Standard Operating Procedure
for the X-Ray Fluorescence Analysis
of Particulate Matter Deposits on Teflon Filters

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* RTI International is a trade name of Research Triangle Institute.

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1.0   Scope and Application

This standard operating procedure addresses the application of energy dispersive X-ray fluorescence (EDXRF) spectrometry to the determination of trace elements in particulate matter (PM) deposits on Teflon filters. This technique is capable of quantitative analysis of elements with atomic numbers 11 (sodium) through 92 (uranium). The 33 elements specific to this project are listed in Table 1.

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

Element	Element	Element	Element
Sodium (Na)	Titanium (Ti)	Arsenic (As)	Indium (In)
Magnesium (Mg)	Vanadium (V)	Selenium (Se)	Antimony (Sb)
Aluminum (Al)	Chromium (Cr)	Bromine (Br)	Cesium (Cs)
Silicon (Si)	Manganese (Mn)	Rubidium (Rb)	Barium (Ba)
Phosphorus (P)	Iron (Fe)	Strontium (Sr)	Cerium (Ce)
Sulfur (S)	Cobalt (Co)	Zirconium (Zr)	Lead (Pb)
Chlorine (Cl)	Nickel (Ni)	Silver (Ag)	
Potassium (K)	Copper (Cu)	Cadmium (Cd)	
Calcium (Ca)	Zinc (Zn)	Tin (Sn)	

1.1   Principle

The basis of X-ray fluorescence (XRF) 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 the emission of X-rays that are 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 provides 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 versus energy) on a personal computer (PC). 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 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 PM 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

The first step is to check the energy calibration to ensure that peak energies are accurately tied to specific elements. Energy adjustment is performed using a ThermoNoran copper (Cu) calibration standard. This procedure is run every day before any analysis is performed. The energy adjustment involves measuring the Cu Kα line (8041), and then determining the difference between the measured peak energy value and the ideal value and if any adjustments are required, the instrument software performs it automatically.

Filter samples are removed from cold storage and are loaded into the sample cups. Sample information is entered into the instrument logbook. The filters (in their sample cups) are loaded into the XRF sample tray in the same order as they are 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 filter deposit analysis is then initiated.

This analysis protocol consists of each filter being analyzed five separate times using five different excitation conditions (See Section 6.2, *Method Setup*). 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 excitation energies. Each analytical run, which includes nine samples, has a multi-element thin film standard to verify overall method and instrumentation performance.

Quantitative calibration for the elements is based on the use of thin film, elemental standards available from Micromatter, Inc. Recalibration of the instrument is required when the quality control samples or the National Institute of Standards and Technology standard falls 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 recalibration frequency is on the order of once every 6 to 12 months.

2.0   Safety

Operating the ThermoNoran QuanX XRF analyzer under normal operations and following Good Laboratory Practices to provide a safe working environment, but the following cautions should be noted.

ThermoNoran QuanX XRF analyzer 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. Monthly the RTI Radiation Safety Officer performs area monitoring around each instrument to check for any leaking radiation. Also, the operator wears one to monitor his or her exposure. If any problems arise with the "X-RAYS 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. Because this window is 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, it is important to note that Be metal is poisonous. Use extreme caution when collecting pieces of Be and consult the instrument service engineer for advice on cleaning up the broken window and replacing it.

3.0   Filter Sample Considerations

It is assumed that the PM material is uniformly deposited on the filter and that the position of the PM filter and the standards in the instrument is the same. It is important that care be taken when loading filters into the sample 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 sample cups and that these cups rest flat on the instrument sample-positioning wheel.

4.0   Interferences and Intensity Corrections

The following sections describe potential sources of error in the procedure:

4.1   Spectral Interferences

Spectral interferences with analyte line intensity determination include 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 10 blank, unused Teflon filters. These filters are analyzed on the XRF instrument for the 33 elements. Only those elements for which the average laboratory blanks values is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for each of the select elements with a background above three times the uncertainty, and this median value is subtracted from the measured value for each of these elements to make the corrections. The correction values are entered into the software for automatic correction of field sample data.

4.3　Particle Size Effects

The X-ray production efficiency is affected by particle size for the lightest elements, such as aluminum; however, PM particle size effects are substantially less than 1 percent for most elements. Because 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.

4.4　Attenuation Correction

X-ray attenuation occurs when incoming (excitation) x-ray photons are absorbed by the sample before causing the desired fluorescence and when outgoing (fluorescent) photons are absorbed by the sample before escaping the sample. The net effect is that the instrument detects less signal from an element than would be expected if there is no attenuation correction; smaller values indicate a greater attenuation effect. RTI Attenuation correction software accounts for the excitation energies used in the RTI ThermoNoran QuanX XRF instruments. The software, which is a modification of a routine used by EPA, determines attenuations and their uncertainties for both thin, homogeneous deposits principally from aerosol condensation and also from deposits that contain particles with diameters in the high end of the $PM_{2.5}$ size range. The software is applied to RTI's XRF data post measurement to correct for the attenuation before that data is posted in the AQS.

5.0　Instruments

Three ThermoNoran QuanX XRF analyzers (i.e., bench top, laboratory grade, EDXRF spectrometers) are used for this procedure. Each instrument uses a high flux rhodium 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, a 10-position sample filter wheel, and pulse-processing electronics that communicate spectral data to a PC, which displays and processes spectral information and outputs elemental concentration data. Each analyzer contains the following major components:

- ThermoNoran QuanX cabinet that contains the detector, X-ray tube, and sample changer and electronics for system control and signal processing.

- PC with the ThermoNoran WinTrace software.
- Vacuum pump.
- Printer for analysis reports.
- Uninterruptible power supply, which supplies the instrument, PC, and the vacuum pump with 6 hours of uninterruptible power.

6.0   Instrument Calibration

6.1   Standards

Standards used for calibration consist of single or two non-interfering elements deposited as thin film standards from Micromatter, Inc; the standards are prepared by vacuum deposition resulting in highly uniform deposits. The 31 Micromatter standards used for calibration at RTI are listed in Table 2.

Table 2. Micromatter Calibration Standards

Analyte	Analyte	Analyte	Analyte
Sodium or chlorine as NaCl	Titanium as Ti metal	Zinc as ZnTe	Indium as In metal
Magnesium as Mg metal	Vanadium as V metal	Arsenic as GaAs	Tin as Sn metal
Aluminum as Al metal	Chromium as Cr metal	Selenium as Se metal	Antimony as Sb metal
Silicon as SiO	Manganese as Mn metal	Bromine or cesium as CsBr	Cesium as CsF_2
Phosphorus or gallium as GaP	Iron as Fe metal	Rubidium as RbI	Barium as $Ba F_2$
Sulfur as CuSx	Cobalt as Co metal	Strontium as $Sr F_2$	Cerium as CeF_3
Potassium as KI	Nickel as Ni metal	Silver or mercury as Ag-Hg Amalgam	Lead as Pb metal
Calcium as $Ca F_2$	Copper as Cu metal	Cadmium or selenium as CdSe	

6.2   Method Setup

The standardization procedure consists of following steps:

- Set up reference peak spectra: Acquisition of reference spectra is required when performing calibration. As long as no processing methods have changed, these peak shape references remain valid. The procedure of acquiring reference spectra consists of analyzing thin film standards or pure element material (as listed in Table 2) and acquiring individual elemental spectra that are stored in the Method File with each of the analytical conditions. The reference spectra must be interference free, and the peak count for the

reference spectra must be greater than 30,000 counts. These reference spectra are used in the standard deconvolution and mathematical separation of overlapping peaks of the unknown spectra.

- Select acquisition conditions and analysis technique: Five different excitation conditions are performed during the analysis, as shown in Table 3. 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. When creating the excitation conditions, there are two operational parameters that are typically used and need to be considered (as shown in Table 4). These are determination of live time and atmospheric conditions, which will depend on the elements of concern and the detection limits that need to be achieved. Typically, for the lighter the elements, the live time is set to 300, and the atmospheric condition is set to vacuum.

Table 3. Excitation Conditions

	Condition	Filter	Atmospheric Conditions	Voltage (kV)	Current (mA)	Analytes*
1	Low Za	None	Vacuum	4	1.98	Na and Mg
2	Low Zb	Graphite	Vacuum	10	1.98	Al, Si, P, S Cl, K, and Ca
3	Mid Za	Pd thin	Vacuum	30	1.66	Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cs, Ba, and Ce
4	Mid Zc	Pd thick	Vacuum	50	1.00	As, Se, Br, Rb, Sr, and Pb
5	High Za	Cu thin	Vacuum	50	1.00	Zr, Ag, Cd, In, Sn, and Sb

Cs, Ba, Ce, Pb, are quantified from L-lines; all other elements are quantified from the K-lines.

Table 4. Operational Parameters

Parameter	Description
Live time	This is pre-set in the Method File; for the unknown samples, each excitation condition is set to between 200 and 300 seconds live time
Atmosphere	This is pre-set in the Method File; for the unknown samples, each excitation condition will operate under vacuum

- Set up standards file: The Micromatter standards listed in Table 2 are manually entered into a Standards Library and imported into the Method File. The information provided in the Standards Library is the standard name, identification number, and certified concentration of the particular standard. The software will not allow the measurement of

the standards until the standard file is imported into the Method File.

- Measurement of standards: After the Standards Library is imported into the Method File, the analyst proceeds with calibration by clicking the calibrate icon. The software will prompt to acquire all spectra for the standards. Verify that the standards are placed in the sample tray correctly, then start the acquisition. The software will acquire all the necessary spectra to perform the calibration. Because the method is quantifying for 33 elements and the sample tray is for 10 samples, the software will prompt for the next tray to be loaded after finishing the first 10 standards.

- Determine background correction: Laboratory background correction is determined using 10 blank, unused Teflon filters. These filters are analyzed for the 33 elements. Only the elements for which the average laboratory blank value is above three times the uncertainty calculated by ThermoNoran software are subjected to background correction. A median value is determined for the select elements with background levels above three 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 manually added into the software under the Coefficients view, for automatic correction of the data.

- Validate calibration: After the standards and reference spectra have been acquired and the background correction has been applied, the round-robin samples (See Section 12 regarding the round-robin program) and the NIST 1832, along with Micromatter standards (as unknowns) are analyzed to verify calibration and check recoveries for each element of concern. A typical adjustment to the calibration is due to the +/- 5% error with the Micromatter standards. If an element's recovery is too high or low when the standard has been analyzed as an unknown, then an adjustment is made within the Coefficients view of the Method File to accurately correct for the error with the standard.

- Run unknowns: After the instrument has successfully performed calibration, quantitative analysis can be performed on real-world samples.

6.3   Calibration Frequency

Calibration is performed only when the quality assurance/quality control (QA/QC) 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 6 months to 1 year.

7.0   Filter Handling

Teflon filters are received from RTI's Gravimetric Laboratory after being weighed to determine the mass (loading) of the filter. Custody of the Teflon filters is transferred to RTI's XRF Laboratory by signing 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 are allowed to come to room temperature. With a 10-tray autosampler, the QA standard will always be loaded into position 10, and the unknowns will start out with position 1 and will continue to position 9. The analyst will wear powder-free gloves when working with the filters and samples holders. Before any filters are loaded into the sample 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 sample cup, first remove the top of the Petri slide. Next, turn over the Petri slide into the sample 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. If a filter is stuck in the Petri slide, cleaned forceps are used to gently grab the filter by the outer ring and to place it face down into the sample cup. Place the sample cup in the next available tray position and write down the filter aliquot number in the instrument's logbook. Recording the tray position and filter aliquot number in the logbook will allow the operator to cross check the information 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 cups and loaded into the sample tray, a Method Tray List is created in Acquisition Manager within the WinTrace software. The Method Tray List will allow for automated quantitative analysis in conjunction with a Method File. The Method Tray List is created by entering the first sample identification and choosing the Method File from the directory. After the Method File is opened by Acquisition Manager and the sample position is verified in the tray as being correct, then proceed to enter the next sample on the next line. The program automatically fills in the Method File specified for the previous sample.

After the Method Tray List is set up, click the spectrum icon on the toolbar to start the acquisition. The chamber lid will latch and the "X-RAYS ON" warning light will illuminate and the vacuum pump will click on. After a 300-second warm up, acquisition will begin starting with the lowest power condition.

9.0   Data Acquisition and Calculations

After all the spectra have all been acquired (they are saved in the respective 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.

To obtain the analytical results of the unknowns, go into Method Explorer and open the respective Method File. Under sample lists, identify the samples needed, and then click on the analysis report item to obtain the results in an rtf format. Save the report onto the hard drive. The

results file must be converted from the rtf format to a csv format to be able to upload to the RTI XRF database. ThermoNoran provided RTI with an external program to complete the conversion. After the data has been converted, it is an acceptable format to upload into the RTI XRF database for report generation, uncertainty determinations, attenuation correction through EPA provided software, and perform QC analysis. During report generation, the unit concentration $\mu g/cm^2$ is multiplied by the sample area, 11.3 cm^2, to obtain the value for μg/filter.

The WinTrace XRF software does not calculate uncertainty values when the peak and concentration result is zero (i.e., peak area ≤ background area). To obtain the uncertainty values for when the result is zero, a calculation is performed during the import into the RTI 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 $\mu g/cm^2$

       t   =   Live time

10.0   Quality Control

Several different QC activities are performed as part of the analysis procedure. These activities, their frequency, the measures of acceptable performance, and action if the item fails performance standards are provided in Table 5.

Table 5. Quality Control Procedures

Item	Inspection Frequency	Inspection Parameter	Action If Item Fails Inspection	Documentation Required
Energy calibration	Daily	Wavelength alignment of the instrument	This is an automated process	Document in the instrument's run logbook
Calibration verification	Monthly	Percentage of recovery of seven elements on thin-film National Institutes of Standards and Technology reference materials	Adjust instrument calibration factors	Document in the instrument's run logbook; results stored in the XRF database
	Monthly	90% to 110% recovery analyzing the PM2.5 calibration standards as unknowns		Results stored in instrument's method file
Ongoing calibration verification	Run with every tray of samples	90% to 110% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10μg/cm^2	Re-check instrument calibration and adjust if necessary; re-analyze samples	Document in the instrument's run log book
Background Determination	Monthly	Analysis of 10 blank, unused Teflon filters. All elements below three times the uncertainty	Adjust instrument background values	Documented in instruments run logbook

11.0 Data Review and Validation

The analytical dataset undergoes Level 0 and Level 1 validations. These levels of validation will ensure that the dataset being reported will be of good quality.

11.1 Level 0 Validation

A Level 0 validation begins with the analyst, who identifies any problems related to the chain-of-custody, the filter, or any mechanical or software problems that might have occurred during the analysis of the filters. If such items are identified, the analyst notes any problems in the instrument logbook, which is reviewed by the Technical Area Supervisor.

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 it will primarily be performed by the Technical Area Supervisor. Using the review criteria developed by the QA Manager, the responsibilities of the analyst and the Technical Area Supervisor are provided in Table 6.

If any discrepancies are noted by the analyst or the Technical Area Supervisor, they will be reported on their respective checklist (Figure 1 and Figure 2).

Table 6. Level 1 Validation Responsibilities

Analyst	Technical Area Supervisor
Verify proper custody documentation is provided in batch folder	Ensure analytical dataset is complete and the proper procedures were followed to analyze the filters
Check sample identifications against COC forms and proper number of samples match given COC	Check that proper paperwork is provided in the batch folder and for any notations regarding the analysis of the batch or flaws with the filters that were analyzed
Confirm mass values for each sample are present on final report	Review precision, accuracy, and replicate data for acceptable limits
Make sure sample identifications are consistent between final report versus pre-attenuation report	Check data for any inconsistencies or trends and report to QA Manager
Review pre and post attenuation reports for disparity with attenuated data	Apply flags to data , if applicable

After two levels of review have been performed on the analytical dataset, it is ready to be submitted for upload into the CSN database.

Batch Creation Date:_____   Batch ID Number:_____

Number of Samples:_____

(circle one, if no leave comment why)

Item #1: Custody Documentation
        Chain-of-Custody form present   Yes   No

            Signed By:_____

            Dated:_____

        Sample Identification
            No. of samples matches number on COC form   Yes   No
            ID#s on COC match Id #s on samples   Yes   No

Item #2: Attenuation Correction
        Sample IDs consistent with pre-attenuation report   Yes   No
        Mass values present on report   Yes   No

Item #3: Data Comparison Pre-attenuation vs Attenuated Data
        Results consistent between pre and post attenuation   Yes   No

Comments Regarding Data:_____

_____

_____

_____

Reviewer Signature:_____   Date Signed:_____

Figure 1. EDXRF Analysis Analyst Checklist.

COC Form No. _____   Report Date: _____

Data Review:

Sample Filter No. _____   Comments: _____

Sample Filter No. _____   Comments: _____

Sample Filter No. _____   Comments: _____

Sample Filter No. _____   Comments: _____

Sample Filter No. _____   Comments: _____

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 _____ Notes: _____

Filter-Loading Masses: Yes _____ No _____ Notes: _____

Reviewed by: _____   _____
                                                                        Date

Figure 2. EDXRF Analysis Technical Area Supervisor Checklist.

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 Chemical Speciation Network (CSN) Program. Exposed (real-world) filters obtained from the CSN archive are used to provide the most realistic samples possible. According to the contract with EPA, filters and aliquots must be kept for 5 years in case the state monitoring agencies want to re-analyze them or have them returned to the respective agency.

12.1 Selection of Filters

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

- Represents 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)
- Represents a range of different concentrations, from low to high (but above the uncertainty levels)
- No data validity flags or codes
- In good condition by visual inspection.

12.2 Distribution of Filters, Data Tracking, and Reporting

The selected filters in their Petri slides are in the CSN archive based on their box numbers, which can be obtained from the CSN database. Filters are already in Petri slides and are marked by their original aliquot numbers (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 conducted 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 CSN Program can analyze them on all of their instruments before sending them back to RTI.

The aliquot number is linked in the database to measurement request ID number R28598T. Using a special measurement request ID allows data to be easily retrieved after the round-robin filters have been analyzed.

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

Each round-robin filter should be analyzed at least once by every participating laboratory (and instrument). 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 participating XRF laboratories, including RTI, along with all the regular data. The round-robin data are uploaded into the CSN 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 CSN 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 Microsoft Excel or another 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 versus the median of results for all reporting laboratories and instruments. The original result is usually included in the dataset from which the median is determined.

Systematic problems are defined as particular element/laboratory/instrument combinations that are consistently above the median by a significant amount. This amount 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 a set of elements appears to be systematically high or low relative to the median results as previously described, the laboratory with the bias (same procedures for all participating XRF laboratories, including RTI) is contacted and is asked to recalibrate 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 that requires recalibration, it will recalculate all data for the affected elements during the questioned time period and will resubmit the data to RTI, where it will be uploaded into the CSN database, replacing the previous data.