

Standard Operating Procedure for the X-Ray Fluorescence Analysis of PM2.5 Deposits on Teflon Filters

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1.0 SCOPE AND APPLICATION

This standard operating procedure addresses the application of energy dispersive X-ray fluorescence spectrometry (EDXRF) to the determination of trace elements in PM 2.5 deposits on Teflon filters. This technique is capable of quantitative analysis of elements with atomic numbers 11 (sodium) through 92 (uranium). The 48 elements specific to this project are listed in Table 1.

Table 1. Project-Specific Elements Analyzed for the PM2.5 Speciation Program

Sodium (Na)	Chromium (Cr)	Strontium (Sr)	Lanthanum (La)
Magnesium (Mg)	Manganese (Mn)	Yttrium (Y)	Cerium (Ce)
Aluminum (Al)	Iron (Fe)	Zirconium (Zr)	Samarium (Sm)
Silicon (Si)	Cobalt (Co)	Niobium (Nb)	Europium (Eu)
Phosphorus (P)	Nickel (Ni)	Molybdenum (Mo)	Terbium (Tb)
Sulfur (S)	Copper (Cu)	Silver (Ag)	Hafnium (Hf)
Chlorine (Cl)	Zinc (Zn)	Cadmium (Cd)	Tantalum (Ta)
Potassium (K)	Gallium (Ga)	Indium (In)	Tungsten (W)
Calcium (Ca)	Arsenic (As)	Tin (Sn)	Iridium (Ir)
Scandium (Sc)	Selenium (Se)	Antimony (Sb)	Gold (Au)
Titanium (Ti)	Bromine (Br)	Cesium (Cs)	Mercury (Hg)
Vanadium (V)	Rubidium (Rb)	Barium (Ba)	Lead (Pb)

1.1 Principle

The basis of X-ray fluorescence spectrometry is the interaction of X-ray photons from a separate excitation source with atoms of the elements of interest found in the sample (filter deposit). When these excitation photons interact with the atoms in the sample, the photons cause the ejection of inner shell electrons. Outer shell electrons then fall into these vacancies. These transitions result in emission of X-rays characteristic of the element. The energy of the characteristic X-ray is equal to the difference in the electron binding energies of the two electron shells involved in the transition. Because the electron binding energies are a function of the atomic number, the energy of the X-ray is characteristic of the element. The number or intensity of X-rays produced at a given energy provide a measure of the amount of the element present by comparisons with standards.

The X-rays are detected with a semiconductor material, lithium-drifted silicon. The X-ray passing into the detector produces a pulse of electrical current; the more energetic the X-ray, the larger the pulse of electrical current. The electrical pulses are measured and counted with appropriate electronics. These analyzer electronics further process the signals and display the X-ray energy spectrum (numbers of

X-rays vs. energy) on a personal computer. The computer software determines the energy and intensity of the characteristic X-ray peaks and then calculates the elemental concentrations through comparison to calibration parameters. The analysis of PM 2.5 filter deposits is based on the assumption that the thickness of the deposit is small with respect to the analyte characteristic X-ray transmission thickness. It is assumed that the overall production of fluorescence X-rays is equivalent for PM2.5 samples and thin film, elemental standards. Therefore, the concentration of analytes in an unknown sample is determined by first calibrating the spectrometer with thin film standards to determine sensitivity factors and then analyzing the unknown samples under identical excitation conditions as used to determine the calibration factors.

1.2 Method Overview

Filter samples are removed from cold storage and loaded into the sample spinner cups. Sample information is entered into the instrument logbook. The filters (in their spinner cups) are loaded into the XRF sample tray in the same order written into the instrument logbook. The instrument is then prepared for analysis by entering each filter aliquot number into the Method Tray List within the WinTrace software. The PM 2.5 filter deposit analysis is then initiated.

This analysis protocol consists of each filter being analyzed five separate times using five different excitation conditions. The specific excitation conditions have been optimized for specific groups of elements listed in Table 1. The different excitation conditions are used to maximize the sensitivity of the measurement of the different groups of elements, which fluoresce over a wide range of energies.

Energy calibration is performed using a ThermoNoran copper (Cu) calibration standard. This procedure is run every day before any analysis is performed. The energy calibration involves measurement of the Cu K α line (8041) and then determination of the difference between the measured peak energy value and the ideal value.

Quantitative calibration for the elements is based on use of thin film, elemental standards available from Micromatter. Recalibration of the instrument is required when the quality control samples or the U.S. National Institutes of Standards and Technology (NIST) standards fall outside their acceptance limits, when the detector or tube is replaced, or when the instrument undergoes significant repair or other changes in the hardware. Typical re-calibration frequency is on the order of once every six to twelve months.

2.0 Safety

Operating the ThermoNoran QuanX under normal operations and following good laboratory practice provides a safe working environment, but the following cautions should be noted:

QuanX operators are protected from accidental exposure to X-rays by a lid lock and front and back door interlocks when the instrument is in operation. There are three dosimeter badges placed around the instrument to check for any leaking radiation. Also, the operator wears one to monitor her/his exposure. If any problems arise with the "X-RAY ON" indicator light on the sample chamber lid or the interlock system, contact the instrument service engineer.

A beryllium (Be) window is present to separate the sample chamber from the X-ray tube and detector. The window is very fragile and brittle. Do not allow sample or debris to fall onto the window, and avoid using compressed air to clean the window because it will cause the window to rupture. If the window should rupture, note that Be metal is poisonous. Use extreme caution when collecting pieces of Be and consult the service engineer for advice on cleanup of the broken window and replacement.

3.0 Filter Sample Considerations

It is assumed that the PM 2.5 material is uniformly deposited on the filter, and that the position of the PM2.5 filters and the standards in the instrument are the same. It is important that care be taken when loading filters into the sample spinner cups so that the deposit is not scraped, smudged, or smeared in any way. Care also needs to be taken to assure that the filters are placed flat in the spinner cups, and that these cups rest flat on the instrument sample-positioning wheel.

4.0 Interferences and Intensity Corrections

The following are potential sources of error in the procedure:

4.1 Spectral interferences

Spectral interferences with analyte line intensity determination included elemental peak overlap, escape peak, and sum peak interferences. These interferences are automatically corrected within the method program. No action is required by the XRF operator once these interferences have been addressed within the method.

4.2 Background Correction

The laboratory background correction is determined using blank, unused Teflon filters. The blank filters are analyzed on the XRF instrument for the 48 elements. Only the elements for which the average laboratory blank value is above three (3) times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for the select elements above 3 times

the uncertainty and this median value is subtracted from the measured value for each of these elements to make the correction. The correction is added into the ThermoNoran method software for automatic correction of the data.

4.3 Particle Size Effects

The X-ray production efficiency is affected by particle size for the very lightest elements such as aluminum. However, PM 2.5 particle size effects are substantially less than 1 percent for most elements. Since the true particle size distribution cannot be determined for any given filter without microscopic analysis of that filter, no correction for particle size is performed.

5.0 Instruments

Two ThermoNoran QuanX X-ray fluorescence analyzers are used for this procedure. They are a bench top, laboratory grade, energy-dispersive X-ray fluorescence (EDXRF) spectrometers. Each instrument utilizes a high flux rhodium (Rh) anode X-ray tube, which is positioned to direct excitation X-rays through one of five preselected filters onto the sample. Standard equipment for each instrument includes an electronically cooled lithium drifted silicon [Si(Li)] solid-state X-ray detector, 10 position sample filter wheel, and pulse processing electronics that communicate spectral data to a personal computer. The personal computer displays and processes spectral information, and outputs elemental concentration data. Each analyzer contains the following major components:

- ThermoNoran QuanX cabinet containing the detector, X-ray tube, sample changer and electronics for system control and signal processing.
- Personal computer with the ThermoNoran WinTrace software.
- Vacuum pump.
- Printer for analysis reports.
- Uninterruptible Power Supply (UPS), which supplies the QuanX, computer, and the vacuum pump with 25 minutes of uninterruptible power.

6.0 Instrument Calibration

6.1 Standards

Standards used for calibration consist of thin film standards from Micromatter, Inc; the standards were prepared by vacuum deposition resulting in highly uniform deposits.

The 40 Micromatter standards used for calibration are listed in the following table:

Analyte	Analyte	Analyte	Analyte
Sodium or Chlorine as NaCl	Vanadium as V metal	Bromine or Cesium as CsBr	Antimony as Sb metal
Magnesium as Mg metal	Chromium as Cr metal	Rubidium as RbI	Barium as BaF2
Aluminum as Al metal	Manganese as Mn metal	Strontium as SrF2	Lanthanum as LaF3
Silicon as SiO	Iron as Fe metal	Yttrium as YF3	Cerium as CeF3
Phosphorus or Gallium as GaP	Cobalt as Co metal	Niobium as Nb2O3	Samarium as SmF3
Sulfur as CuSx	Nickel as Ni metal	Molybdenum as MoO3	Europium as EuF3
Potassium as KI	Copper as Cu metal	Silver or Mercury as Ag-Hg Amalgam	Terbium as TbF3
Calcium as CaF2	Zinc as ZnTe	Cadmium or Selenium as CdSe	Tungsten as WO3
Scandium as ScF3	Arsenic as GaAs	Indium as In metal	Gold as Au metal
Titanium as Ti metal	Selenium as Se metal	Tin as Sn metal	Lead as Pb metal

6.2 Reference Peak Spectra

Acquisition of reference spectra is required only during the normal calibration. As long as no processing methods have changed, these peak shape references remain valid. The procedure consists of placing the standards in the instrument and acquiring individual elemental spectra that are stored in the method file with each of the analytical conditions. These reference spectra are used in the standard deconvolution and mathematical separation of overlapping peaks of the unknown spectra.

6.3 Method Set-Up

The standardization procedure consists of following steps:

- Select acquisition conditions
- Set up standards file
- Measurement of standards
- Set up reference and spectrum processing file
- Validate calibration
- Determine background correction
- Run unknowns

6.4 Calibration Frequency

Calibration is performed only when the QC/QA limits are exceeded, or if there is a change in the excitation and/or detection conditions, such as a change in the tube, detector, X-ray filters, or signal processor. Calibrations are typically valid for six months to a year.

7.0 Filter Handling

Teflon filters are received from the Gravimetric Laboratory, after being weighed to determine the mass (loading) of the filter. Custody of the Teflon filters are transferred to the XRF Laboratory by the signing of the appropriate chain of custody forms. The filters are placed in cold storage (refrigerator in Building 6) until they are scheduled for analysis. Note that the filters are analyzed at room temperature, and under vacuum conditions.

8.0 Filter Preparation and Analysis

8.1 Preparation

Filters scheduled for analysis are removed from cold storage and allowed to come to room temperature. While the filters are acclimating, the first nine filters in the batch are pulled and prepared for analysis. With a 10-tray position wheel, the quality assurance standard will always be loaded into position 10 and the unknowns will start out with position 1 and continue to 9. Before any filters are loaded in the spinner cups, the cups must be wiped with a Kimwipe to remove any residue left behind from the previous filters. This will eliminate potential cross-contamination. To load a filter into a spinner cup, first remove the top of the petri slide. Next, turn over the petri slide into the spinner cup with the exposed area of the filter now face down in the cup and ready for analysis. The filter will gently fall from the petri slide into the cup. Place the spinner cup in the next available tray position and write down the

filter aliquot number in the instruments logbook. Recording the tray position and filter aliquot numbers in the logbook will allow for a cross check when entering the filter information into the WinTrace software for analysis. No other preparation of the samples is required.

8.2 Analysis

After the filters are loaded into the sample spinner cups and loaded into the sample tray, a Method Tray List is created in the Acquisition Manager within the WinTrace software. The Method Tray List will allow for automated quantitative analysis in conjunction with a Method File. The spectra are saved directly within the respective method file. The Method File contains the five (5) excitation conditions appropriate for the analysis of the Teflon filters. The table below illustrates the five (5) excitation conditions as set-up in the method to analyze the unknowns.

Condition	Filter	Voltage (kV)	Current (mA)	Analytes
1	Low Za	Voltage varies for each condition on each instrument	Current varies for each condition on each instrument	Analytes will vary for each condition on each instrument
2	Low Zb			
3	Pd Thin			
4	Pd Thick			
5	Cu Thin			

The operational parameters typically used are listed in the following table:

Parameter	Description
Live time	This is preset in the method file. For the unknown samples, each excitation condition is set to 300 seconds live time.
Atmosphere	This is preset in the method file. For the unknown samples, each excitation condition will operate under vacuum.

Once the method tray list is set-up, press the icon on the toolbar to start the acquisition. The chamber lid will latch and the “X-RAYS ON” warning light will illuminate.

9.0 Data Acquisition and Calculations

After all the spectra have all been acquired (they are saved in the method file), Method Explorer will process the spectrums and display the analytical results in a specific format. The instrumental analysis report details the analyte, concentration, uncertainty, peak counts per second (cps), and background cps. The concentration in $\mu\text{g}/\text{cm}^2$ is multiplied by the sample area, 11.3 cm^2 , to obtain the value for $\mu\text{g}/\text{filter}$.

The XRF software does not calculate uncertainty values when the peak and concentration result is zero (i.e., peak area \leq background area). To obtain the uncertainty values for when the result is zero a calculation is performed during import of the data into the XRF database. The calculation is:

$$\text{Uncertainty} = \text{Slope} * A * \text{sqrt}(3 * \text{sqrt}(B * t) + B * t) / t$$

Where:

Slope is the response slope calculated in the method

B = background count rate (cps)

A = scaling factor for converting to ug/cm²

t = livetime

To obtain the analytical results of the unknowns, go into Method Explorer and open the air filter analysis method. Under sample lists, identify the samples needed and then click on the analysis results item to obtain the raw results in a table format. Copy the table and paste in an Excel spreadsheet. The data is now in an acceptable format to apply calculations and format for generating reports for EPA database.

10.0 Quality Control

Several different quality control activities are performed as part of the analysis procedure. These activities, their frequency and the measures of acceptable performance are given in the following table.

Activity	Frequency	Measure of Acceptable Performance
Energy Calibration	Daily	This procedure is a wavelength alignment of the instrument. It is an automated process.
Blank Filters (new)	Weekly	All elements below three times the uncertainty
QC Check Sample	Analyzed with every tray of samples.	Coefficient of Variation for the batch must be within 5%.
NIST	Weekly	90-110% recovery

11.0 Data Review and Validation

The analytical data set goes through a Level 0 and a Level 1 validations. These levels of validation will ensure the data set being reported will be of good quality.

11.1 Level 0 Validation

A Level 0 validation begins with the analyst. The analyst identifies any problems related to the chain-of-custody (COC), the filter, or any mechanical or software problems that might have arisen during the analysis of the filters. If such items are identified, validation flags will be applied to single out any problems and these flags will be considered when using the data. A Level 0 checklist is presented as Figure 1.

11.2 Level 1 Validation

A Level 1 validation is a more technical review of the analytical data. This review starts with the analyst, but will primarily be performed by the Technical Area Supervisor. Using the review criteria developed by the QA Manager, the Technical Area Supervisor will check the analytical data set for completeness, the data for reasonableness, that QC sample results (checks of precision, accuracy [recovery], and reproducibility) are within acceptance limits, and that the procedure to analyze the filters was followed. If any discrepancies are noted and would have a direct affect on the data, the Technical Area Supervisor would apply validation flags to the data. A Level 1 checklist is presented as Figure 2.

After the analytical data set has gone through the two levels of review, both the analyst and the Technical Area Supervisor sign off on the data set and it is ready to be submitted for upload into the database.

12.0 XRF Round-Robin Comparison Program

The XRF round robin filter exchange program is intended to provide an ongoing comparison of analysis results generated by the two laboratories that analyze XRF samples for the STN program. Exposed ("real-world") filters obtained from the STN archive are used in order to provide the most realistic samples possible. Archived filters for round robin testing are those filters that are less than 1 year old. According to the contract with EPA, filters and aliquots must be kept for 5 years in case the state monitoring agencies wish to re-analyze them or have them returned to them.

Sample Delivery Date _____

COC Form Number _____

Number of Samples _____

(circle one)

Item #1: Custody Documentation

Chain-of-Custody Form Present	Y	N	N/A
Signed	Y	N	N/A
Dated	Y	N	N/A
Sample Identification			
No. of Samples Matches Number on COC Form	Y	N	N/A
ID#s on Form Match ID #s on Samples	Y	N	N/A

Item #2: Sample Integrity

Sample Containers Intact	Y	N	N/A
Filters Intact	Y	N	N/A

Item #4: Corrective Actions

Investigation Due to Mismatching Sample ID Numbers	Y	N	N/A
Investigation Due to Broken Sample Container(s)	Y	N	N/A
Investigation Due to Damaged Sample(s)	Y	N	N/A
Investigation Due to Missing Net Mass(es)	Y	N	N/A

Item #5: Log-In Completion

Chain of Custody Form			
Signed	Y	N	N/A
Date Noted	Y	N	N/A
Form Placed in Job File	Y	N	N/A

Signed _____

Notes: _____

Figure 1. PM2.5 Chemical Speciation Project Level 0 Checklist

COC Form No. _____ Report Date: _____

Data Review:

Sample Filter No. _____ Comments: _____

Quality Control Review:

Precision Data Acceptable: Yes ___ No ___ Notes: _____

Accuracy Data Acceptable: Yes ___ No ___ Notes: _____

Replicate Data Acceptable: Yes ___ No ___ Notes: _____

Chain - of - Custody Data - Cover Letter: Yes No

Filter Loading Masses: Yes ___ No ___ Notes: _____

Reviewed by: _____ Date _____

Approved by: _____ Date _____

Figure 2. Energy Dispersive X-ray Fluorescence Elemental Analysis Level 1 Checklist.

12.1 Selection of Filters

To find filters that are likely to yield the most useful data, the data base is periodically searched for filter samples having the following characteristics:

- a. Over 6 months old and less than 1 year
- b. Representing a range of different elements at levels above the analytical uncertainties (queries have been designed to select filter sets that maximize the number of different measurable elements)
- c. Representing a range of different concentrations, from low to high (but above the uncertainty levels)
- d. No data validity flags or codes
- e. In good condition by visual inspection

A series of queries have been developed that screen the database for criteria a through d. These are run as often as new round robin filters are needed which is, approximately every 3 to 6 months.

12.2 Distribution of Filters, Data Tracking, and Reporting

The selected filters in their petri slides are located in the STN archive based on their box number, which can be obtained from the STN database. Filters are already in petri slides, and are marked by their original aliquot number (assigned when the filter was received from the field). Filters are visually inspected before further processing, and any defective filters are not used as round robins. Filters are assigned a new aliquot number and are transferred into new petri slides labeled with new barcode stickers. This is done in an effort to make the sample partially "blind" to the laboratories when they are re-analyzed. However, filters are identified as round robin samples so that laboratories operating two or more XRF instruments for the STN program can analyze them on all their instruments before sending them back to RTI.

The aliquot number is linked in the database to measurement request ID number R28598T. Use of a special measurement request ID allows easy retrieval of the data after the round robin filters have been analyzed.

The filters are incorporated into normal shipments to the XRF laboratories. On average, at least two round robin filter per moth are analyzed by each laboratory. Laboratories with multiple XRF instruments analyze the round robin filters on each instrument. The filter

distribution coordinator keeps a notebook to track the filters, but once the data have been entered into the database, manual tracking records are not required in order to analyze the Round Robin data.

Each round robin filter should be analyzed by every participating laboratory (and instrument) at least once. Analysis of the same filter multiple times by the same laboratory is not considered to be a problem; however, filters are rotated out of use after approximately 6 months of use, and are replaced by new round robin filters selected as described in Section 12.1 above.

Data are reported back from the XRF laboratories along with all the regular data. The round robin data uploaded into the STN database along with all the regular data. Round robin results are "ignored" by the data processing routines used for validating and reporting routine and blank filter data. The round robin data are accessible in the STN database using the unique measurement request number assigned to the round robin program.

Database queries have been developed that extract the round robin XRF data as well as the original values reported for the filter, and report them in a tabular format suitable for importing into Excel or other data management and analysis tool.

12.3 Interpretation of Results and Corrective Actions

The most effective means of interpreting the results has been found to be plots of individual round robin results vs. the median of results for all reporting Labs and instruments. The original result is usually included in the data set from which the median is determined.

Systematic problems are defined as particular element/lab/instrument combinations that are consistently above the median by a significant amount. The significance is assessed relative to the uncertainty values that are reported along with the concentration data. Identification of problems is similar to the technique used with control charts: a potential problem would be indicated under the following conditions, where "1-sigma" is the uncertainty value for the element reported by the laboratory:

- one sample beyond 3-sigma
- two samples beyond 2-sigma (both in the same direction)
- five samples beyond 1-sigma (all in the same direction)

Whenever an element or set of elements appears to be systematically high or low relative to the median results as described above, the laboratory is contacted and is asked to re-calibrate the instrument and/or to review its QC data for the time period during which the questioned round robin samples were analyzed. If the laboratory identifies a problem requiring re-calibration, it will re-calculate all data for the affected elements during the questioned time period and will resubmit the data to RTI where it will be uploaded to the STN database, replacing the previous data.