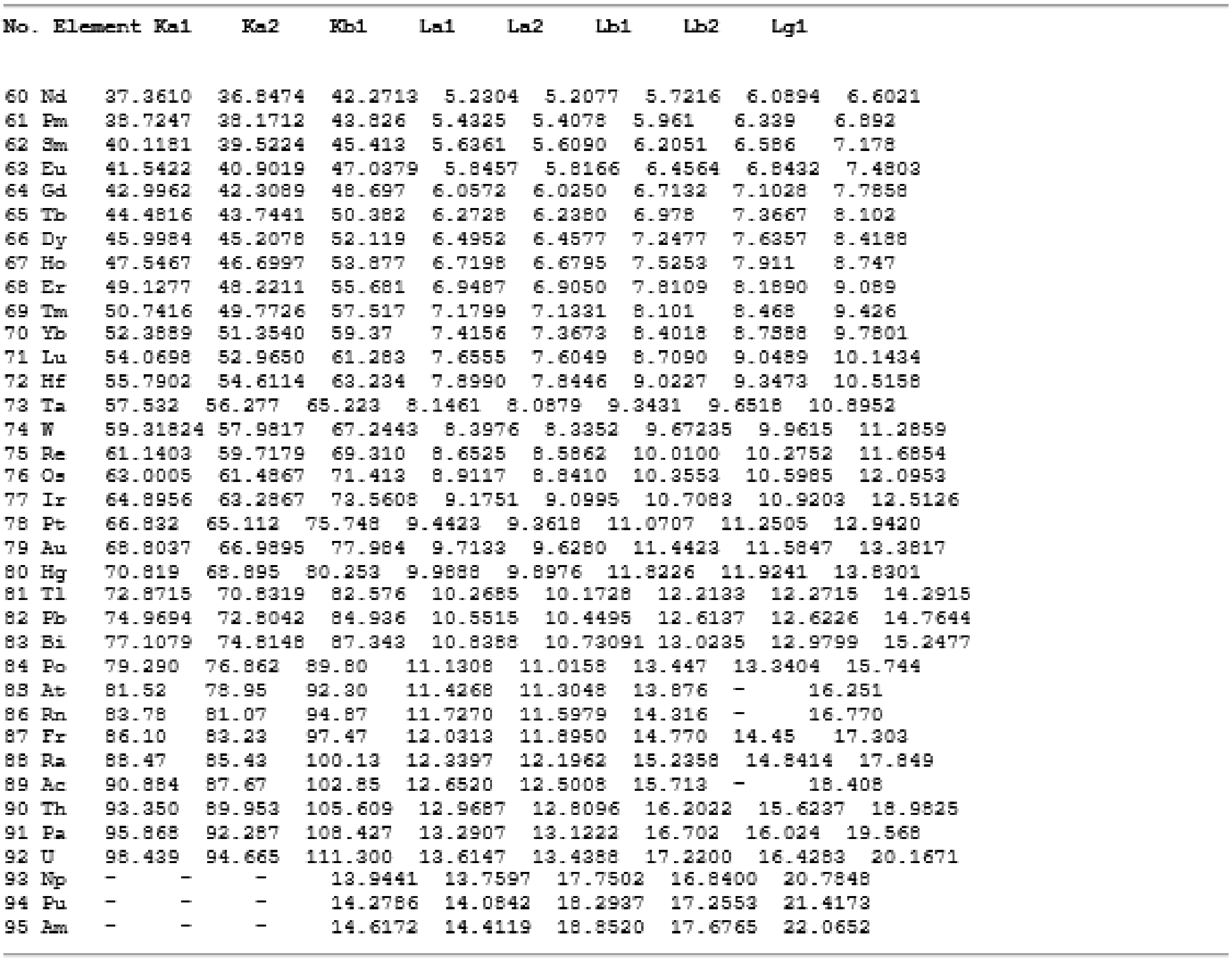
19.16 Standard Operating Procedure for the Determination of PM2.5 Mass and PM Coarse Mass by Gravimetric Analysis, MLD055 Rev. 2.0, April 13, 2022 (or current).

Appendix A

TABLE A-1: X-Ray Emission Lines - *K*-level and *L*-level emissionlines in KeV



No.	Element	Ka1	Ka2	Kb1	La1	La2	Lb1	Lb2	Lg1
3	Li	0.0543							
4	Be	0.1085							
5	B	0.1833							
6	C	0.277							
7	N	0.3924							
8	O	0.5249							
9	F	0.6768							
10	Ne	0.8486	0.8486						
11	Na	1.04098	1.04098	1.0711					
12	Mg	1.25360	1.25360	1.3022					
13	Al	1.48670	1.48627	1.55745					
14	Si	1.73998	1.73938	1.83594					
15	P	2.0137	2.0127	2.1391					
16	S	2.30784	2.30664	2.46404					
17	Cl	2.62239	2.62078	2.8156					
18	Ar	2.95770	2.95563	3.1905					
19	K	3.3138	3.3111	3.5896					
20	Ca	3.69168	3.68809	4.0127	0.3413	0.3413	0.3449		
21	Sc	4.0906	4.0861	4.4605	0.3954	0.3954	0.3996		
22	Ti	4.51084	4.50486	4.93181	0.4522	0.4522	0.4584		
23	V	4.95220	4.94464	5.42729	0.5113	0.5113	0.5192		
24	Cr	5.41472	5.405509	5.94671	0.5728	0.5728	0.5828		
25	Mn	5.89875	5.88765	6.49045	0.6374	0.6374	0.6488		
26	Fe	6.40384	6.39084	7.05798	0.7050	0.7050	0.7185		
27	Co	6.93032	6.91530	7.64943	0.7762	0.7762	0.7914		
28	Ni	7.47815	7.46089	8.26466	0.8515	0.8515	0.8688		
29	Cu	8.04778	8.02783	8.90529	0.9297	0.9297	0.9498		
30	Zn	8.63886	8.61578	9.5720	1.0117	1.0117	1.0347		
31	Ga	9.25174	9.22482	10.2642	1.09792	1.09792	1.1248		
32	Ge	9.88642	9.85532	10.9821	1.18800	1.18800	1.2185		
33	As	10.54372	10.50799	11.7262	1.2820	1.2820	1.3170		
34	Se	11.2224	11.1814	12.4959	1.37910	1.37910	1.41923		
35	Br	11.9242	11.8776	13.2914	1.48043	1.48043	1.52590		
36	Kr	12.649	12.598	14.112	1.5860	1.5860	1.6366		
37	Rb	13.3953	13.3358	14.9613	1.69413	1.69256	1.75217		
38	Sr	14.1650	14.0979	15.8357	1.80656	1.80474	1.87172		
39	Y	14.9584	14.8829	16.7378	1.92256	1.92047	1.99584		
40	Zr	15.7751	15.6909	17.6678	2.04236	2.0399	2.1244	2.2194	2.3027
41	Nb	16.6151	16.5210	18.6225	2.16589	2.1630	2.2574	2.3670	2.4618
42	Mo	17.47934	17.3743	19.6083	2.29316	2.28985	2.39481	2.5183	2.6235
43	Tc	18.3671	18.2508	20.619	2.4240	-	2.5368	-	-
44	Ru	19.2792	19.1504	21.6568	2.55855	2.55431	2.68323	2.8360	2.9645
45	Rh	20.2161	20.0737	22.7236	2.69674	2.69205	2.83441	3.0013	3.1438
46	Pd	21.1771	21.0201	23.8187	2.83861	2.83325	2.99022	3.17179	3.3287
47	Ag	22.16292	21.9903	24.9424	2.98431	2.97821	3.15094	3.34781	3.51959
48	Cd	23.1736	22.9841	26.0955	3.13373	3.12691	3.31657	3.52812	3.71686
49	In	24.2097	24.0020	27.2759	3.28694	3.27929	3.48721	3.71381	3.92081
50	Sn	25.2713	25.0440	28.4860	3.44398	3.43542	3.66280	3.90486	4.13112
51	Sb	26.3591	26.1108	29.7256	3.60472	3.59532	3.84357	4.10078	4.34779
52	Te	27.4723	27.2017	30.9957	3.76933	3.7588	4.02958	4.3017	4.5709
53	I	28.6120	28.3172	32.2947	3.93765	3.92604	4.22072	4.5075	4.8009
54	Xe	29.779	29.458	33.624	4.1099	-	-	-	-
55	Cs	30.9728	30.6251	34.9869	4.2865	4.2722	4.6198	4.9359	5.2804
56	Ba	32.1936	31.8171	36.3782	4.46626	4.45090	4.82753	5.1565	5.5311
57	La	33.4418	33.0341	37.8010	4.65097	4.63423	5.0421	5.3835	5.7885
58	Ce	34.7197	34.2789	39.2573	4.8402	4.8230	5.2622	5.6134	6.052
59	Pr	36.0263	35.5502	40.7482	5.0337	5.0135	5.4889	5.850	6.3221



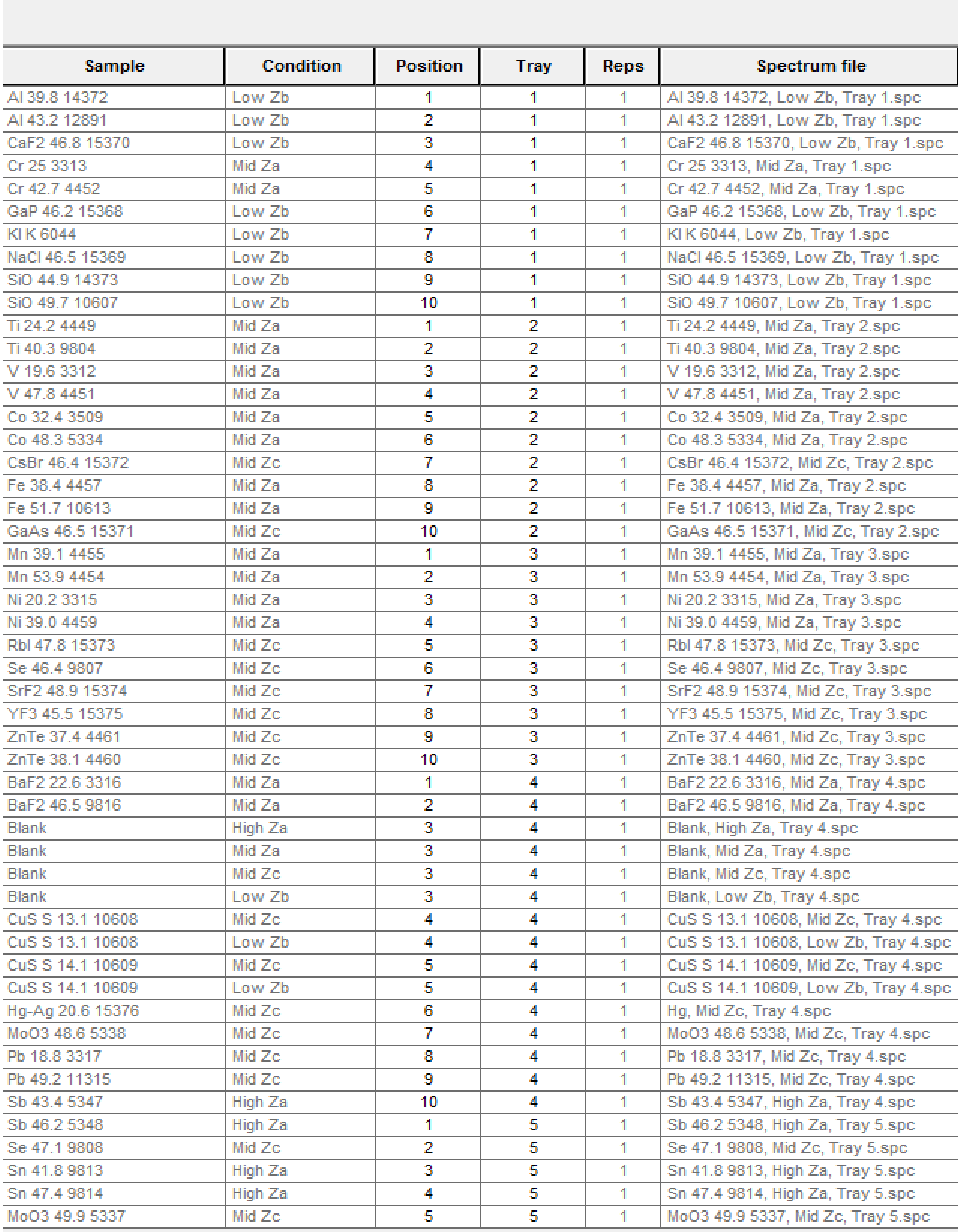
No.	Element	Ka1	Ka2	Kb1	La1	La2	Lb1	Lb2	Lg1
60	Nd	37.3610	36.8474	42.2713	5.2304	5.2077	5.7216	6.0894	6.6021
61	Pm	38.7247	38.1712	43.826	5.4325	5.4078	5.961	6.339	6.892
62	Sm	40.1181	39.5224	45.413	5.6361	5.6090	6.2051	6.586	7.178
63	Eu	41.5422	40.9019	47.0379	5.8457	5.8166	6.4564	6.8432	7.4803
64	Gd	42.9962	42.3089	48.697	6.0572	6.0250	6.7132	7.1028	7.7858
65	Tb	44.4816	43.7441	50.382	6.2728	6.2380	6.978	7.3667	8.102
66	Dy	45.9984	45.2078	52.119	6.4952	6.4577	7.2477	7.6357	8.4188
67	Ho	47.5467	46.6997	53.877	6.7198	6.6795	7.5253	7.911	8.747
68	Er	49.1277	48.2211	55.681	6.9487	6.9050	7.8109	8.1890	9.089
69	Tm	50.7416	49.7726	57.517	7.1799	7.1331	8.101	8.468	9.426
70	Yb	52.3889	51.3540	59.37	7.4156	7.3673	8.4018	8.7588	9.7801
71	Lu	54.0698	52.9650	61.283	7.6555	7.6049	8.7090	9.0489	10.1434
72	Hf	55.7902	54.6114	63.234	7.8990	7.8446	9.0227	9.3473	10.5158
73	Ta	57.532	56.277	65.223	8.1461	8.0879	9.3431	9.6518	10.8952
74	W	59.31824	57.9817	67.2443	8.3976	8.3352	9.67235	9.9615	11.2859
75	Re	61.1403	59.7179	69.310	8.6525	8.5862	10.0100	10.2752	11.6854
76	Os	63.0005	61.4867	71.413	8.9117	8.8410	10.3553	10.5985	12.0953
77	Ir	64.8956	63.2867	73.5608	9.1751	9.0995	10.7083	10.9203	12.5126
78	Pt	66.832	65.112	75.748	9.4423	9.3618	11.0707	11.2505	12.9420
79	Au	68.8037	66.9895	77.984	9.7133	9.6280	11.4423	11.5847	13.3817
80	Hg	70.819	68.895	80.253	9.9888	9.8976	11.8226	11.9241	13.8301
81	Tl	72.8715	70.8319	82.576	10.2685	10.1728	12.2133	12.2715	14.2915
82	Pb	74.9694	72.8042	84.936	10.5515	10.4495	12.6137	12.6226	14.7644
83	Bi	77.1079	74.8148	87.343	10.8388	10.73091	13.0235	12.9799	15.2477
84	Po	79.290	76.862	89.80	11.1308	11.0158	13.447	13.3404	15.744
85	At	81.52	78.95	92.30	11.4268	11.3048	13.876	-	16.251
86	Rn	83.78	81.07	94.87	11.7270	11.5979	14.316	-	16.770
87	Fr	86.10	83.23	97.47	12.0313	11.8950	14.770	14.45	17.303
88	Ra	88.47	85.43	100.13	12.3397	12.1962	15.2358	14.8414	17.849
89	Ac	90.884	87.67	102.85	12.6520	12.5008	15.713	-	18.408
90	Th	93.350	89.953	105.609	12.9687	12.8096	16.2022	15.6237	18.9825
91	Pa	95.868	92.287	108.427	13.2907	13.1222	16.702	16.024	19.568
92	U	98.439	94.665	111.300	13.6147	13.4388	17.2200	16.4283	20.1671
93	Np	-	-	-	13.9441	13.7597	17.7502	16.8400	20.7848
94	Pu	-	-	-	14.2786	14.0842	18.2937	17.2553	21.4173
95	Am	-	-	-	14.6172	14.4119	18.8520	17.6765	22.0652

Values are from J. A. Bearden, "X-Ray Wavelengths", *Review of Modern Physics*, (January 1967) pp. 86-99.

TABLE A-2: NIST Calibration Standards

Element	ID	ug/cm^2	Element	ID	ug/cm^2
Al	*Al 14372*	39.8	Ni	*Ni 4459*	39
Al	*Al 12891*	43.2	Cu	*CuS 10608*	41.6
Si	*SiO 14373*	28.6	Cu	*CuS 10609*	42.7
Si	*SiO 10607*	31.7	Zn	*ZnTe 4461*	12.7
P	*GaP 15368*	15.4	Zn	*ZnTe 4460*	12.9
S	*CuS 10608*	13.1	As	*GaAs 15371*	33.8
S	*CuS 10609*	14.1	Se	*Se 9807*	46.4
Cl	*NaCl 15369*	28.2	Se	*Se 9808*	47.1
K	*KI 6044*	11.6	Br	*CsBr 15372*	17.4
K	*KI 6045*	12.3	Rb	*RbI 15373*	19.2
Ca	*CaF2 15370*	24	Sr	*SrF2 15374*	34.1
Ti	*Ti 4449*	24.2	Y	*YF3 15375*	27.7
Ti	*Ti 9804*	40.3	Mo	*MoO3 5338*	32.4
V	*V 3312*	19.6	Mo	*MoO3 5337*	33.3
V	*V 4451*	47.8	Sn	*Sn 9813*	41.8
Cr	*Cr 3313*	25	Sn	*Sn 9814*	47.4
Cr	*Cr 4452*	42.7	Sb	*Sb 5347*	43.4
Mn	*Mn 4455*	39.1	Sb	*Sb 5348*	46.2
Mn	*Mn 4454*	53.9	Ba	*BaF2 3316*	17.7
Fe	*Fe 4457*	38.4	Ba	*BaF2 9816*	36.4
Fe	*Fe 10613*	51.7	Hg	*HgAg 15376*	20.6
Co	*Co 3509*	32.4	Pb	*Pb 3317*	18.8
Co	*Co 5334*	48.3	Pb	*Pb 11315*	49.2
Ni	*Ni 3315*	20.2	-	-	-

TABLE A-3: Calibration Sequence



Sample	Condition	Position	Tray	Reps	Spectrum file
Al 39.8 14372	Low Zb	1	1	1	Al 39.8 14372, Low Zb, Tray 1.spc
Al 43.2 12891	Low Zb	2	1	1	Al 43.2 12891, Low Zb, Tray 1.spc
CaF2 46.8 15370	Low Zb	3	1	1	CaF2 46.8 15370, Low Zb, Tray 1.spc
Cr 25 3313	Mid Za	4	1	1	Cr 25 3313, Mid Za, Tray 1.spc
Cr 42.7 4452	Mid Za	5	1	1	Cr 42.7 4452, Mid Za, Tray 1.spc
GaP 46.2 15368	Low Zb	6	1	1	GaP 46.2 15368, Low Zb, Tray 1.spc
KI K 6044	Low Zb	7	1	1	KI K 6044, Low Zb, Tray 1.spc
NaCl 46.5 15369	Low Zb	8	1	1	NaCl 46.5 15369, Low Zb, Tray 1.spc
SiO 44.9 14373	Low Zb	9	1	1	SiO 44.9 14373, Low Zb, Tray 1.spc
SiO 49.7 10607	Low Zb	10	1	1	SiO 49.7 10607, Low Zb, Tray 1.spc
Ti 24.2 4449	Mid Za	1	2	1	Ti 24.2 4449, Mid Za, Tray 2.spc
Ti 40.3 9804	Mid Za	2	2	1	Ti 40.3 9804, Mid Za, Tray 2.spc
V 19.6 3312	Mid Za	3	2	1	V 19.6 3312, Mid Za, Tray 2.spc
V 47.8 4451	Mid Za	4	2	1	V 47.8 4451, Mid Za, Tray 2.spc
Co 32.4 3509	Mid Za	5	2	1	Co 32.4 3509, Mid Za, Tray 2.spc
Co 48.3 5334	Mid Za	6	2	1	Co 48.3 5334, Mid Za, Tray 2.spc
CsBr 46.4 15372	Mid Zc	7	2	1	CsBr 46.4 15372, Mid Zc, Tray 2.spc
Fe 38.4 4457	Mid Za	8	2	1	Fe 38.4 4457, Mid Za, Tray 2.spc
Fe 51.7 10613	Mid Za	9	2	1	Fe 51.7 10613, Mid Za, Tray 2.spc
GaAs 46.5 15371	Mid Zc	10	2	1	GaAs 46.5 15371, Mid Zc, Tray 2.spc
Mn 39.1 4455	Mid Za	1	3	1	Mn 39.1 4455, Mid Za, Tray 3.spc
Mn 53.9 4454	Mid Za	2	3	1	Mn 53.9 4454, Mid Za, Tray 3.spc
Ni 20.2 3315	Mid Za	3	3	1	Ni 20.2 3315, Mid Za, Tray 3.spc
Ni 39.0 4459	Mid Za	4	3	1	Ni 39.0 4459, Mid Za, Tray 3.spc
RbI 47.8 15373	Mid Zc	5	3	1	RbI 47.8 15373, Mid Zc, Tray 3.spc
Se 46.4 9807	Mid Zc	6	3	1	Se 46.4 9807, Mid Zc, Tray 3.spc
SrF2 48.9 15374	Mid Zc	7	3	1	SrF2 48.9 15374, Mid Zc, Tray 3.spc
YF3 45.5 15375	Mid Zc	8	3	1	YF3 45.5 15375, Mid Zc, Tray 3.spc
ZnTe 37.4 4461	Mid Zc	9	3	1	ZnTe 37.4 4461, Mid Zc, Tray 3.spc
ZnTe 38.1 4460	Mid Zc	10	3	1	ZnTe 38.1 4460, Mid Zc, Tray 3.spc
BaF2 22.6 3316	Mid Za	1	4	1	BaF2 22.6 3316, Mid Za, Tray 4.spc
BaF2 46.5 9816	Mid Za	2	4	1	BaF2 46.5 9816, Mid Za, Tray 4.spc
Blank	High Za	3	4	1	Blank, High Za, Tray 4.spc
Blank	Mid Za	3	4	1	Blank, Mid Za, Tray 4.spc
Blank	Mid Zc	3	4	1	Blank, Mid Zc, Tray 4.spc
Blank	Low Zb	3	4	1	Blank, Low Zb, Tray 4.spc
CuS S 13.1 10608	Mid Zc	4	4	1	CuS S 13.1 10608, Mid Zc, Tray 4.spc
CuS S 13.1 10608	Low Zb	4	4	1	CuS S 13.1 10608, Low Zb, Tray 4.spc
CuS S 14.1 10609	Mid Zc	5	4	1	CuS S 14.1 10609, Mid Zc, Tray 4.spc
CuS S 14.1 10609	Low Zb	5	4	1	CuS S 14.1 10609, Low Zb, Tray 4.spc
Hg-Ag 20.6 15376	Mid Zc	6	4	1	Hg, Mid Zc, Tray 4.spc
MoO3 48.6 5338	Mid Zc	7	4	1	MoO3 48.6 5338, Mid Zc, Tray 4.spc
Pb 18.8 3317	Mid Zc	8	4	1	Pb 18.8 3317, Mid Zc, Tray 4.spc
Pb 49.2 11315	Mid Zc	9	4	1	Pb 49.2 11315, Mid Zc, Tray 4.spc
Sb 43.4 5347	High Za	10	4	1	Sb 43.4 5347, High Za, Tray 4.spc
Sb 46.2 5348	High Za	1	5	1	Sb 46.2 5348, High Za, Tray 5.spc
Se 47.1 9808	Mid Zc	2	5	1	Se 47.1 9808, Mid Zc, Tray 5.spc
Sn 41.8 9813	High Za	3	5	1	Sn 41.8 9813, High Za, Tray 5.spc
Sn 47.4 9814	High Za	4	5	1	Sn 47.4 9814, High Za, Tray 5.spc
MoO3 49.9 5337	Mid Zc	5	5	1	MoO3 49.9 5337, Mid Zc, Tray 5.spc