

# CHESTER LabNet

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## Standard Operating Procedure XR-002.05

Analysis of Elements in Air Particulates  
by X-Ray Fluorescence (Kevex 770 & 772)  
US EPA IO 3.3

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### Approvals:

 _____ Author	<u>11-23-13</u> _____ Date
 _____ Lead Analyst	<u>10-17-13</u> _____ Date
 _____ QA/QC	<u>11-25-13</u> _____ Date

Effective from: 11-25-13  
Effective until: present



Analysis of Elements in Air Particulates  
by X-Ray Fluorescence (Kevex 770 & 772)  
US EPA IO 3.3

**1.0 Introduction**

- 1.1 Test Method Reference ID: US EPA Inorganics Compendium Method 3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectrometry.
- 1.2 Applicability: This method is applicable to the quantitative analysis of aerosols deposited on a variety of filter types for the elements Na through U.
- 1.3 Detection Limit: XRF does not utilize detection limits as commonly defined, rather all results are reported with an associated uncertainty which varies based upon filter matrices and interferences present in the deposit.
- 1.4 Method Performance: Refer to referenced method.

**2.0 Summary**

- 2.1 Scope and Application: The intended use of this method is for the quantitative analysis of aerosols deposited on a variety of filter types for the elements Na through U. This method is also applicable to the quantitative analysis of resuspended solids deposited on a variety of filter types for the elements Na through U, when first resuspended onto a variety of filter media following SOP XR-001.
- 2.2 Summary of Method: Electrons in the sample are excited from their ground state to higher energy levels by X-radiation from an X-ray tube. These excited electrons emit discrete energy X-rays as they return to their normal ground state energy level. The energy of these emitted X-rays is characteristic of each element and is used to identify the element in the spectrum.

A silicon-lithium crystal detector measures the change in the electronic field generated by the release of the eV charge during elemental excitation. This change in the field is proportional to the energy of excited electrons, and is used to identify specific elements in the deposit.

The frequency of any given energy level is used to quantify that element through direct comparison with thin film standards.

- 2.3 Interferences: As with all emissions spectrometry, secondary, tertiary, quaternary emission lines may overlap primary lines depending on the amount of interferent present.
- 2.4 Sample collection/preservation/shipment/storage: Collection, field preservation and shipment of samples is performed by the client. Chester LabNet has no control over the actions of the client in the field. Upon receipt, samples are stored either at room temperature, or in refrigerators.

### **3.0 Safety**

- 3.1 Follow the Chester LabNet Chemical Hygiene Plan. Always treat samples of unknown origin and/or constitution as hazardous.
- 3.2 This method presents no safety risk beyond typical laboratory safety hazards.
- 3.3 No carcinogenic reagents are used in this method.
- 3.4 Although X-rays are produced by the instrument at dangerous levels, the X-rays will not turn on unless all interlocks are fully locked, thus ensuring the user is shielded from the X-rays. All users must wear dosimeter badges. To date, Chester LabNet has not had a dosimeter badge showing any radiological exposure of any XRF technician. Normal operation of the instrument will not expose the user to X-rays generated by the instrument. Radiation shielding should only be removed by qualified personnel while servicing the instrument, and must always be in place during routine analysis. Removal of DiLithium crystals may only be performed by Mr. Scott or one of his staff.

### **4.0 Pollution Prevention and Waste Management**

- 4.1 The smallest quantity of chemical feasible is removed from its primary container for use.
- 4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

4.4 Larger quantities of known hazards are returned to the client for disposal.

## **5.0 Apparati, Equipment and Supplies**

5.1 Instrument. Kevex Model Delta 770 energy dispersive XRF (EDXRF) equipped with a water-cooled end-window X-ray tube with a rhodium anode and a peak operating power of 60kV and 3.3 mA. The system was modified by IXRF Inc. to operate using Windows based software to control instrument operation. Chester LabNet currently operates two of these instruments, informally named "770" and "772". 770 is the original instrument. Its computer operates on Windows 95 and 772 operates on Windows 98. Both instruments use Ethernet connections to transfer the data files to the processing computer.

### 5.2 Accessories

- 5.2.1 HDPE filter holders with retaining rings purchased from VHG Labs to hold 37mm (part # PFM-37) or 47mm (part # PFM-47) diameter filters at a fixed distance from the X-ray source. Each retaining ring has a unique identifier written on it.
- 5.2.2 Gepe Model 4302 slide storage chest.
- 5.2.3 46mm diameter punch for sampling larger media
- 5.2.4 Forceps.
- 5.2.5 25mm filter holder adapters
- 5.2.6 Kimwipes

### 5.3 Thin Film Calibration Standards

- 5.3.1 Micromatter Inc. vapor deposit of single or two non-interfering elements onto thin Mylar film.
- 5.3.2 EPA organo-metallic acetate film, usually with two non-interfering elements.
- 5.3.3 NIST SRM's 1832 and 1833 multi-element vapor deposits on glass films.

## 6.0 Reagents and Standards

- 6.1 95% ethanol
- 6.2 Liquid Nitrogen

## 7.0 Preparation, Calibration and Standardization

### 7.1 Sample loading

- 7.1.1 Obtain an XRF Analysis Request Form (Figure 1.).
- 7.1.2 Retrieve the samples indicated in the LIMS ID column of the request form.
- 7.1.3 Prepare the work area: Filter loading is done in the laminar flow hood.
  - 7.1.3.1 Turn the hood blower and lights on
  - 7.1.3.2 Clean the work surface with a Kimwipe and ethanol
  - 7.1.3.3 Clean a pair of forceps and the filter loading block with Kimwipes and ethanol.
  - 7.1.3.4 Place the filters to be analyzed, the slide storage chest, the XRF request form and a pen in the hood.
- 7.1.4 Load the filters:
  - 7.1.4.1 Clean all XRF sample holders with ethanol-soaked Kimwipes, being careful to not erase the filter holder IDs.
  - 7.1.4.2 Place appropriate sized filter holder on the filter loading block and then select the filter to be loaded.

- 7.1.4.3 Remove the filter from its container and place deposit side down in the filter holder.
- 7.1.4.4 Use forceps and handle the filter only around its perimeter. If the forceps touch the deposit, clean forceps before proceeding.
- 7.1.4.5 Ensure that deposit area is within the analysis area (e.g. near the center of the filter).
- 7.1.4.6 Choose the appropriate retaining ring and snap it into place so that the filter is held in place without wrinkles or other misalignment. The retaining rings are labeled in batches with a letter/symbol and numbers (1-10). For example, the first set of rings is labeled A1, A2, A3...A10, the second set is labeled B1, B2, B3...B10, etc.
- 7.1.4.7 Note the condition of the filter and record any comments on the XRF request form that may apply to the XRF analysis, such as non-uniform deposit, wrinkled filter, etc. Do NOT analyze filters with loose deposits.
- 7.1.4.8 Place the numbered filter holder in the slot that the retaining ring was taken from. IT IS EXTREMELY IMPORTANT TO MATCH FILTER NUMBER TO LOCATION NUMBER ON XRF REQUEST FORM.
- 7.1.4.9 The filter container should be returned to the tray in which it was originally stored.
- 7.1.4.10 Continue steps 7.1.4.1 through 7.1.4.9 for the remaining filters (maximum of ten).
- 7.1.4.11 The quality assurance standard (QS) is permanently loaded in the XRF sample tray and is not stored in the sample case.
- 7.1.4.12 Write the batch letter/character (A, B, etc.) in the upper left-hand corner of the XRF request form and initial and date the line labeled "Load" on the upper right-hand section of the XRF request form.

SH  
1.21.15

7.1.5 Queue samples:

7.1.5.1 Place the slide storage chest in the appropriate staging area (active sample refrigerator or on the counter in the XRF area) awaiting XRF analysis.

7.1.5.2 Place the XRF request form(s) in the associated instrument specific queue.

7.1.5.3 Return the filter containers back to where they were originally stored.

7.2 KeveX Start Up - This is the procedure for starting the KeveX if the X-rays have been off for more than 12 hours.

7.2.1 With instrument off, carefully raise the chamber lid until the latch at the far left end of the chamber catches.

7.2.2 Initiate Spectrometer:

7.2.2.1 Turn the key ON. If the key already is ON, then turn it OFF and then back ON.

7.2.2.2 The sample tray should now be located at position 1, the X-ray tube should be in the secondary excitation position, and the secondary target should be zero.

7.2.3 Carefully close the chamber lid on the KeveX. If the lid is suddenly dropped, the resulting pressure may be sufficient to rupture the thin Be windows on the X-ray tube and detector.

7.2.4 Adjust the pulse processing rate on the IXRF Systems control box, which is next to the computer.

7.2.4.1 On the 770, set the pulse processing rate to '3' by pressing the switch located at the center right of the pulse processor module until the LED

indicates the correct number.

7.2.4.2 On the 772, set the pulse processing rate to '3' by pressing the switch located at the center right of the pulse processor module until the LED indicates the correct number.

7.2.5 Reinitialize electronics communications:

7.2.5.1 Cold reboot the PC

7.2.5.2 Initiate Windows

7.2.5.3 Open the IXRF Operating Program.

7.2.6 Begin x-ray tube warm up:

7.2.6.1 In the IXRF Operating Program, set the 'mA' to '0.2', and then set the 'kV' to '10'.

7.2.6.2 Press the white 'X-RAY ON' button at the front panel of the Kevex. This should cause the red 'X-RAY ON' light to come on at the front panel of the Kevex.

7.2.6.3 To prevent undue wear on the X-ray tube anode, slowly ramp up the x-ray tube as per page 2-6 of the Kevex 'X-RAY TUBE, HIGH VOLTAGE POWER SUPPLY AND HEAT EXCHANGER USER'S MANUAL'. (See Appendix A)

## **8.0 Procedure**

8.1 Kevex Operating Procedure - the Kevex operating manual should be reviewed before operating the instrument. One should be familiar with the hazards of incorrect operation and the safety systems of the instrument.

## 8.2 Start Analysis Run

- 8.2.1 Using the IXRF software, turn the 'mA' to '0.2' and the kV to '10'. Set 'atm' (atmosphere) to 'air'
- 8.2.2 When conditions have stabilized, press the red 'X-rays Off' button on the front panel of the Kevex and carefully raise the chamber lid until the latch engages.
- 8.2.3 Remove the sample tray from the Kevex chamber.
- 8.2.4 Place the sample tray in the staging area and remove any samples that may be residing in the sample positions, returning the samples to their proper positions in the proper sample case. The quality assurance standard (QS) remains in the tray and always resides in position '16'.
- 8.2.5 Transfer each filter holder in sequence to the like numbered position in the Kevex sample tray. The number of each filter holder should correspond to the number on the tray, and should be oriented at the front-right. The Kevex tray has 16 positions, so that up to 15 samples may be analyzed along with the QS during each analysis run. When properly loaded, the deposit side of the filter should be facing down.
- 8.2.6 Insert the proper detector collimator for the excitation condition(s) to be utilized during analysis. Only qualified personnel may attempt this task and extreme care must be exercised to prevent damage to the fragile detector window. The purpose of the Ag collimator is to reduce or eliminate background counts in the spectral region between 8.0 and 9.5 KeV produced by the Ta collimator. For both the 770 and 772, the Ta collimator is used for <sup>All</sup> excitation conditions 4. The Ag collimator is used for excitation conditions 0, 1, 2 and 3. *except for the Rh prefilter direct excitation condition, which uses the Ag collimator. (RHS 1.8.15)*
- 8.2.7 Replace the sample tray in the Kevex chamber, being careful to orient the two holes in the tray to the correct posts on the sample-advance motor. Carefully lower the chamber lid.
- 8.2.8 If the analysis calls for vacuum, set 'atm' to 'vac' in the IXRF program and make sure the lid is sealed by trying to lift it. If the lid is not sealed, check that the

gasket is properly positioned and hold lid down until sealed.

8.2.9 Make sure that the current and voltage are set at 0.2 mA and 10 kV. Turn X-rays 'ON' at Kevex front panel.

8.2.10 Setup the XRF analysis run in the IXRF program.

8.2.10.1 In the upper left area of the iXRF screen, select 'Setup', then 'Sample Tray'. This brings up a table with columns listing position, name, and template.

8.2.10.2 Enter the LIMS ID into the name column for each sample position as recorded on the XRF request form. Position 16 should be labeled as QSxxx, where xxx = the run number (1 - 999). For example, if the run number on the XRF request form is: A001-005, then the proper identification for the QS would be 'QS005'

8.2.10.3 Enter the analysis protocol ('.ana' file) indicated in the XRF request form for each sample by highlighting the position numbers to be run at a specific protocol (click the icon on the left of each position number), then selecting the ".ana" file in the 'template' window, then finally clicking on the 'set template' icon. The QS has its own discrete analysis protocol. Each protocol dictates the X-ray tube power settings as well as the counting times for each excitation condition.

8.2.10.4 After the analysis has been set up, save the table by selecting 'save' and entering the run number as the file identification.

8.2.10.5 Next click on 'exit' to return to the main program.

8.2.11 The analysis is ready to begin. Select 'analyze', then 'tray'. This brings up the analysis matrix created in setup with columns for Position, Name, Target, Filter, kV, and mA. Check the settings to ensure that the proper analysis protocol has been chosen, remove sample IDs that are not run with the collimator in use, and select 'start' to begin the analysis.

8.2.12 On the XRF request form record the analyst's initials, the date and the time in the space labeled "Primary," "Ag collimator" or "Ta collimator", as appropriate.

8.2.13 In the Kevex Logbook enter the date, time, analyst's initials, run number, analysis protocol, sample holder ID letter, and number of samples.

8.3 Completion of the run:

8.3.1 When the run has finished, change the vacuum "atm" setting to "air".

8.3.2 After the run has successfully completed, the spectral files will be located in the IXRF subdirectory on the hard drive. For both the 770 and 772, the files are transferred directly using the Ethernet.

8.3.3 At this point, process the QS data as described in SOP XR-005.

8.3.4 Chose a sample for replicate analysis and analyze that sample using the same protocol. For example, if the sample was analyzed using Protocol 6, analyze the replicate using Protocol 6.

*Rotate the sample 90° prior to re-analysis RB 1.8.15*

8.4 After ensuring that the QS sample has passed for the run, unload the XRF:

8.4.1 Remove the Kevex sample tray

8.4.2 Remove the samples from the sample tray and place back in the appropriate sample box. It is extremely important to match filter number to location number to XRF request form.

8.4.3 The samples are now ready to be transferred from the XRF sample holders back into their storage containers and either archived or returned to the client.

8.5 At this point, the next scheduled XRF analysis may be initiated.

## 8.6 Instrument shut-down.

8.6.1 When the XRF instrument is not in use, the X-rays are ~~kept on~~ <sup>turned OFF</sup> at a low 'standby' power setting which acts to prolong the life of the X-ray tube. *Aut 1-8-14*

8.6.2 Ensure the lid is shut and the interlock is on (white interlock light is on)

8.6.3 Set 'atm' to "air"

8.6.4 Set the tube power to 10 kV and 0.2 mA.

*8.6.7 Set to "pump off"*

8.6.5 Set the tube to the secondary target position

*8.6.8 close out both XRF windows JS 1-14-16*

8.6.6 Set the target wheel to position zero.

*8.6.9 Turn XRF instrument to off position using the KEY*

*8.6.10 Turn off pulse processor by switching button on unit face*

## 9.0 QA/QC

*8.6.11 Do NOT turn off the computer.*

9.1 Quality Assurance Standard (QS). The QS is a multi-element thin film vapor-deposited standard on Mylar manufactured by Micromatter Inc. The QS measurements are considered to be a reliable approximation of the precision of the instrument between the time of analysis and the time of calibration.

9.1.1 Frequency: once, at the end of each analytical run

9.1.2 QC statistic: percent recovery

9.1.3 Control limits: 90-110 %

9.1.4 Corrective action: terminate analysis, determine cause of QS failure. Failure necessitates re-analysis of any excitation condition(s) falling outside the limit. Repeated failure requires a recalibration of any excitation condition(s) not meeting the required limits and reanalysis of the samples associated with the failed QS. See analyst's note 13.1 for possible sources of QS failures.

9.1.5 Note: See section 10 for a description of the QS true value determinations.

9.2 Laboratory Replicate. This is a sample which is analyzed twice.

- 9.2.1 Frequency: once per analytical batch of ten client samples.
- 9.2.2 QC Statistic: relative percent difference (RPD) of both the sample results and the uncertainties of the sample results ( $\delta_{RPU}$ ) for all results greater than three times the uncertainty of that analyte.
- 9.2.3 Control limits: Average analyte score for the sample must exceed 1.5. See section 10.2 for the calculations relating to scoring of samples.
- 9.2.4 Corrective action: re-analyze a different sample and replicate. If control limits are still exceeded, troubleshoot the instrument and reanalyze all samples associated with that replicate.

9.3 NIST weekly accuracy check (NIST check). These standards are thin film standard prepared and certified by NIST. The frequency of this analysis is limited by the fragile nature of the standards. Elements analyzed are Al, Si, S, K, Ca, Ti, V, Mn, Fe, Cu, Zn, and Pb. Each element is analyzed in each pertinent excitation condition.

- 9.3.1 Frequency: once per week
- 9.3.2 QC statistic: analytical result
- 9.3.3 Control limits: within the NIST certified uncertainty for each analyte
- 9.3.4 Corrective action: terminate analysis, recalibrate the excitation condition in which the failure occurs.

## 10.0 Calculations

10.1 Calculation of QS standard percent recovery:

The QS multi-element thin film standard is analyzed several times during calibration, and the gross counts for elements Si, Ti, Fe, Se, and Cd in their  $K\alpha$  windows, and Pb in its  $L\beta$  window are averaged. These averaged values are entered into the QS data processing program. The QS is then run concurrent with each analytical run of samples and the gross counts for each element in each excitation condition are compared with those obtained during calibration.

Percent recoveries are calculated as follows:

$$R_{i,j} = U_{i,j} / C_{i,j} * 100$$

where:  $R_{i,j}$  = recovery for element i in excitation condition j.  
 $U_{i,j}$  = gross counts per second for element i in excitation condition j obtained during analysis of samples.  
 $C_{i,j}$  = the averaged gross counts per second for element i in excitation condition j from the calibration runs.

## 10.2 Scoring of Replicate Samples:

For a given sample, all analyte results which exceed three times the uncertainty for that analyte are given both a score and a qualifier. The score is a numerical value assigned to a qualifier to aid in determining the overall score of the replicate sample. The qualifier and score is determined by comparing the relative percent difference of the analyte result to the relative percent *uncertainty* of the analyte result.

10.2.1 The relative percent difference (RPD) of the analyte result is calculated as follows:

$$RPD = [(X_1 - X_2) / ((X_1 + X_2) / 2)] * 100$$

where:  $X_1$  = original sample concentration  
 $X_2$  = replicate sample concentration

10.2.2 The relative percent uncertainty (RPU) of the uncertainties is calculated as follows:

$$\delta_{RPU} = [((\delta_o^2 + \delta_r^2)^{1/2}) / ((X_1 + X_2) / 2)] * 100$$

where:  $\delta_{RPU}$  = the relative percent uncertainty of each analyte  
 $\delta_o$  = the uncertainty for a particular analyte for the original analysis  
 $\delta_r$  = the uncertainty for a particular analyte for the replicate analysis  
 $X_1$  = the original sample concentration  
 $X_2$  = the replicate sample concentration

10.2.3 Each replicate analyte is graded and qualified as follows:

Condition	Score	Qualifier
$RPD \leq \delta_{RPU}$	+2	+
$\delta_{RPU} < RPD \leq 2 \times \delta_{RPU}$	+1	0
$2 \times \delta_{RPU} < RPD \leq 3 \times \delta_{RPU}$	-1	-
$RPD > 3 \times \delta_{RPU}$	-2	--

10.2.4 The intermediate score of the replicate is calculated as follows:

$$S_f = \frac{\sum S_i}{n}$$

where:  $S_f$  = the intermediate grade

$S_i$  = each individual analyte score ('+2', '+1', '-1', or '-2')

$n$  = the total number of analytes whose original concentration exceeds 3x its uncertainty

$$S_d = S_f / \text{average RPD}$$

where:  $S_d$  = the determinate score

$$\text{average RPD} = \frac{|\text{RPD} / \text{RPD}|}{n}$$

## 11.0 References

11.1 Kevex Operator's Manual

11.2 Practical X-Ray Spectrometry, R. Jenkins and J.L. De Vries, second edition, Philips Technical Library, Springer-Verlag New York Inc.

11.3 X-Ray Fluorescence Analysis of Environmental Samples, Jaklevic, et al, Ed. by T.G. Dzubay, Ann Arbor Sci.

- 11.4 Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, T.G. Dzubay and R.O. Nelson, in Advances in X-Ray Analysis, Vol 18, 619-631.
- 11.5 Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon Membrane Filters by X-Ray Fluorescence Analysis, J.A. Cooper, L.M. Valdovinos, J.R. Sherman, W.L. Pollard, R.H. Sarver, and J.K. Weider, report by NEA, Inc., Beaverton, OR, July 15, 1987.
- 11.6 Round Robin Evaluation: Elemental Analysis of Bulk Samples and PM<sub>10</sub> Loaded Teflon Filters, presented at the 82nd Annual Meeting of AWMA, Anaheim, CA, June 24-30, 1989.
- 11.7 US EPA Inorganics Compendium Method IO 3.3; Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectrometry

## 12.0 Definitions

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.
- 12.3.1 Analytical Batch: a group of prepared samples (extracts/digests etc) that are analyzed together as a group, although they may have been prepared separately.
- 12.4 Blank: a clean aliquot of the same matrix as the digested samples. A blank is subjected to the usual analytical and measurement processes.
- 12.4.1 Calibration Blank: An unspiked clean matrix of similar constitution as the sample extracts or digests (e.g. DI Water, 5% HNO<sub>3</sub> etc) used to establish the zero intercept of the calibration curve.
- 12.4.2 Field Blank: A blank prepared by the client in the field. This blank is treated as a sample by the laboratory.
- 12.5 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.

- 12.6 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.
- 12.7 Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements where possible.
- 12.8 Calibration Standard: a substance or reference material used to calibrate and instrument.
- 12.9 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.
- 12.10 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.
- 12.11 Correlation Coefficient: the statistical representation of how closely a set of x,y coordinates comes to a true line. A correlation coefficient of 1.000 is considered a perfectly straight line. Correlation coefficients above 0.995 are usually attainable by most instruments.
- 12.12 Duplicate: A second aliquot of a sample, taken through all steps of the method, including digestion/preparatory stages.
- 12.13 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.
- 12.14 Laboratory Information Management System (LIMS): a comprehensive computerized database system that a laboratory uses for sample tracking and data management, from sample receipt to reporting and archiving.
- 12.15 Matrix/Matrices: the component or substrate that contains the analyte of interest.
- 12.16 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.17 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.
- 12.18 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.
- 12.19 Standard: a solution or matrix of a known amount of analyte(s).
- 12.19.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.

### 13.0 Analysts' Notes

13.1 QS and NIST failures indicative of XRF system malfunctions may include:

- 13.1.1 Processing of sample through incorrect spreadsheet. Prior to any other troubleshooting, analyst should verify that the QS or NIST standard was processed through the appropriate spreadsheet (e.g. a Teflon QS will fail if processed through the quartz QS spreadsheet).
- 13.1.2 Vacuum failure/decay where the lower energy elements Si and Ti are readily absorbed by the Ar in the atmosphere. Si will exhibit the lowest recovery, then Ti < Fe < Se < Pb < Cd.
- 13.1.3 Channel drifting will cause peaks to shift so that recoveries are low for all elements. Check the QS spectra for shifting and correct by recalibrating the channels (see SOP XR-004).
- 13.1.4 Degradation in peak intensity in all excitation conditions can signal a decline in X-ray tube performance.
- 13.1.5 Loss of resolution (peak broadening) is a sign of detector degradation, and may indicate a low liquid nitrogen level, or loss of vacuum behind the Be window.

### XRF Analysis Request Form

Date of Request:	<b>Initial/Date:</b>
Date Results Required:	Load: _____
Client Name:	Ag Collimator: _____
Run Number:	Ta collimator: _____
Protocol:	Resume: _____
Sample Description:	QA: _____
Total # of Samples:	Unload: _____
Report Number:	
Date Data Processed:	
Date Worklist Released:	
Comments:	

	<b>a</b>	<b>b</b>
Cond	Date/ Time	Date/ Time

Pos.	LIMS ID	S	Deposit Area	Mass	Client ID	Comments
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16	<i>QS001</i>					

Figure 1. XRF Run Sheet

C:\IXRF\QS024.sp0					sp0
Livetime	Target	Filter	kV	mA	
50	Direct	Cel	7.5	0.1	5
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery		
Si 9004	1801	1706	1.056		PASS

C:\IXRF\QS024.sp1					sp1
Livetime	Target	Filter	kV	mA	
50	Direct	Cu	20	0.2	2
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery		
Si 416	41.6				
Ti 8621	862.1	871.9261	0.989		PASS
Fe 17790	1779.0	1822.317	0.976		PASS

C:\IXRF\QS024.sp2					sp2
Livetime	Target	Filter	kV	mA	
50	Ge	0	30	1	2
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery		
Ti 10138	202.76	205.4454	0.987		PASS
Fe 24524	490.48	493.9854	0.993		PASS

C:\IXRF\QS024.sp3					sp3
Livetime	Target	Filter	kV	mA	
50	8	Rh	35	1	1
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery		
Ti 3566	71.32	68.11	1.047		PASS
Fe 8901	178.0	176.8	1.007		PASS
Se 10624	212.5	206.8	1.027		PASS
Pb 13075	261.5	260.8	1.003		PASS

C:\IXRF\QS024.sp4					sp4
Livetime	Target	Filter	kV	mA	
50	Direct	W	55	0.6	0
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery		
Cd 5561	185.4	187.7	0.987		PASS

Figure 2. Example QS results page

Figure 3. Replicate sample report.

REPLICATE REPORT

Original ID: 02-T5786

Replicate ID: RT5786

Deposit Mass: 214 µg

Deposit Area: 11.3 cm<sup>2</sup>

Particle Size: F

Element	Original ug/cm2		Replicate ug/cm2		Difference ug/cm2		RPD						
Na	0.0921	+-	0.0452	0.0381	+-	0.0476	0.0540	+-	0.0656				
Mg	0.0000	+-	0.0158	0.0325	+-	0.0176	-0.0325	+-	0.0236				
Al	0.0271	+-	0.0077	0.0173	+-	0.0083	0.0098	+-	0.0114	+	44.0	+-	51.2
Si	0.0965	+-	0.0116	0.0957	+-	0.0118	0.0007	+-	0.0165	+	0.8	+-	17.2
P	0.0000	+-	0.0026	0.0000	+-	0.0030	0.0000	+-	0.0040				
S	0.5519	+-	0.0623	0.5804	+-	0.0658	-0.0285	+-	0.0906	+	-5.0	+-	16.0
Cl	0.0104	+-	0.0038	0.0124	+-	0.0046	-0.0019	+-	0.0059				
K	0.0527	+-	0.0062	0.0589	+-	0.0071	-0.0061	+-	0.0094	+	-11.0	+-	16.8
Ca	0.0437	+-	0.0052	0.0446	+-	0.0055	-0.0009	+-	0.0076	+	-2.1	+-	17.2
Sc	0.0000	+-	0.0010	0.0006	+-	0.0013	-0.0006	+-	0.0017				
Ti	0.0089	+-	0.0011	0.0109	+-	0.0015	-0.0020	+-	0.0019	0	-20.6	+-	18.8
V	0.0011	+-	0.0006	0.0002	+-	0.0009	0.0009	+-	0.0011				
Cr	0.0006	+-	0.0006	0.0013	+-	0.0008	-0.0007	+-	0.0010				
Mn	0.0004	+-	0.0009	0.0040	+-	0.0012	-0.0036	+-	0.0015				
Fe	0.1003	+-	0.0053	0.1014	+-	0.0056	-0.0011	+-	0.0076	+	-1.1	+-	7.6
Co	0.0000	+-	0.0008	0.0000	+-	0.0010	0.0000	+-	0.0013				
Ni	0.0000	+-	0.0005	0.0001	+-	0.0007	-0.0001	+-	0.0008				
Cu	0.0899	+-	0.0046	0.0902	+-	0.0048	-0.0003	+-	0.0067	+	-0.3	+-	7.4
Zn	0.0023	+-	0.0007	0.0033	+-	0.0010	-0.0010	+-	0.0012	+	-37.3	+-	43.9
Ga	0.0000	+-	0.0015	0.0000	+-	0.0022	0.0000	+-	0.0026				
As	0.0028	+-	0.0010	0.0001	+-	0.0013	0.0027	+-	0.0017				
Se	0.0013	+-	0.0008	0.0005	+-	0.0012	0.0007	+-	0.0015				
Br	0.0044	+-	0.0009	0.0034	+-	0.0012	0.0010	+-	0.0015	+	25.1	+-	38.4
Rb	0.0000	+-	0.0009	0.0000	+-	0.0012	0.0000	+-	0.0015				
Sr	0.0000	+-	0.0010	0.0001	+-	0.0014	-0.0001	+-	0.0018				
Y	0.0015	+-	0.0012	0.0000	+-	0.0017	0.0015	+-	0.0021				
Zr	0.0029	+-	0.0015	0.0000	+-	0.0020	0.0029	+-	0.0025				
Nb	0.0005	+-	0.0017	0.0000	+-	0.0023	0.0005	+-	0.0029				
Mo	0.0028	+-	0.0019	0.0000	+-	0.0027	0.0028	+-	0.0033				
Ag	0.0000	+-	0.0037	0.0042	+-	0.0055	-0.0042	+-	0.0066				
Cd	0.0017	+-	0.0039	0.0000	+-	0.0054	0.0017	+-	0.0066				
In	0.0000	+-	0.0041	0.0000	+-	0.0055	0.0000	+-	0.0068				
Sn	0.0192	+-	0.0070	0.0148	+-	0.0068	0.0044	+-	0.0097				
Sb	0.0021	+-	0.0055	0.0058	+-	0.0074	-0.0037	+-	0.0092				
Cs	0.0091	+-	0.0144	0.0174	+-	0.0199	-0.0083	+-	0.0245				
Ba	0.0189	+-	0.0196	0.0466	+-	0.0275	-0.0277	+-	0.0338				
La	0.0000	+-	0.0265	0.0000	+-	0.0368	0.0000	+-	0.0453				
Ce	0.0071	+-	0.0373	0.1106	+-	0.0529	-0.1035	+-	0.0647				
Hg	0.0000	+-	0.0017	0.0000	+-	0.0023	0.0000	+-	0.0029				
Pb	0.0005	+-	0.0022	0.0006	+-	0.0030	-0.0001	+-	0.0038				

RPD: Relative Percent Difference  $(X1-X2)/[(X1+X2)/2]*100$ . RPD is calculated when original value is greater than three times its uncertainty.

Figure 4. Weekly NIST accuracy standard report.

*Chester LabNet - Portland*

XRF-770

**XRF Analytical Quality Assurance Report**

Client: Weekly NIST Check

Analysis Period: through April 3, 2002

**1. Precision Data**

Micromatter Multi-elemental Quality Control Standard: QS285

**QC Standard Results**

Analyte	n	Counts per Second			c.v.	%E
		Calib.	Meas.	S.D.		
Si(0)	13	185.90	179.67	2.92	1.63	-3.35
Si(1)	13	11.44	11.45	0.19	1.62	0.15
Ti(2)	13	132.64	134.36	1.38	1.03	1.29
Fe(3)	13	179.51	178.77	2.36	1.32	-0.41
Se(4)	12	42.27	41.58	0.88	2.11	-1.63
Pb(4)	12	30.54	30.63	0.86	2.81	0.29
Cd(5)	13	42.52	42.60	0.64	1.50	0.17

**2. Accuracy Data**

NIST Standard Reference Materials: SRM 1832, SRM 1833

Analyte/ SRM	n	Certified Value( $\mu\text{g}/\text{cm}^2$ )	Measured Value ( $\mu\text{g}/\text{cm}^2$ )				% Rec.
			High	Low	Average		
Al 1832	45	14.6 +/- .97	15.90	13.86	14.44	+/- 0.46	98.9
Si 1832	45	34.0 +/- 1.1	38.01	33.37	34.59	+/- 1.04	101.7
Si 1833	45	33.0 +/- 2.1	33.16	30.67	32.25	+/- 0.49	97.7
S 2708	45	2.46 +/- .25	2.57	2.28	2.44	+/- 0.08	99.0
K 1833	45	17.3 +/- 1.64	17.44	16.09	16.91	+/- 0.34	97.7
Ca 1832	45	19.4 +/- 1.30	21.35	19.95	20.74	+/- 0.34	106.9
Ti 1833	45	12.8 +/- 1.79	12.85	11.72	12.28	+/- 0.37	95.9
V 1832	45	4.70 +/- .49	4.95	4.37	4.64	+/- 0.17	98.6
Mn 1832	45	4.54 +/- .49	4.84	4.56	4.69	+/- 0.06	103.3
Fe 1833	45	14.2 +/- .45	14.49	13.97	14.21	+/- 0.13	100.1
Cu 1832	45	2.43 +/- .16	2.49	2.31	2.43	+/- 0.04	99.8
Zn 1833	45	4.01 +/- .23	4.07	3.82	3.95	+/- 0.05	98.4
Pb 1833	45	16.7 +/- .85	18.26	15.97	16.94	+/- 0.46	101.5

NIST: National Institute of Standards and Technology

% Rec: Percent Recovery = (Experimental/Given) x 100

n: Number of Observations

S.D.: Standard Deviation

c.v.: Coefficient of Variation = (S.D./Measured) x 100

% E: Percent Error = [(Measured-Calibrated)/Calibrated] x 100

Stepwise warm up data for xray tube

Step	KV/mA	Time (min)
1	10 / 0.2	1
2	20 / 0.2	1
3	30 / 0.6	1
4	40 / 1.3	2
5	45 / 1.6	2
6	50 / 2.0	2
7	50 / 2.5	2
(8)	Add 2 kV each 30 seconds	

Appendix A: Deviations from Promulgated Method  
(Inorganics Air Compendium Method IO3.3)

Item	Promulgated requirement	SOP	Justification
1	Section 3: The instrument is a commercially available KeveX EDX-771 energy dispersive x-ray spectrometer which utilizes secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements.	Use four direct excitation with filtered X-rays as well as Ge target excitation.	Most secondary targets give inferior count rates requiring longer counting times. Damage to Teflon membranes is not evident.
2	Section 3: Spectral deconvolution is accomplished by a least squares algorithm which fits stored pure element library spectra and background to the sample spectrum under analysis.	Peaks are integrated using linear background subtraction.	Chester LabNet has participated in ongoing round robin trials from 2001 to present in conjunction with EPA's PM <sub>2.5</sub> Speciation Network which has demonstrated statistically significant comparability to the promulgated requirement.
3	Section 3: X-ray attenuation corrections are tailored to the fine particle layer and the discrete coarse particle fraction.	Use single particle size correction for PM <sub>2.5</sub> and PM <sub>10</sub> in conjunction with mass absorption (thickness) attenuation correction.	Analysis of Al <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , and SiO <sub>2</sub> particle standards indicate equal particle size effect between PM <sub>2.5</sub> and PM <sub>10</sub> deposits after correction for mass absorption effects.
4	Section 6: To minimize radiation damage to delicate aerosol samples only the secondary mode is used.	Use four direct excitation with filtered X-rays as well as Ge target excitation.	Most secondary targets give inferior count rates requiring longer counting times. Damage to Teflon membranes is not evident.

Item	Promulgated requirement	SOP	Justification
5	Section 6: Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background.	Use Vacuum.	Helium purge presents problems with degradation of vacuum behind the Beryllium windows of the X-ray tube and detector. Although there is a potential for loss of volatile species (most notably, Cl), Teflon filters are not recommended for collecting volatile materials.
6	Section 6: The machine is operated by procedure files (or programs) written in Kevex's proprietary Job Control Language (JCL) which runs in a Windows 3.1 environment and provides setting of the analytical conditions and data acquisition. Using the JCL language, procedures have been written in-house to perform all the functions necessary to acquire spectra and to assign to them file names in a structured manner to facilitate future spectral processing	Use iXRF PC software to control Kevex 770 spectrometers. XRF770 uses Windows 95, while XRF772 uses Windows 98. Spectral processing takes place in a proprietary EXCEL program written in-house.	PC's were upgraded to enable Ethernet connection for transferring spectral data to a central processing.

Item	Promulgated requirement	SOP	Justification
7	<p>7.3 In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.</p>	<p>Use direct W-filtered excitation.</p>	<p>This delivers higher count rates for the analytes of interest (Rh through Ce) which reduces signal to noise ratio and yields lower detection limits as well as lower overlap uncertainties for K, Ca, Sc, Ti, V, and Cr.</p>
8	<p>9.1 Spectra are acquired in sets of 15 samples each. Up to 7 spectra are acquired for each sample depending on how many secondary excitation targets are selected. Utilizing all seven fluorescers requires approximately 4 hours machine time for 44 elements analyzed plus atmospheric argon.</p>	<p>Use four direct excitation with filtered X-rays as well as Ge target excitation.</p>	<p>Most secondary targets give inferior count rates requiring longer counting times. Damage to Teflon membranes is not evident. Analysis times are on the order of 1 hour per sample.</p>

Item	Promulgated requirement	SOP	Justification
9	<p>9.2 Elemental intensities are determined by spectral deconvolution with a least squares algorithm which utilizes experimentally determined elemental shape functions instead of the mathematical Gaussian function. This approach has been successfully implemented for many years on an earlier machine and is described in Section 15, Citation 10.</p>	<p>Peaks are integrated using linear background subtraction.</p>	<p>Chester LabNet has participated in ongoing round robin trials from 2001 to present in conjunction with EPA's PM<sub>2.5</sub> Speciation Network which has demonstrated statistically significant comparability to the promulgated requirement</p>
10	<p>9.3 X-ray attenuation corrections are performed as described in Section 15, Citation 10 and are briefly described here.</p>	<p>Use single particle size correction for PM<sub>2.5</sub> and PM<sub>10</sub> in conjunction with mass absorption (thickness) attenuation correction.</p>	<p>Analysis of Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and SiO<sub>2</sub> particle standards indicate equal particle size effect between PM<sub>2.5</sub> and PM<sub>10</sub> deposits after correction for mass absorption effects. Mass absorption corrections performed as described in IO-3.3, Section 15, Citation 13.</p>

Item	Promulgated requirement	SOP	Justification
11	<p>9.5 When samples are collected by the dichotomous or other samplers using virtual impaction, an additional correction must be employed because these types of samplers do not perfectly separate the fine and coarse particles. Due to virtual impaction requirements, about 10% of the fine particle mass is deposited on the coarse filter. Therefore, the attenuation corrections used for the particles on the coarse filter "over-correct" the attenuation because of these residual fines on the coarse filter. These effects are compensated for by the flow fraction correction.</p>	<p>Use single particle size correction for PM<sub>2.5</sub> and PM<sub>10</sub> in conjunction with mass absorption (thickness) attenuation correction</p>	<p>Analysis of Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>, and SiO<sub>2</sub> particle standards indicate equal particle size effect between PM<sub>2.5</sub> and PM<sub>10</sub> deposits after correction for mass absorption effects. Mass absorption corrections performed as described in IO-3.3, Section 15, Citation 13.</p>
12	<p>10. Data Reporting Elements with concentrations below 3 times the uncertainty are flagged with an asterisk (*) on the printed record.</p>	<p>Elemental concentrations less than 3 times the uncertainty are not routinely flagged.</p>	<p>Clients may request a report format to flag data as MDL when concentrations fall below a specified threshold.</p>

Item	Promulgated requirement	SOP	Justification
13	<p>11.3 The background files which are used for background fitting are created at calibration time. Thirty clean Teflon® and Nuclepore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.</p>	<p>Ten Teflon blanks are used to determine concentrations of elements thought to be artifact to the analysis chamber. These concentrations are averaged, and subtracted then from elemental concentrations during analysis. All concentrations are derived using linear background subtraction.</p>	<p>Teflon blanks do not present a uniform background. Significant background subtraction errors can arise when the thickness of the deposit or of the Teflon membrane itself causes X-ray scatter to increase.</p>
14	<p>11.4 The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum.</p>	<p>Micromatter standards are used to profile each element's characteristic K, L, M lines. Peak centroids and Full-Width at Half Max peaks plotted versus atomic number.</p>	<p>Peak properties are well known, and are consistent throughout the life of the detector.</p>
15	<p>12. Detection Limits The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty (<math>\pm 5\%</math>); long term system stability (<math>\pm 5\%</math>);</p>	<p>No long term system stability uncertainty calculation is performed.</p>	<p>Peak and background subtraction uncertainties are considered sufficient in approximating long term stability uncertainty. Quality Assurance Standard analysis is an adequate monitor of long term stability.</p>

# CHESTER LabNet

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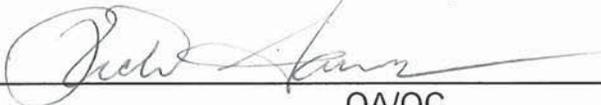
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## Standard Operating Procedure XR-004.02

### KEVEX XRF SPECTROMETER CALIBRATION CHESTER LABNET PROPRIETARY METHOD

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#### Approvals:

 _____	<u>11-25-13</u> _____
Author	Date
 _____	<u>10.17.13</u> _____
Lead Analyst	Date
 _____	<u>10.17.13</u> _____
QA/QC	Date

Effective from: 11-25-13  
Effective until: present



## KEVEX XRF SPECTROMETER CALIBRATION CHESTER LABNET PROPRIETARY METHOD

### 1.0 Introduction

- 1.1 Test Method Reference ID: Chester LabNet Proprietary Method.
- 1.2 Applicability: This method is applicable to the calibration of Kevex Model Delta 770 energy dispersive XRF (EDXRF) for all thin film matrices analyzed by Chester LabNet.
- 1.3 Detection Limit: N/A
- 1.4 Method Performance: Specificity is achieved by the KeV of each electron excitation, which is unique to each electron for each element.

### 2.0 Summary

- 2.1 Scope and Application: The intended use of this method is for the calibration of Kevex Model Delta 770 energy dispersive XRF (EDXRF). Chester LabNet currently operates two of these instruments, informally named "770" and "772". The process by which each instrument is calibrated is identical. *This method meets its intended use 11-9-15*
- 2.2 Summary of Method:
  - 2.2.1 The instruments are configured for the analytes of interest, then a series of standards and matrices are analyzed to determine the peak energies of each analyte. A response factor for each element at each excitation utilized condition is determined, and that factor is entered into the IXRF operational software. *12/1/14*
  - 2.2.2 Also determined are inter-elemental interferences and matrix differences. These factors are entered into the LabNet proprietary software, which corrects for these issues.
  - 2.2.3 Full calibration will take a minimum of 2 working days to complete.

2.2.4 Calibration should be performed only by trained operators with experience in data interpretation and instrument functioning. This SOP is designed only as a guide, and should not be used in lieu of proper training.

2.3 Interferences: As with all emissions spectrometry, secondary, tertiary, quaternary emission lines may overlap primary lines depending on the amount of interferent present.

2.4 Sample collection/preservation/shipment/storage: Thin film standards are stored at room temperature in the XRF laboratory.

### **3.0 Safety**

3.1 Follow the Chester LabNet Chemical Hygiene Plan. Always treat samples of unknown origin and/or constitution as hazardous.

3.2 This method presents no safety risk beyond typical laboratory safety hazards.

3.3 No carcinogenic reagents are used in this method.

3.4 Although X-rays are produced by the instrument at dangerous levels, the X-rays will not turn on unless a built-in interlock is fully locked, thus ensuring the user is shielded from the X-rays. Users should never remove the front cover of the instrument while the X-rays are operational, nor should they ever attempt to disable the interlock device. All users wear dosimeter badges. To date, Chester LabNet has never had a dosimeter badge showing any radiological exposure of any XRF technician.

### **4.0 Pollution Prevention and Waste Management**

4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

- 4.3.1 Acidic and Basic wastes are neutralized prior to disposing of them in the sanitary sewer system.
- 4.3.2 Organic liquids are usually primarily used for cleaning purposes. Organic wastes are generated in very small quantities, and evaporate off with no need for more formal disposal.
- 4.4 Larger quantities of known hazards are returned to the client for disposal.
- 4.5 Expired Chemicals:
  - 4.5.1 Dry chemicals beyond their <sup>5/11-9-15</sup> ~~real or arbitrary~~ expiration date are lab packed and disposed of by a qualified chemical disposal company.
  - 4.5.2 Acids and Bases beyond their <sup>5/11-9-15</sup> ~~real or arbitrary~~ expiration date are neutralized prior to being disposed of via the sanitary sewer system.
  - 4.5.3 Organic liquids beyond their <sup>5/11-9-15</sup> ~~real or arbitrary~~ expiration date are disposed of by a qualified chemical disposal company if the volume or type of liquid warrants such disposal. Disposal of organic liquids is rare.

**5.0 Apparati, Equipment and Supplies**

- 5.1 Instrument. Kevex Model Delta 770 energy dispersive XRF (EDXRF) equipped with a water-cooled end-window X-ray tube with a rhodium anode and a peak operating power of 60kV and 3.3 mA. The system was modified by IXRF Inc. to operate using Windows based software to control instrument operation. Chester LabNet currently operates two of these instruments, informally named "770" and "772". 770 is the original instrument. Its computer operates on Windows 95; 772 operates on Windows 98. Both instruments use an Ethernet connection to transfer data files to the data processing computer.
- 5.2 Thin Film Calibration Standards
  - 5.2.1 Micromatter Inc. vapor deposit of single or two non-interfering elements onto thin Mylar film.

~~5.2.2~~ EPA organo-metallic acetate film, usually with two non-interfering elements. *expired*

*Qub  
12/17/19*

5.2.3 NIST SRM's 1832 and 1833 multi-element vapor deposits on glass films.

## 6.0 Reagents and Standards

6.1 95% ethanol

6.2 Liquid Nitrogen

## 7.0 Preparation, Calibration and Standardization

7.1 Ensure the proper excitation conditions are configured within the IXRF software. Different excitation conditions are used in order to maximize the sensitivity of the analysis over a wide range of elements fluorescing at various energies. If only one energy is listed below, it is used for both instruments. The analytes appearing in **bold** type are in their most favorable excitation condition.

7.1.1 Excitation conditions for 'low-density' filter media (Teflon, Nucleopore, Mylar).

7.1.1.1 sp0: direct Rh  $L\alpha$  excitation with two Whatman no. 41 cellulose filters used as a prefilter to absorb low-energy X-rays from source. Energy: 7.5 kV. Analytes of interest: **Na, Mg, Al, Si, P, S**. Tube geometry (incident beam angle):  $\theta = 21^\circ$ .

7.1.1.2 sp1: direct Cu  $K\alpha$  excitation with 0.1mm thick Cu foil used as a prefilter. Energy: 20 kV. Analytes of interest: Al, Si, P, **S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cs, Ba, La, Ce.** Tube geometry:  $\theta = 21^\circ$

7.1.1.3 sp2: Ge secondary target. Energy 35 kV for 770, 30kV for 772. Analytes of interest: K, Ca, Ti, V, Cr, Mn, Fe, **Co, Ni, Cu, Zn, Sm, Eu, Tb**. Tube geometry:  $\theta = 45^\circ$

7.1.1.4 sp3: direct Rh  $K\alpha$  excitation with 0.15mm thick Rh foil prefilter. Energy: 35 kV. Analytes of interest: K, Ca, Ti, V, Cr, Mn, Fe, **Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Hf, Ta, W, Ir, Au, Hg, Pb**. Tube

geometry:  $\theta = 21^\circ$

7.1.1.5 sp4: direct Rh bremsstrahlung excitation with .1 mm W foil prefilter.  
Energy: 55 kV. Analytes of interest: **Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I,**  
**Cs, Ba, La, Ce.** Tube geometry:  $\theta = 21^\circ$

7.1.2 Excitation conditions for 'high-density' filter media (quartz, glass fiber, carbon impregnated).

7.1.2.1 sp0: Fe secondary target. Energy: ~~35 kV for 770~~; 25kV for ~~772~~. Analytes of interest: **Al, Si, P, S, Cl, K, Ca, Ti, V, Cr.** Tube geometry:  $\theta = 45^\circ$

7.1.2.2 sp1: Ge secondary target. Energy 35 kV for 770, 30kV for 772. Analytes of interest: K, Ca, Ti, V, Cr, **Mn, Fe, Co, Ni, Cu, Zn.** Tube geometry:  $\theta = 45^\circ$

7.1.2.3 sp2: direct Rh  $K\alpha$  excitation with 1.5 mm Rh foil prefilter. Energy: 35 kV. Analytes of interest: K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, **Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Mo, Hg, Pb.** Tube geometry:  $\theta = 21^\circ$

7.1.2.4 sp3: direct Rh bremsstrahlung excitation with .1 mm W foil prefilter.  
Energy: 55 kV. Analytes of interest: **Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I,**  
**Cs, Ba, La, Ce.** Tube geometry:  $\theta = 21^\circ$

7.2 Preparation of standards for analysis: standards are permanently mounted in sample holders and stored in a tray labeled "standards" in the XRF lab.

7.3 Characterizing peak energies:

7.3.1 Peak energies should only have to be determined if the instrument is brand new, ~~or~~ if the peaks have shifted due to detector "drift", or if the detector has been replaced. Detector "drift", or broadening of the peaks, is usually a prelude to detector failure. Characterization of peak energies should ONLY be performed by analysts with extensive knowledge of the instrument. The description below is only a brief overview of the technique.

7.3.2 Operate the XRF in manual mode.

7.3.3 Set the system up as follows:

7.3.3.1 Pressure = vacuum

7.3.3.2 Energy = defined by elements of interest

7.3.3.3 mA and kV set to approximate that needed by given element

7.3.3.4 set the filter appropriately for the element of interest

7.3.3.5 set the target appropriately for the element of interest.

7.3.3.6 Start the X-rays and acquire spectrum until the peak is of the desired height.

7.4 Obtaining Calibration Counts:

7.4.1 Analyze each standard following the protocols in SOP XR-002 (ELEMENTAL ANALYSIS OF AIR FILTERS BY X-RAY FLUORESCENCE USING A KEVEX-770 SPECTROMETER AND IXRF OPERATING SYSTEM)

7.4.2 Use the QS analytical protocol to analyze the standards at reduced power (mA).

7.5 After transferring the raw data into the Excel workbook, determine the net counts.

## 8.0 Procedure

8.1 Determine energies for each analyte/excitation condition. Energy calibration is performed using Kevex Standard No. 2036 and the Kevex software calibration option in which a low energy line is measured at the Al  $K\alpha$  line (1.487 KeV) and a high energy line is measured at the Cu  $K\alpha$  line (8.047 KeV). The program will then assign channel number 149 as the Al peak centroid, and channel 805 as the Cu peak centroid, thereby calibrating each channel increment at 10 eV.

8.2 Identify KeV location of peaks: Peak calibration is performed by analyzing thin film standards containing the elements of interest (see section 5.2). Peaks should be Gaussian-shaped with at least 2000 counts in the central channel (centroid).

8.2.1 Determine channel numbers associated with each analyte:

- 8.2.1.1 Calculate the Full-Width-at-Half-Maximum (FWHM) window for each element by dividing the number of counts in the most intense channel (usually the centroid) by two (HM).
- 8.2.1.2 Next, find the channel on the low energy side of the peak closest in counts to HM = LEHM (low-energy-at half-max).
- 8.2.1.3 Repeat this procedure for the HEHM (high-energy-at half-max).
- 8.2.1.4 The area between and including LEHM and HEHM represents the FWHM window for that element where LEHM and HEHM are defined as channel numbers. The sum of the counts in these channels should represent approximately 70% of the total area of the peak. *net* *12/27/14*
- 8.2.2 Determine peak centroids associated with analytes of interest:
- 8.2.2.1 Determine the peak centroid for each analyte contained in the standard by the following equation:  $(LEHM + HEHM) / 2$ .
- 8.2.2.2 Plot a graph of atomic number along the x-axis, versus peak centroid on the y-axis.
- 8.2.2.3 This graph should yield a smoothly varying curve sloping upward.
- 8.2.2.4 Visual interpretation of the graph, or algebraic regression can be used to approximate peak positions for elements not represented by standards.
- 8.2.3 Determine peak widths associated with analytes of interest:
- 8.2.3.1 Determine the peak width for each analyte contained in the standard by the following equation:  $(HEHM - LEHM) + 1$ .
- 8.2.3.2 Plot a graph of atomic number along the x-axis, versus peak width on the y-axis.
- 8.2.3.3 This graph should yield a smoothly varying curve sloping upward.

8.2.3.4 Visual interpretation of the graph, or algebraic regression can be used to approximate peak widths for elements not represented by standards.

8.2.3.5 Note that separate plots should be made for  $K\alpha$ ,  $L\alpha$ , and  $L\beta$  peaks.

*for each  
excitation  
condition  
Set 11-9-15*

8.2.3.6 Some peak widths and centroids for LabNet's 770 Kevex instrument are:

Analyte line	centroid (channel #)	width (no. of channels)
Si $K\alpha$	174.5	12
Fe $K\alpha$	640.5	16
Pb $L\beta$	1263.0	19
Cd $K\alpha$	2312.5	32
La $K\alpha$	3334.0	53

8.3 Determine calibration response factors for each analyte of interest:

8.3.1 Determine the calibration factor for each analyte normalized to 1.0 mA. See Section 10.4 for calculations.

8.3.2 Plot the calibration curves associated with analytes of interest:

8.3.2.1 Determine the sensitivity factor at 1mA for each analyte contained in the standard by the following equation:  $S_n = 1 / (\text{Calibration Factor} \times \text{Calibration Current (mA)})$ .

8.3.2.2 Plot a graph of atomic number along the x-axis, versus the log of the sensitivity factor on the y-axis.

8.3.2.3 This graph should yield a smoothly varying curve sloping upward, except for Tungsten filtered 55 kV, which slopes downward.

8.3.2.4 Visual interpretation of the graph, or algebraic regression can be used to approximate calibration factors for elements not represented by standards as long as the atomic number of the analyte is within the range represented on the graph. Sensitivity values lying outside the curve

should be checked by analyzing additional standards

8.3.2.5 Note that separate plots should be made for  $K\alpha$ ,  $L\alpha$ , and  $L\beta$  peaks. *for each excitation condition* *CAZ 12/17/14*

8.4 Calculate interference factors from the thin film standards used for calibration using the equations in section 10.6.

8.5 Determine the correction for  $PM_{2.5}$  particle size for Aluminum.

8.5.1 Analyze the 'fine' fractions of particulate matter deposited onto 37mm Teflon filters in the form of  $Al_2O_3$  and  $Al_2Si_2O_7$ .

8.5.2 Create the deposits by suspending the particulate matter and 'sampling' with a Sierra-Andersen dichotomous sampler. See SOP XR-001 for suspension of particulate matter onto filters.

8.5.3 The particle size attenuation effect for Al is then calculated for each standard following the equations in section 10.7.

8.6 Update the Chester LabNet XRF Data Processing MSEXcel Workbook with the newly acquired factors as follows:

8.6.1 Save the previous Calibration Workbook into the "Previous Calibration" subdirectory.

8.6.2 The peak location data are entered into the file labeled 'peaks' within the LabNet XRF Data Processing workbook.

8.6.2.1 The first column contains the element of interest.

8.6.2.2 The next four columns define:

8.6.2.2.1 the low-energy-background (LEB), where L = the low-energy channel,

8.6.2.2.2 H = the high energy channel,

8.6.2.2.3 C = the LEB centroid; and

8.6.2.2.4 # denotes the number of channels in the LEB window.

- 8.6.2.3 The next four columns represent the analyte peak and the following four columns labeled 'HEB' define the high-energy-background channels.
- 8.6.3 The calibration factors data are entered into the tab labeled 'peaks' within the LabNet XRF Data Processing workbook.
- 8.6.3.1 The column at the far right contains the calibration factors for the elements of interest normalized to 1.0 mA current.
- 8.6.3.2 The next column to the left contains the calibration factors normalized to the current (mA) used in the analysis of that excitation condition.
- 8.6.4 Enter the interference factors into the tab labeled 'IEC' within the LabNet XRF Data Processing workbook.
- 8.7 Enter the size correction factor for Al into the size/absorption correction algorithm in the LabNet XRF Data Processing Program.
- 8.8 Create a new subdirectory version and save the new MSEXcel Data Processing workbook into the new subdirectory (e.g. "Version 5", "Version 6").

## 9.0 QA/QC

- 9.1 Curve shapes for all graphs: All graphs of analyte atomic number vs. other parameter should yield a smooth quadratic line. If the graph is not quadratic, all operating parameters must be verified and the calibration performed from the beginning

## 10.0 Calculations

- 10.1 Full-Width-at Half-Maximum (FWHM) window. The area between and including LEHM and HEHM represents the FWHM window for that element. Note that the counts as described here refer to the net counts (background subtracted).

HM = [counts in the most intense channel (usually the centroid)] ÷ 2.

LEHM = [channel on the low energy side of the peak closest in counts to HM]

HEHM = [channel on the high energy side of the peak closest in counts to HM]

where: HM = counts at half maximum  
 LEHM = Low-energy-half-maximum channel number  
 HEHM = High-energy-half-maximum channel number

Note that the sum of the counts in these channels should represent approximately 70% of the total area of the peak.

10.2 Peak centroid channel number:

$$\text{Centroid} = (\text{LEHM} + \text{HEHM}) / 2$$

where: LEHM = Low-energy-half-maximum channel number  
 HEHM = High-energy-half-maximum channel number

10.3 The peak width in channels:

$$\text{Width} = (\text{HEHM} - \text{LEHM}) + 1$$

where: LEHM = Low-energy-half-maximum channel number  
 HEHM = High-energy-half-maximum channel number

10.4 Calibration factors are calculated as follows:

$$I_n = I_g - I_b$$

Where:  $I_n$  = net counts

$I_g$  = the gross counts (sum of all counts in FWHM window)

$I_b$  = the background counts (average background counts multiplied by peak width)

$$F = V / (I_n / t)$$

Where:  $F$  = the calibration factor [ $(\mu\text{g}/\text{cm}^2)/(\text{counts}/\text{second})$ ]

$t$  = the counting livetime (seconds)

$V$  = the surface equivalent value (SEV) of the element in the standard.

SEV is the absorption corrected value. Absorption effects will be discussed later in the text.

The calibration factor is then normalized to 1.0 mA as follows:

$$F_n = F \times C_c$$

Where:  $F_n$  = the calibration factor at 1.0 mA

$C_c$  = the current (mA) used during calibration

10.5 Sensitivity factors are calculated as follows:

$$S_n = 1 / F_n \text{ where } S_n \text{ represents the sensitivity factor at 1.0 mA}$$

10.6 Interference factors are calculated for spectral overlap using the data from the thin film standards used for calibration:

$$L_i = N_i / N_j$$

Where:  $L_i$  = the interference correction factor (counts/second in the window

of element i due to element j)

$N_i$  = net counts/second in window of element i

$N_j$  = net counts/sec in window of element j (interfering element)

Most spectral overlap is the result of the  $K\beta$  line of element j overlapping the  $K\alpha$  line of element i. Another common interference occurs when an L-line of element j from one excitation condition overlaps the  $K\alpha$  line of element i in a separate excitation condition. In the latter case it is necessary to normalize the correction factor (L) to 1.0 mA per second as follows:

$$L_i = (N_i / C_i T_i) / (N_j / C_j T_j)$$

Where:  $C_i$  = the current (mA) used in the excitation condition in which element i is measured.

$C_j$  = the current (mA) used in the excitation condition in which element j is measured.

$T_i$  = livetime (sec) for the excitation condition in which the element is measured.

$T_j$  = livetime (sec) for the excitation condition in which element j is

measured.

10.7 The mass absorption effect for Al and Si (independently) is then calculated for each particle size attenuation standard as follows:

10.7.1 Mass absorption coefficient

$$\mu = \sum (\mu_i w_i)$$

Where:  $\mu$  = the total mass absorption coefficient of all elements present on the incoming X-rays ( $\text{cm}^2/\text{g}$ )

$\mu_i$  = the mass absorption coefficient of each element  $i$  on the incoming X-rays

$w_i$  = the weight percent of element  $i$  in the deposit ( $0 < w_i < 1$ )

10.7.2 Total Mass absorption coefficient

$$\mu' = \sum (\mu_{i,j} w_i)$$

Where:  $\mu'$  = the total mass absorption coefficient of all elements present on the exiting (fluorescing) X-rays from element  $j$

$\mu_{i,j}$  = the mass absorption coefficient of each element  $i$  on the exiting X-rays from element  $j$ .

10.7.3 Total Mass absorption coefficient by area

$$\underline{\mu} = (\mu \csc \theta) + (\mu' \csc \theta')$$

where:  $\underline{\mu}$  = the total mass absorption coefficient ( $\text{cm}^2/\text{g}$ )

$\theta$  = the angle at which the incoming X-rays strike the sample

$\theta$  is described in sections 6.1 and 6.2 for each excitation condition

$\theta'$  = the angle at which the exiting X-rays travel to the detector and is fixed at  $45^\circ$

10.7.4 Mass absorption:

$$A = (1 - e^{-\underline{\mu}m}) / \underline{\mu}m$$

where:  $m$  = the areal density of the deposit ( $\text{g}/\text{cm}^2$ )

$A$  = mass absorption

$e$  = natural log exponent (mathematical  $e$ )

10.7.5 The net counts are corrected for the calculated absorption for each standard as follows:

$$N_c = N / A$$

Where:  $N_c$  = the absorption corrected intensity (net counts/second)

$N$  = the uncorrected net count counts/second

$A$  = mass absorption (from section 10.7.4)

10.7.6 Determine final size correction:

10.7.6.1 Plot the empirical concentration of Al for each standard along the x-axis versus the absorption corrected intensity along the y-axis.

10.7.6.2 Perform a linear regression, forcing the line through zero, such that

$$y = mx.$$

Where:  $m$  = the sensitivity factor  $[(\text{cts/s})/(\mu\text{g}/\text{cm}^2)]$ .

10.7.6.3 Calculate the size correction factor as follows:

$$A_{i,p} = S_t / S_p$$

Where:  $A_{i,p}$  = the size attenuation factor for element  $i$  at particle size  $p$

$S_t$  = the thin film calibration sensitivity factor for element  $i$

$S_p$  = the particle standard sensitivity factor which is the slope of the line derived from the linear regression above.

Simply stated, the attenuation for mass absorption has been taken into account, so that if there were no additional attenuation due to the size of the particles, then  $S_p = S_t$  and  $A_{i,p} = 1$ . Any additional attenuation would then be due to individual

particle size, and  $A_{i,p} < 1$ .  $A_p \cong 0.667$  for Al  $PM_{2.5}$ , and  $A_p \cong 1$  for Si  $PM_{2.5}$ .

## 11.0 References

- 11.1 Kevex Operator's Manual
- 11.2 Practical X-Ray Spectrometry, R. Jenkins and J.L. De Vries, second edition, Philips Technical Library, Springer-Verlag New York Inc.
- 11.3 X-Ray Fluorescence Analysis of Environmental Samples, Jaklevic, et al, Ed. by T.G. Dzubay, Ann Arbor Sci.
- 11.4 Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, T.G. Dzubay and R.O. Nelson, in Advances in X-Ray Analysis, Vol 18, 619-631.
- 11.5 Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon Membrane Filters by X-Ray Fluorescence Analysis, J.A. Cooper, L.M. Valdovinos, J.R. Sherman, W.L. Pollard, R.H. Sarver, and J.K. Weider, report by NEA, Inc., Beaverton, OR, July 15, 1987.
- 11.6 Round Robin Evaluation: Elemental Analysis of Bulk Samples and  $PM_{10}$  Loaded Teflon Filters, presented at the 82nd Annual Meeting of AWMA, Anaheim, CA, June 24-30, 1989.

## 12.0 Definitions

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.4 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.

12.5 Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements where possible.

12.6 Calibration Standard: a substance or reference material used to calibrate and instrument.

12.7 Detection Limit: the lowest concentration of an analyte of interest that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value.

12.7.1 Instrument Detection Limit (IDL): Three times the uncertainty of the measurement of a given analyte at a given concentration.

12.8 Matrix/Matrices: the component or substrate that contains the analyte of interest. In this case, the matrix should consist of a bicarbonate impregnated cellulose filter.

12.9 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.

12.10 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.

12.11 Standard: a solution or matrix of a known amount of analyte(s).

12.11.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.

### **13.0 Analysts' Notes**

13.1 N/A

Figure 1. Final calibration data sheet

SP0	LEB				Analyte				HEB				Avg Counts				Calibration	
	L	H	C	#	L	H	C	#	L	H	C	#	LEB	HEB	m	b	Factors	
Na	91	93	92	3	95	110	102.5	16	114	116	115	3	69.3	61.0	-0.3623	102.6667	0.04273	0.03205
Mg	114	116	115	3	118	133	125.5	16	133	134	133.5	2	61.0	67.0	0.3243	23.7027	0.01930	0.01447
Al	137	139	138	3	142	157	149.5	16	158	160	159	3	47.7	60.0	0.5873	-33.3810	0.00932	0.00699
Si	158	160	159	3	167	182	174.5	16	188	191	189.5	4	60.0	79.5	0.6393	-41.6557	0.00516	0.00387
P	191	192	191.5	2	193	209	201.0	17	210	211	210.5	2	78.0	98.5	1.0789	-128.6184	0.00336	0.00252
S	199	201	200	3	223	239	231.0	17	249	251	250	3	75.7	179.3	2.0733	-339.0000	0.00245	0.00184
SP1																		
Al	113	117	115	5	142	157	149.5	16	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.19094	0.57283
Si	113	117	115	5	167	182	174.5	16	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.10518	0.31555
P	113	117	115	5	193	209	201.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.06828	0.20484
S	113	117	115	5	223	239	231.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.04921	0.14764
Cl	113	117	115	5	254	270	262.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.03526	0.10577
K	298	302	300	5	324	341	332.5	18	414	416	415	3	63.6	208.3	1.2586	-313.9652	0.01943	0.05829
Ca	298	302	300	5	361	378	369.5	18	414	416	415	3	63.6	208.3	1.2586	-313.9652	0.01460	0.04381
Ti MS	113	117	115	5	443	460	451.5	18	524	528	526	5	88.8	11.4	-0.1883	110.4569		
SP2																		
K	298	302	300	5	324	341	332.5	18	421	425	423	5	78.2	55.4	-0.1854	133.8098	0.01706	0.05117
Ca	298	302	300	5	361	378	369.5	18	421	425	423	5	83.2	55.4	-0.2260	151.0049	0.01300	0.03900
Sc	298	302	300	5	401	418	409.5	18	421	425	423	5	83.2	55.4	-0.2260	151.0049	0.01026	0.03077
Ti	421	425	423	5	443	460	451.5	18	517	521	519	5	55.4	85.4	0.3125	-76.7875	0.00809	0.02427
V	421	425	423	5	487	505	496.0	19	517	521	519	5	55.4	85.4	0.3125	-76.7875	0.00633	0.01900
Cr	512	521	516.5	10	533	551	542.0	19	564	573	568.5	10	79.4	123.7	0.8519	-360.6183	0.00491	0.01474
Fe MS	316	320	318	5	631	650	640.5	20	737	741	739	5	77.8	24.6	-0.1264	117.9843		
SP3																		
Cr	420	424	422	5	533	551	542.0	19	564	568	566	5	41.4	21.4	-0.1389	100.0111	0.01279	0.03838
Mn	564	568	566	5	581	599	590.0	19	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.01033	0.03100
Fe	564	568	566	5	631	650	640.5	20	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.00826	0.02478
Co	564	568	566	5	684	703	693.5	20	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.00660	0.01981
Ni	667	671	669	5	738	758	748.0	21	767	771	769	5	20.8	27.0	0.0620	-20.6780	0.00563	0.01690
Cu	767	771	769	5	795	815	805.0	21	833	837	835	5	27.0	44.0	0.2576	-171.0758	0.00483	0.01450
Zn	833	837	835	5	854	875	864.5	22	883	887	885	5	44.0	102.8	1.1760	-937.9600	0.00404	0.01211
Sm	516	520	518	5	554	572	563.0	19	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.02698	0.08095
Eu	516	520	518	5	575	593	584.0	19	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.03800	0.11401
Tb	516	520	518	5	688	708	698.0	21	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.02563	0.07690
Ge MS	725	734	734	10	978	999	988.5	22	1136	1140	1138	5	25.7	10.6	-0.0244	38.3158		
SP4																		
Zn	767	771	769	5	854	875	864.5	22	891	895	893	5	24.2	25.4	0.0097	16.7581	0.01733	0.05200
Ga	891	895	893	5	915	936	925.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.01483	0.04450
Ge	891	895	893	5	978	999	988.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.01298	0.03895
As	1017	1021	1019	5	1044	1065	1054.5	22	1153	1157	1155	5	25.6	21.8	-0.0279	54.0721	0.01166	0.03497
Se	1017	1021	1019	5	1111	1133	1122.0	23	1153	1157	1155	5	25.6	21.8	-0.0279	54.0721	0.01086	0.03257
Br	1153	1157	1155	5	1181	1204	1192.5	24	1227	1231	1229	5	21.8	19.2	-0.0351	62.3811	0.00991	0.02973
Rb	1299	1303	1301	5	1327	1352	1339.5	26	1376	1379	1377.5	4	26.0	37.8	0.1536	-173.8268	0.00850	0.02550
Sr	1376	1379	1377.5	4	1404	1430	1417.0	27	1454	1458	1456	5	37.8	67.8	0.3828	-489.5605	0.00784	0.02351
Y	1454	1458	1456	5	1481	1508	1494.5	28	1533	1537	1535	5	67.8	105.0	0.4709	-617.8101	0.00733	0.02200
Zr	1533	1537	1535	5	1562	1590	1576.0	29	1615	1619	1617	5	105.0	158.2	0.6488	-890.8780	0.00678	0.02034
Hg	891	895	893	5	989	1010	999.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.02201	0.06604
Pb	1222	1231	1226.5	10	1252	1273	1262.5	22	1296	1305	1300.5	10	20.9	29.4	0.1149	-119.9818	0.02563	0.07688
SP5																		
Pd	2061	2080	2070.5	20	2095	2130	2112.5	36	2145	2164	2154.5	20	13.4	14.5	0.0137	-14.9961	0.01458	0.04373
Ag	2158	2177	2167.5	20	2192	2229	2210.5	38	2244	2263	2253.5	20	13.6	13.7	0.0012	11.0797	0.01402	0.04205
Cd	2258	2277	2267.5	20	2292	2331	2311.5	40	2346	2365	2355.5	20	13.8	13.7	-0.0011	16.3767	0.01375	0.04125
In	2360	2379	2369.5	20	2394	2435	2414.5	42	2450	2469	2459.5	20	14.0	15.5	0.0161	-24.1753	0.01375	0.04125
Sn	2463	2482	2472.5	20	2497	2540	2518.5	44	2555	2574	2564.5	20	15.9	18.5	0.0288	-55.3688	0.01415	0.04246
Sb	2569	2588	2578.5	20	2603	2649	2626.0	47	2664	2683	2673.5	20	17.5	23.1	0.0589	-134.5458	0.01503	0.04508
Cs	3021	3040	3030.5	20	3055	3112	3083.5	58	3127	3146	3136.5	20	39.2	49.1	0.0934	-243.8373	0.02475	0.07424
Ba	3143	3162	3152.5	20	3177	3236	3206.5	60	3251	3270	3260.5	20	47.5	55.0	0.0699	-172.9331	0.03037	0.09110
La	3265	3284	3274.5	20	3299	3361	3330.0	63	3376	3395	3385.5	20	58.3	58.7	0.0041	44.9750	0.03836	0.11508

Figure 2. Overlap correction data.

Analyte to be corrected	sp	Interferent	sp	Factor	Amount Subtracted	Corrected Net Counts	Corrected Uncertainty
K	1	Cd	5	0	0.00	0	0.00
Sn	5	Ag	5	0	0.00	110	0.00
K	1	Sn	4	0	0.00	0	0.00
Ca	1	Sn	4	0	0.00	0	0.00
Sb	5	Cd	5	0.13207	1.98	12	4.41
K	1	Sb	5	0	0.00	0	0.00
Ca	1	SB	5	0	0.00	0	0.00
Ca	1	K	1	0.07171	0.00	0	4.32
Ca	2	K	2	0.07171	5.37	45	3.05
Sc	2	Ca	2	0.092	4.12	0	4.59
Ba	5	I	5	0	0.00	10	0.00
Ti	2	BA	5	0.3332	0.00	345	0.00
Ti	2	Fe MS	2	0.0012	381.35	0	0.68
V	2	BA	5	0.1321	0.00	0	0.00
V	2	TI	2	0.13371	0.00	0	8.58
Cr	2	V	2	0.13568	0.00	0	6.69
Mn	3	CR	3	0.1257	18.74	65	4.15
Fe	3	MN	3	0.08087	5.27	415	2.50
Cu	3	Ge MS	3	0.0017	209.02	32	0.60
Pb	4	SE	4	0.07656	0.00	0	2.32
S	1	PB	4	0.11478	0.00	0	8.20
Cl	1	PB	4	0.02922	0.00	689	2.09
Cl	1	S	1	0.0175	0.00	689	0.86
Cl	1	Ti MS	1	0.0021	645.80	43	1.17
S	1	CL	1	0	0.00	0	0.00
Co	3	FE	3	0.06992	29.00	0	2.61
Sm	3	Cr	3	0.0762	11.36	0	2.51
Sm	3	Mn	3	0.0172	1.12	0	0.53
Eu	3	Cr	3	0.0611	9.11	0	2.02
Eu	3	Mn	3	0.8262	53.88	0	25.50
Tb	3	Fe	3	0.1	41.47	0	3.74
Tb	3	Co	3	0.9369	0.00	0	28.34
Co	4	FE	4	0.06007	10.75	0	2.18
Ga	4	PB	4	0.06488	0.00	28	2.16
As	4	PB	4	1.200648	0.00	0	0.00
Ge	4	ZN	3	0	0.00	0	0.00
Ge	4	Hg	4	0	0.00	0	0.00
Br	4	AS	4	0.04556	0.00	43	1.40
Rb	4	BR	4	0.13207	5.73	24	4.24
Y	4	PB	4	0.06959	0.00	0	1.78
Y	4	RB	4	0	0.00	0	0.00
Hf	4	Pb	4	0.0174	0.00	0	0.58
Hf	4	Cu	4	0.0883	13.99	0	3.05
Ga	4	Ta	4	0.65672	41.21	0	22.59

Figure 3. Interelement energy absorption table (see section 10.7)

## Kevex Absorption Table

	Incom	Incom	Exit	Exit	Exit	Exit	Exit	Exit	Exit	Exit	Exit	Exit
	Rh L $\alpha$	Ti K $\alpha$	Na K $\alpha$	Mg K $\alpha$	Al K $\alpha$	Si K $\alpha$	P K $\alpha$	S K $\alpha$	Cl K $\alpha$	K K $\alpha$	Ca K $\alpha$	Ti K $\alpha$
csc	1.071	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142	1.4142
C	116	26	1780	1050	640	400	263	175	125	61	45	26
O	275	63	4000	2440	1520	965	633	435	300	162	115	63
Na	650	163	8160	4925	3395	2100	1480	1030	715	366	276	163
Mg	850	212	580	350	4050	2660	1794	1330	930	490	367	212
Al	1035	263	850	500	330	3170	2223	1610	1130	595	450	263
Si	1265	328	1230	740	480	315	2645	1960	1375	735	556	328
P	1435	389	1640	1015	650	435	300	2180	1570	850	648	389
S	1770	453	2100	1320	795	525	355	250	1920	1030	671	453
Cl	190	512	2500	1570	960	635	435	300	210	1140	870	512
K	280	689	3425	2120	1300	855	593	425	305	162	606	689
Ca	320	780	3850	2380	1500	980	710	480	345	185	142	780
Ti	425	114	4680	2975	2000	1300	905	645	455	250	190	114
V	480	129	5050	3260	2200	1460	1020	730	520	280	215	129
Cr	550	153	5480	3510	2470	1670	1165	835	590	320	247	153
Mn	675	171	5895	3790	2700	1920	1310	935	665	360	279	171
Fe	700	193	6275	4100	2910	2040	1465	1070	760	410	317	193
Co	735	198	6640	4380	3070	2195	1565	1160	790	435	341	198
Ni	830	244	6800	4540	3140	2225	1675	1260	900	490	379	244
Cu	885	262	7550	5035	3450	2415	1780	1350	960	530	419	262
Zn	1050	292	0	5235	3645	2510	1915	1460	1130	595	480	292
Ga	1145	300	0	0	3810	2645	2025	1575	1225	700	508	300
Ge	1210	325	0	0	3995	2750	2145	1670	320	760	543	325
As	1310	340	1580	1020	0	2880	2490	1795	1420	820	595	340
Se	1380	380	1740	1110	0	3010	2620	1930	1530	925	660	380
Br	1410	480	1875	1190	840	0	2528	2060	1615	1025	703	480
Rb	1630	455	2200	1380	950	710	0	2330	1810	1190	805	455
Sr	1740	180	2400	1500	1020	760	0	2465	1910	1260	875	180
Y	1875	515	2555	1820	1080	810	648	0	2020	1310	938	515
Zr	1940	580	2755	1740	1155	855	688	0	2125	1390	995	580
Mo	0	720	3180	2005	1315	990	788	630	0	1540	1190	720
Pd	550	890	4100	2590	1675	1260	1000	800	590	0	683	890
Ag	585	925	4230	2700	1800	1350	1058	860	625	355	1365	925
Cd	620	1025	4660	2930	1880	1415	1120	890	665	385	0	1025
In	650	1065	4880	3080	1975	1480	1175	930	700	400	170	1065
Sn	720	1020	5300	3360	2280	1475	1235	990	760	435	348	1020
Sb	730	0	5510	3500	2355	1660	1310	1050	780	455	368	0
Te	770	0	5825	3650	2500	1740	1375	1100	825	480	385	0
I	805	265	0	3870	2645	1840	1453	1160	870	505	405	265
Cs	0	0	0	0	0	2010	0	0	0	0	0	0
Ba	940	310	0	0	0	2130	1680	1345	1010	585	473	310
La	980	325	0	0	0	2210	1760	1400	1055	610	495	325
Hg	0	880	0	0	0	0	0	0	0	0	1435	880
Pb	0	935	0	0	0	0	0	0	0	0	1500	935
$\Sigma$	35506	17549	131275	92680	72480	64755	51324	44600	37550	24576	23043	17549

Appendix A: Deviations from Promulgated Method  
(Inorganics Air Compendium Method IO3.3)

Item	Promulgated requirement	SOP	Justification
1	Section 3: The instrument is ... calibrated with thin metal foils and salts for 44 chemical elements.	Instruments are calibrated using primarily vapor deposited Mylar standards.	Vapor deposits yield a more uniform deposit than salt deposits. Mylar has negligible background.
2	Section 3: Spectral deconvolution is accomplished by a least squares algorithm which fits stored pure element library spectra and background to the sample spectrum under analysis.	Peaks are integrated using linear background subtraction.	Chester LabNet has participated in ongoing round robin trials from 2001 to present in conjunction with EPA's PM <sub>2.5</sub> Speciation Network which has demonstrated statistically significant comparability to the promulgated requirement.
3	Section 6: Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background.	Use Vacuum.	Helium purge presents problems with degradation of vacuum behind the Beryllium windows of the X-ray tube and detector. Although there is a potential for loss of volatile species (most notably, Cl), Teflon filters are not recommended for collecting volatile materials.

Item	Promulgated requirement	SOP	Justification
4	<p>Section 6: The machine is operated by procedure files (or programs) written in KeveX's proprietary Job Control Language (JCL) which runs in a Windows 3.1 environment and provides setting of the analytical conditions and data acquisition. Using the JCL language, procedures have been written in-house to perform all the functions necessary to acquire spectra and to assign to them file names in a structured manner to facilitate future spectral processing</p>	<p>Use iXRF PC software to control KeveX 770 spectrometers. XRF770 uses Windows 95, while XRF772 uses Windows 98. Spectral processing takes place in a proprietary EXCEL program written in-house.</p>	<p>PC's were upgraded to enable Ethernet connection for transferring spectral data to a central processing.</p>
5	<p>7.3 In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.</p>	<p>Use direct W-filtered excitation.</p>	<p>This delivers higher count rates for the analytes of interest (Rh through Ce) which reduces signal to noise ratio and yields lower detection limits as well as lower overlap uncertainties for K, Ca, Sc, Ti, V, and Cr.</p>

Item	Promulgated requirement	SOP	Justification
6	9.2 Elemental intensities are determined by spectral deconvolution with a least squares algorithm which utilizes experimentally determined elemental shape functions instead of the mathematical Gaussian function. This approach has been successfully implemented for many years on an earlier machine and is described in Section 15, Citation 10.	Peaks are integrated using linear background subtraction.	Chester LabNet has participated in ongoing round robin trials from 2001 to present in conjunction with EPA's PM <sub>2.5</sub> Speciation Network which has demonstrated statistically significant comparability to the promulgated requirement
7	11.2 Approximately 200 calibration standards for 44 elements are in use (see Table 4.) and the acquisition of their spectra requires several days.	Approximately 60 standards are used for calibration.	The standards in use have proved to be sufficient in providing a reliable calibration.

Item	Promulgated requirement	SOP	Justification
8	<p>11.3 The background files which are used for background fitting are created at calibration time. Thirty clean Teflon® and Nucleopore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.</p>	<p>Ten Teflon blanks are used to determine concentrations of elements thought to be artifact to the analysis chamber. These concentrations are averaged, and subtracted then from elemental concentrations during analysis. All concentrations are derived using linear background subtraction.</p>	<p>Teflon blanks do not present a uniform background. Significant background subtraction errors can arise when the thickness of the deposit or of the Teflon membrane itself causes X-ray scatter to increase.</p>
9	<p>11.4 The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum.</p>	<p>Micromatter standards are used to profile each element's characteristic K, L, M lines. Peak centroids and Full-Width at Half Max peaks plotted versus atomic number.</p>	<p>Peak properties are well known, and are consistent throughout the life of the detector.</p>
10	<p>12. Detection Limits The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty (<math>\pm 5\%</math>); long term system stability (<math>\pm 5\%</math>);</p>	<p>No long term system stability uncertainty calculation is performed.</p>	<p>Peak and background subtraction uncertainties are considered sufficient in approximating long term stability uncertainty. Quality Assurance Standard analysis is an adequate monitor of long term stability.</p>

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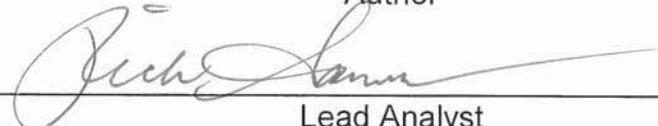
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## Standard Operating Procedure XR-005.02

### KEVEX SPECTROMETER DATA GENERATION, INTERPRETATION AND REPORTING CHESTER LABNET PROPRIETARY METHOD

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#### Approvals:

 _____ Author	<u>12-6-13</u> _____ Date
 _____ Lead Analyst	<u>12-9-13</u> _____ Date
 _____ QA/QC	<u>12-6-13</u> _____ Date

Effective from: 12-9-13  
Effective until: present



# KEVEX SPECTROMETER DATA GENERATION, INTERPRETATION AND REPORTING CHESTER LABNET PROPRIETARY METHOD

## 1.0 Introduction

- 1.1 Test Method Reference ID: Chester LabNet Proprietary method
- 1.2 Applicability: This method is applicable to data generated by the Kevex Model Delta 770 energy dispersive XRF (EDXRF).
- 1.3 Detection Limit: N/A
- 1.4 Method Performance: N/A

## 2.0 Summary

- 2.1 Scope and Application: This intended use of this method is for the production, interpretation and reporting of data generated by the Kevex Model Delta 770 energy dispersive XRF (EDXRF). Chester LabNet currently operates two of these instruments, informally named "770" and "772". The process by which data is processed from each of these instruments is essentially identical. This SOP should never be performed by anyone lacking extensive XRF data processing and interpretation skills. *This method meets its intended use. See 11.9.15*
- 2.2 Summary of Method: Once analysis is complete, data is transferred to a data processing computer, where it is processed from raw counts to final concentrations. During this process, the data is checked for spectral interferences and corrected for interelement interferences as well as particle size and self-absorption affects. The final processed data is then transferred to the LIMS.
- 2.3 Interferences: N/A.
- 2.4 Sample collection/preservation/shipment/storage: N/A

### 3.0 Safety

3.1 This method poses no risks beyond those normally associated with computer usage.

### 4.0 Pollution Prevention and Waste Management

4.1 No chemicals are utilized in this method.

### 5.0 Apparati, Equipment and Supplies

5.1 Data processing computer <sup>SH 11-9-15</sup> ~~loaded with~~ <sup>running a</sup> Windows compatible operating system, Microsoft excel and Chester LabNet's proprietary data processing spreadsheets.

5.2 Flash drive(s)

### 6.0 Reagents and Standards

6.1 N/A

### 7.0 Preparation, Calibration and Standardization

7.1 Samples should already be analyzed as per SOP XR-002.

### 8.0 Procedure

8.1 Transfer the spectral files:

8.1.1 From the 770 and 772 data collection computer, copy all spectral files associated with the analytical run onto the proper subdirectory on the data processing computer. Spectral file names have a ".sp" extension in their names.

8.2 Process the QS data.

8.2.1 Open the QS processing workbook in Excel.

- 8.2.2 Enter the QS (Quality Standard) ID to be processed in the cell labeled "QGSNIST".
- 8.2.3 click 'Start'.
- 8.2.4 After processing is complete, verify that the QS data has passed QC by checking the data in the QS tab of the worksheet. Print out the QS data sheet and keep it with the XRF request form for that particular analysis.
- 8.2.5 Enter the date of analysis and the normalized gross counts per second for each element in each excitation condition. Next, enter the XRF run number, analysis protocol, and number of samples analyzed into the proper '770QS' or '772QS' archive file.

### 8.3 Process Sample Data.

- 8.3.1 Open the appropriate LabNet XRF Data Processing workbook and select the 'IDs' worksheet. Also open a blank report workbook and rename it as ANNN-XXX where:

A = the client letter prefix

NNN = the client number, and

XXX = the run number

Save this file as a .xls file.

- 8.3.2 In the LabNet XRF Data Processing workbook, return to the 'IDs' worksheet.
- 8.3.3 In the 'IDs' worksheet, enter the following demographics for each sample, as expressed on the XRF runsheet: file name, LIMS ID, Particle Size, deposit mass, deposit area.
- 8.3.4 After all demographics have been entered, highlight and copy them to the 'SAMPLE LOG' worksheet in the workbook created in section 8.3.1.

8.3.5 Return to the 'IDs' worksheet in the Processing workbook and left click on the *Start* button.

8.3.6 When the calculations have been completed, the program will move to the 'LIMS(2)' window. At this point:

- the peaks have been integrated and corrected for spectral overlap interference as described in section 10.1.
- the particle size corrections have been made for Al, Na, Mg and Si as described in section 10.3.
- the net uncertainty for each final concentration has been determined as described in section 10.4.

8.3.7 Create a report file:

8.3.7.1 Select the proper LIMS format worksheet within the processing workbook (XRF, RTI, Precise, etc). Highlight the data, along with the header, and copy to the LIMS worksheet in the report workbook created in 8.3.1. This worksheet will automatically calculate the best candidates for the replicate sample analysis. The number of analytes which are both greater than 3x their uncertainty and greater than the mean value for each analyte in the group of samples analyzed will be displayed in a column at the far right-hand side of the file. Once the replicate sample has been chosen, perform the analysis using the same analysis protocol.

8.3.7.2 Amend the "SAMPLE LOG" worksheet in the report workbook with the replicate ID (normally the original sample ID with an "R" prefix) and the proper demographics. If the replicate is run on a different instrument, use the prefix "X" and the original sample ID. Once the replicate analysis has been performed, the processing can commence by copying the updated demographics to the ID worksheet in a newly opened processing workbook, and pressing "START" as in 8.3.5.

8.3.7.3 When the processing is completed, go to the "result (2)" worksheet. This file contains the raw data as well as corrected concentrations for each

excitation condition for each sample. Create a copy of the raw data in the proper format for printing on the <sup>dot matrix if 24 pins</sup> line printer by executing the following commands:

- 8.3.7.3.1 edit
- 8.3.7.3.2 move or copy sheet
- 8.3.7.3.3 create a copy
- 8.3.7.3.4 to book (new book)
- 8.3.7.3.5 ok
- 8.3.7.3.6 Save this file as a .prn file using the same filename as the report workbook (ANNN-XXX.prn).

8.3.7.4 Move the .prn file to the report workbook using the following commands:

- 8.3.7.4.1 edit
- 8.3.7.4.2 move or copy sheet
- 8.3.7.4.3 to book (ANNN-XXX.xls)
- 8.3.7.4.4 In the report workbook, go to the raw sample analysis (ANNN-XXX) worksheet and scroll down to the replicate "Corrected Conc." Section (bottom of page).
- 8.3.7.4.5 Highlight the area starting one row above the "Lab ID" header, down through the uncertainty for the last analyte in the "Corrected Conc." Column.
- 8.3.7.4.6 Copy the highlighted portion to the "Replicate" worksheet in the report workbook and *paste values* into cell "A1". (note: using the normal paste function rather than the paste values function will cause errors in the worksheet).

8.3.7.5 Return to the raw data worksheet (ANNN-XXX) and scroll up to the "Corrected Conc." section of the original analysis. Highlight and copy the data to the "Original" worksheet as described in 8.3.7.4.

8.3.7.6 Proceed to the "report" worksheet within the report workbook. The replicate report will appear, ready to print. Print the replicate report on the Laser Jet printer.

8.3.7.7 Save and close the report file.

8.3.7.8 Print the entire raw data file using the "Command Prompt" program.

8.3.7.8.1 Go to the subdirectory into which the file has been saved (XRF or 772) using the command "cd/XRF" or "cd/772."

8.3.7.8.2 Print the raw data on the dot matrix printer using the command "p ANNN-XXX.prn."

8.3.7.9 Keep all printouts with the XRF run sheet prior to inspection, QA, and LIMS entry.

8.4 At this point, the processed data is checked for anomalies and corrections made in the 'LIMS' worksheet of the run file. Some anomalies include:

8.4.1 Over-subtraction of very intense peaks. Peaks that exceed 10000x the background counts can become over-corrected for background counts as the background subtraction channels begin to 'ride' up the sides of the analyte peak.

8.4.2 'False positives' for analytes in the 'noisier' background regions of the spectra; most notably Rh through La in the high energy (55 kV) excitation condition, and Y through Mo in the 35 kV direct excitation condition.

8.4.3 *Only a qualified XRF spectroscopist should critique the XRF spectra. Data corrections are made in red ink on the XRF printout. The data is then amended with the corrections.*

8.5 Once the data file has been amended and saved, transfer the data to the LIMS.

8.5.1 When all data changes and corrections have been made and saved in the XRF Run workbook, save a copy of the LIMS data for importing into the LIMS.

8.5.1.1 Go to the LIMS worksheet in the run file workbook.

8.5.1.2 Select all Sample IDs, concentrations and uncertainties and copy to a new workbook. Do not select the header row (Row 1).

8.5.1.3 Save this new workbook into the worklist directory as WWWW.csv, where WWWW is the worklist name.

8.5.2 Transfer the worklist from the worklist directory onto the LIMS as described in SOP AD-007, "Laboratory Information Management System"

8.6 Archive raw data:

8.6.1 Hardcopy data is archived by client name, project number, and analysis date. In each file the following documents are kept: run sheets, QS reports, replicate reports and the XRF data printouts. These files are held for three years prior to disposal, unless otherwise requested.

8.6.2 Electronic data is archived on the C drive of the data processing computer and on a flash drive. Each instrument has an associated subdirectory for archived data. The data files are moved into a subdirectory and named after the report number. The files are copied onto the LIMS computer, which is backed up weekly, for archiving.

## 9.0 QA/QC

9.1.1 N/A

## 10.0 Calculations

10.1 Peaks are integrated and corrected for spectral overlap interference in the following sequence:

$G_{i,j}$  = the sum of all counts in the FWHM window for element  $i$  in excitation condition  $j$  (gross counts)

$$B_{i,j} = n_{i,j} (mx + b) = \text{the background counts}$$

where:  $n_{i,j}$  = the number of channels in the FWHM window for element  $i$  in excitation condition  $j$ .

$x$  = the channel number of the centroid of the FWHM window for element  $i$  in excitation condition  $j$ .

$$m = \text{the slope of the background} = (\Sigma_h - \Sigma_l) / (C_h - C_l)$$

where:  $\Sigma_h$  = the sum of the counts in the HEB window for element  $i$  in excitation condition  $j$  (see figure 1).

$\Sigma_l$  = the sum of the counts in the LEB window for element  $i$  in excitation condition  $j$ .

$C_h$  = the centroid for the HEB window for element  $i$  in excitation condition  $j$ .

$C_l$  = the centroid for the LEB window for element  $i$  in excitation condition  $j$ .

$b$  = the y-intercept of the background =  $\Sigma_h - (m C_h)$

$$N_{i,j} = G_{i,j} - B_{i,j}$$

where:  $N_{i,j}$  = net counts in the FWHM window for element  $i$  in excitation condition  $j$ .

$$N_{c,i,j} = N_{i,j} - \Sigma(L_{n,i,j} N_j)$$

where:  $N_{c,i,j}$  = the interference corrected net counts for element  $i$  in excitation condition  $j$ .

$L_{n,i,j}$  = the normalized interference correction factor for element  $i$  from element  $j$ .

$N_j$  = the net counts for interfering element  $j$ .

$$L_{n,i,j} = L_{i,j} [(t_i C_i) / (t_j C_j)]$$

where:  $L_{i,j}$  = the interference correction factor for element  $i$  from element  $j$ .  
 $t_i$  = the counting livetime for the excitation condition in which element  $i$  was analyzed.

$C_i$  = the current (mA) used for the excitation condition in which element  $i$  was analyzed.

$t_j$  = the counting livetime for the excitation condition in which the interfering element  $j$  was analyzed.

$C_j$  = the current (mA) used for the excitation condition in which the interfering element  $j$  was analyzed.

$$C = (N_{c,i,j} F_n C_i) / t$$

where:  $C$  = the empirical concentration ( $\mu\text{g}/\text{cm}^2$ )

$F_n$  = the normalized calibration factor  $[(\mu\text{g}/\text{cm}^2) / (\text{cts}/\text{sec})]$   
 $t$  = the counting livetime (sec)

10.2 The absorption corrected concentration is calculated using the mass absorption coefficients:

$$C_a = C / A$$

where:  $C_a$  = the absorption corrected concentration ( $\mu\text{g}/\text{cm}^2$ )  
 $C$  = the empirical concentration ( $\mu\text{g}/\text{cm}^2$ )  
 $A$  = the absorption correction factor

The absorption correction algorithm is iterative and begins its corrections with  $C_a$ . All detected analytes are divided by the areal density of the deposit ( $\mu\text{g}/\text{cm}^2$ ) to determine their mass fractions. The carbon mass fraction ( $mf_c$ ) is then estimated:

$$mf_c = (1 - (\sum mf_i + \sum mf_{io})) / 1.3$$

where:  $mf_i$  = the mass fraction of element  $i$   
 $mf_{io}$  = the mass fraction of oxygen related to element  $i$

The oxygen mass fraction ( $mf_o$ ) is then estimated:

$$mf_o = 1 - (\sum mf_i + mf_c)$$

The absorption correction algorithm then takes the corrected  $C_a$  concentration into account as it sequentially moves to correct K, then Cl...to Na

10.3 The particle size corrections for Na, Mg, Al, Si are determined as follows:

$$C_{a,s} = C_a / A_p$$

where:  $C_{a,s}$  = the size and absorption corrected concentration ( $\mu\text{g}/\text{cm}^2$ )  
 $A_p$  = size correction factor

10.4 The net uncertainty for each final concentration is determined as follows:

$$\delta_{\text{conc}} = (\delta_{\text{net}} F_n) / t$$

where:  $\delta_{\text{conc}}$  = the net concentration uncertainty ( $\mu\text{g}/\text{cm}^2$ )

$F_n$  = the normalized calibration factor (Section 6.4.4)

$t$  = counting livetime

$$\delta_{\text{net}} = (\delta_c^2 + \delta_l^2 + \delta_s^2 + \delta_a^2)^{1/2}$$

where:  $\delta_{\text{net}}$  = the net uncertainty (counts)

$$\delta_c = (G+B)^{1/2}$$

where:  $\delta_c$  = is the counting uncertainty expressed as a function of the uncorrected net counts

$G$  = the gross counts in the FWHM window

$B$  = the background counts in the FWHM window

$$\delta_l = \sum (\delta_{c,j} L_{n,j})$$

where:  $\delta_l$  = is the spectral overlap uncertainty (counts)

$\delta_{c,j}$  = the counting uncertainty for each interfering element  $j$ .

$L_{n,j}$  = the normalized spectral overlap correction factor for each interfering element  $j$  (step 6.4.7)

$$\delta_s = 0.05 N_c$$

where:  $\delta_s$  = the calibration uncertainty which is assumed to be 5% as per manufacturer's specification.

$N_c$  = net counts corrected for spectral overlap

$$\delta_a = (\delta_c^2 + \delta_l^2 + \delta_s^2)^{1/2} / (A^2 A_p^2)$$

where:  $\delta_a$  = the absorption correction uncertainty (counts)

$A$  = the absorption correction factor (steps 6.5.1 through 6.5.4)

$A_p$  = the size correction factor

## 11.0 References

11.1 Kevex Operator's Manual

11.2 Practical X-Ray Spectrometry, R. Jenkins and J.L. De Vries, second edition, Philips Technical Library, Springer-Verlag New York Inc.

11.3 X-Ray Fluorescence Analysis of Environmental Samples, Jaklevic, et al, Ed. by T.G. Dzubay, Ann Arbor Sci.

- 11.4 Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, T.G. Dzubay and R.O. Nelson, in Advances in X-Ray Analysis, Vol 18, 619-631.
- 11.5 Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon Membrane Filters by X-Ray Fluorescence Analysis, J.A. Cooper, L.M. Valdovinos, J.R. Sherman, W.L. Pollard, R.H. Sarver, and J.K. Weider, report by NEA, Inc., Beaverton, OR, July 15, 1987.
- 11.6 Round Robin Evaluation: Elemental Analysis of Bulk Samples and PM<sub>10</sub> Loaded Teflon Filters, presented at the 82nd Annual Meeting of AWMA, Anaheim, CA, June 24-30, 1989.

## **12.0 Definitions**

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.4 Laboratory Information Management System (LIMS): a comprehensive computerized database system that a laboratory uses for sample tracking and data management, from sample receipt to reporting and archiving.
- 12.5 Matrix/Matrices: the component or substrate that contains the analyte of interest. In this case, the matrix should consist of a bicarbonate impregnated cellulose filter.
- 12.6 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.7 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.

**13.0 Analysts' Notes**

13.1 N/A

SP0	LEB				Analyte				HEB				Avg Counts				Calibration	
	L	H	C	#	L	H	C	#	L	H	C	#	LEB	HEB	m	b	Factors	
Na	91	93	92	3	95	110	102.5	16	114	116	115	3	69.3	61.0	-0.3623	102.6667	0.04273	0.03205
Mg	114	116	115	3	118	133	125.5	16	133	134	133.5	2	61.0	67.0	0.3243	23.7027	0.01930	0.01447
Al	137	139	138	3	142	157	149.5	16	158	160	159	3	47.7	60.0	0.5873	-33.3810	0.00932	0.00699
Si	158	160	159	3	167	182	174.5	16	188	191	189.5	4	60.0	79.5	0.6393	-41.6557	0.00516	0.00387
P	191	192	191.5	2	193	209	201.0	17	210	211	210.5	2	78.0	98.5	1.0789	-128.6184	0.00336	0.00252
S	199	201	200	3	223	239	231.0	17	249	251	250	3	75.7	179.3	2.0733	-339.0000	0.00245	0.00184
<b>SP1</b>																		
Al	113	117	115	5	142	157	149.5	16	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.19094	0.57283
Si	113	117	115	5	167	182	174.5	16	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.10518	0.31555
P	113	117	115	5	193	209	201.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.06828	0.20484
S	113	117	115	5	223	239	231.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.04921	0.14764
Cl	113	117	115	5	254	270	262.0	17	298	302	300	5	88.8	63.6	-0.1362	104.4649	0.03526	0.10577
K	298	302	300	5	324	341	332.5	18	414	416	415	3	63.6	208.3	1.2586	-313.9652	0.01943	0.05829
Ca	298	302	300	5	361	378	369.5	18	414	416	415	3	63.6	208.3	1.2586	-313.9652	0.01460	0.04381
Ti MS	113	117	115	5	443	460	451.5	18	524	528	526	5	88.8	11.4	-0.1883	110.4569		
<b>SP2</b>																		
K	298	302	300	5	324	341	332.5	18	421	425	423	5	78.2	55.4	-0.1854	133.8098	0.01706	0.05117
Ca	298	302	300	5	361	378	369.5	18	421	425	423	5	83.2	55.4	-0.2260	151.0049	0.01300	0.03900
Sc	298	302	300	5	401	418	409.5	18	421	425	423	5	83.2	55.4	-0.2260	151.0049	0.01026	0.03077
Ti	421	425	423	5	443	460	451.5	18	517	521	519	5	55.4	85.4	0.3125	-76.7875	0.00809	0.02427
V	421	425	423	5	487	505	496.0	19	517	521	519	5	55.4	85.4	0.3125	-76.7875	0.00633	0.01900
Cr	512	521	516.5	10	533	551	542.0	19	564	573	568.5	10	79.4	123.7	0.8519	-360.6183	0.00491	0.01474
Fe MS	316	320	318	5	631	650	640.5	20	737	741	739	5	77.8	24.6	-0.1264	117.9843		
<b>SP3</b>																		
Cr	420	424	422	5	533	551	542.0	19	564	568	566	5	41.4	21.4	-0.1389	100.0111	0.01279	0.03838
Mn	564	568	566	5	581	599	590.0	19	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.01033	0.03100
Fe	564	568	566	5	631	650	640.5	20	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.00826	0.02478
Co	564	568	566	5	684	703	693.5	20	726	730	728	5	21.4	27.6	0.0383	-0.2617	0.00660	0.01981
Ni	667	671	669	5	738	758	748.0	21	767	771	769	5	20.8	27.0	0.0620	-20.6780	0.00563	0.01690
Cu	767	771	769	5	795	815	805.0	21	833	837	835	5	27.0	44.0	0.2576	-171.0758	0.00483	0.01450
Zn	833	837	835	5	854	875	864.5	22	883	887	885	5	44.0	102.8	1.1760	-937.9600	0.00404	0.01211
Sm	516	520	518	5	554	572	563.0	19	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.02698	0.08095
Eu	516	520	518	5	575	593	584.0	19	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.03800	0.11401
Tb	516	520	518	5	688	708	698.0	21	726	730	728	5	34.2	27.6	-0.0314	50.4800	0.02563	0.07690
Ge MS	725	734	518	10	978	999	988.5	22	1136	1140	1138	5	25.7	10.6	-0.0244	38.3158		
<b>SP4</b>																		
Zn	767	771	769	5	854	875	864.5	22	891	895	893	5	24.2	25.4	0.0097	16.7581	0.01733	0.05200
Ga	891	895	893	5	915	936	925.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.01483	0.04450
Ge	891	895	893	5	978	999	988.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.01298	0.03895
As	1017	1021	1019	5	1044	1065	1054.5	22	1153	1157	1155	5	25.6	21.8	-0.0279	54.0721	0.01166	0.03497
Se	1017	1021	1019	5	1111	1133	1122.0	23	1153	1157	1155	5	25.6	21.8	-0.0279	54.0721	0.01086	0.03257
Br	1153	1157	1155	5	1181	1204	1192.5	24	1227	1231	1229	5	21.8	19.2	-0.0351	62.3811	0.00991	0.02973
Rb	1299	1303	1301	5	1327	1352	1339.5	26	1376	1379	1377.5	4	26.0	37.8	0.1536	-173.8268	0.00850	0.02550
Sr	1376	1379	1377.5	4	1404	1430	1417.0	27	1454	1458	1456	5	37.8	67.8	0.3828	-489.5605	0.00784	0.02351
Y	1454	1458	1456	5	1481	1508	1494.5	28	1533	1537	1535	5	67.8	105.0	0.4709	-617.8101	0.00733	0.02200
Zr	1533	1537	1535	5	1562	1590	1576.0	29	1615	1619	1617	5	105.0	158.2	0.6488	-890.8780	0.00678	0.02034
Hg	891	895	893	5	989	1010	999.5	22	1017	1021	1019	5	25.4	25.6	0.0016	23.9825	0.02201	0.06604
Pb	1222	1231	1226.5	10	1252	1273	1262.5	22	1296	1305	1300.5	10	20.9	29.4	0.1149	-119.9818	0.02563	0.07688
<b>SP5</b>																		
Pd	2061	2080	2070.5	20	2095	2130	2112.5	36	2145	2164	2154.5	20	13.4	14.5	0.0137	-14.9961	0.01458	0.04373
Ag	2158	2177	2167.5	20	2192	2229	2210.5	38	2244	2263	2253.5	20	13.6	13.7	0.0012	11.0797	0.01402	0.04205
Cd	2258	2277	2267.5	20	2292	2331	2311.5	40	2346	2365	2355.5	20	13.8	13.7	-0.0011	16.3767	0.01375	0.04125
In	2360	2379	2369.5	20	2394	2435	2414.5	42	2450	2469	2459.5	20	14.0	15.5	0.0161	-24.1753	0.01375	0.04125
Sn	2463	2482	2472.5	20	2497	2540	2518.5	44	2555	2574	2564.5	20	15.9	18.5	0.0288	-55.3688	0.01415	0.04246
Sb	2569	2588	2578.5	20	2603	2649	2626.0	47	2664	2683	2673.5	20	17.5	23.1	0.0589	-134.5458	0.01503	0.04508
Cs	3021	3040	3030.5	20	3055	3112	3083.5	58	3127	3146	3136.5	20	39.2	49.1	0.0934	-243.8373	0.02475	0.07424
Ba	3143	3162	3152.5	20	3177	3236	3206.5	60	3251	3270	3260.5	20	47.5	55.0	0.0699	-172.9331	0.03037	0.09110
La	3265	3284	3274.5	20	3299	3361	3330.0	63	3376	3395	3385.5	20	58.3	58.7	0.0041	44.9750	0.03836	0.11508

Figure 1. Example calibration data used in data processing.

Figure 2. Example overlap correction factors used in data processing.

Analyte to be corrected	sp	Interferent	sp	Factor	Amount Subtracted	Corrected Net Counts	Corrected Uncertainty
K	1	Cd	5	0	0.00	0	0.00
Sn	5	Ag	5	0	0.00	110	0.00
K	1	Sn	4	0	0.00	0	0.00
Ca	1	Sn	4	0	0.00	0	0.00
Sb	5	Cd	5	0.13207	1.98	12	4.41
K	1	Sb	5	0	0.00	0	0.00
Ca	1	SB	5	0	0.00	0	0.00
Ca	1	K	1	0.07171	0.00	0	4.32
Ca	2	K	2	0.07171	5.37	45	3.05
Sc	2	Ca	2	0.092	4.12	0	4.59
Ba	5	I	5	0	0.00	10	0.00
Ti	2	BA	5	0.3332	0.00	345	0.00
Ti	2	Fe MS	2	0.0012	381.35	0	0.68
V	2	BA	5	0.1321	0.00	0	0.00
V	2	TI	2	0.13371	0.00	0	8.58
Cr	2	V	2	0.13568	0.00	0	6.69
Mn	3	CR	3	0.1257	18.74	65	4.15
Fe	3	MN	3	0.08087	5.27	415	2.50
Cu	3	Ge MS	3	0.0017	209.02	32	0.60
Pb	4	SE	4	0.07656	0.00	0	2.32
S	1	PB	4	0.11478	0.00	0	8.20
Cl	1	PB	4	0.02922	0.00	689	2.09
Cl	1	S	1	0.0175	0.00	689	0.86
Cl	1	Ti MS	1	0.0021	645.80	43	1.17
S	1	CL	1	0	0.00	0	0.00
Co	3	FE	3	0.06992	29.00	0	2.61
Sm	3	Cr	3	0.0762	11.36	0	2.51
Sm	3	Mn	3	0.0172	1.12	0	0.53
Eu	3	Cr	3	0.0611	9.11	0	2.02
Eu	3	Mn	3	0.8262	53.88	0	25.50
Tb	3	Fe	3	0.1	41.47	0	3.74
Tb	3	Co	3	0.9369	0.00	0	28.34
Co	4	FE	4	0.06007	10.75	0	2.18
Ga	4	PB	4	0.06488	0.00	28	2.16
As	4	PB	4	1.200648	0.00	0	0.00
Ge	4	ZN	3	0	0.00	0	0.00
Ge	4	Hg	4	0	0.00	0	0.00
Br	4	AS	4	0.04556	0.00	43	1.40
Rb	4	BR	4	0.13207	5.73	24	4.24
Y	4	PB	4	0.06959	0.00	0	1.78
Y	4	RB	4	0	0.00	0	0.00
Hf	4	Pb	4	0.0174	0.00	0	0.58
Hf	4	Cu	4	0.0883	13.99	0	3.05
Ga	4	Ta	4	0.65672	41.21	0	22.59

Figure 3. Example replicate report.

REPLICATE REPORT

Original ID: 02-T5786  
 Replicate ID: RT5786

Deposit Mass: 214 µg  
 Deposit Area: 11.3 cm<sup>2</sup>  
 Particle Size: F

Element	Original		Replicate		Difference		RPD						
	ug/cm2		ug/cm2		ug/cm2								
Na	0.0921	+/-	0.0452	0.0381	+/-	0.0476	0.0540	+/-	0.0656				
Mg	0.0000	+/-	0.0158	0.0325	+/-	0.0176	-0.0325	+/-	0.0236				
Al	0.0271	+/-	0.0077	0.0173	+/-	0.0083	0.0098	+/-	0.0114	+	44.0	+/-	51.2
Si	0.0965	+/-	0.0116	0.0957	+/-	0.0118	0.0007	+/-	0.0165	+	0.8	+/-	17.2
P	0.0000	+/-	0.0026	0.0000	+/-	0.0030	0.0000	+/-	0.0040				
S	0.5519	+/-	0.0623	0.5804	+/-	0.0658	-0.0285	+/-	0.0906	+	-5.0	+/-	16.0
Cl	0.0104	+/-	0.0038	0.0124	+/-	0.0046	-0.0019	+/-	0.0059				
K	0.0527	+/-	0.0062	0.0589	+/-	0.0071	-0.0061	+/-	0.0094	+	-11.0	+/-	16.8
Ca	0.0437	+/-	0.0052	0.0446	+/-	0.0055	-0.0009	+/-	0.0076	+	-2.1	+/-	17.2
Sc	0.0000	+/-	0.0010	0.0006	+/-	0.0013	-0.0006	+/-	0.0017				
Ti	0.0089	+/-	0.0011	0.0109	+/-	0.0015	-0.0020	+/-	0.0019	0	-20.6	+/-	18.8
V	0.0011	+/-	0.0006	0.0002	+/-	0.0009	0.0009	+/-	0.0011				
Cr	0.0006	+/-	0.0006	0.0013	+/-	0.0008	-0.0007	+/-	0.0010				
Mn	0.0004	+/-	0.0009	0.0040	+/-	0.0012	-0.0036	+/-	0.0015				
Fe	0.1003	+/-	0.0053	0.1014	+/-	0.0056	-0.0011	+/-	0.0076	+	-1.1	+/-	7.6
Co	0.0000	+/-	0.0008	0.0000	+/-	0.0010	0.0000	+/-	0.0013				
Ni	0.0000	+/-	0.0005	0.0001	+/-	0.0007	-0.0001	+/-	0.0008				
Cu	0.0899	+/-	0.0046	0.0902	+/-	0.0048	-0.0003	+/-	0.0067	+	-0.3	+/-	7.4
Zn	0.0023	+/-	0.0007	0.0033	+/-	0.0010	-0.0010	+/-	0.0012	+	-37.3	+/-	43.9
Ga	0.0000	+/-	0.0015	0.0000	+/-	0.0022	0.0000	+/-	0.0026				
As	0.0028	+/-	0.0010	0.0001	+/-	0.0013	0.0027	+/-	0.0017				
Se	0.0013	+/-	0.0008	0.0005	+/-	0.0012	0.0007	+/-	0.0015				
Br	0.0044	+/-	0.0009	0.0034	+/-	0.0012	0.0010	+/-	0.0015	+	25.1	+/-	38.4
Rb	0.0000	+/-	0.0009	0.0000	+/-	0.0012	0.0000	+/-	0.0015				
Sr	0.0000	+/-	0.0010	0.0001	+/-	0.0014	-0.0001	+/-	0.0018				
Y	0.0015	+/-	0.0012	0.0000	+/-	0.0017	0.0015	+/-	0.0021				
Zr	0.0029	+/-	0.0015	0.0000	+/-	0.0020	0.0029	+/-	0.0025				
Nb	0.0005	+/-	0.0017	0.0000	+/-	0.0023	0.0005	+/-	0.0029				
Mo	0.0028	+/-	0.0019	0.0000	+/-	0.0027	0.0028	+/-	0.0033				
Ag	0.0000	+/-	0.0037	0.0042	+/-	0.0055	-0.0042	+/-	0.0066				
Cd	0.0017	+/-	0.0039	0.0000	+/-	0.0054	0.0017	+/-	0.0066				
In	0.0000	+/-	0.0041	0.0000	+/-	0.0055	0.0000	+/-	0.0068				
Sn	0.0192	+/-	0.0070	0.0148	+/-	0.0068	0.0044	+/-	0.0097				
Sb	0.0021	+/-	0.0055	0.0058	+/-	0.0074	-0.0037	+/-	0.0092				
Cs	0.0091	+/-	0.0144	0.0174	+/-	0.0199	-0.0083	+/-	0.0245				
Ba	0.0189	+/-	0.0196	0.0466	+/-	0.0275	-0.0277	+/-	0.0338				
La	0.0000	+/-	0.0265	0.0000	+/-	0.0368	0.0000	+/-	0.0453				
Ce	0.0071	+/-	0.0373	0.1106	+/-	0.0529	-0.1035	+/-	0.0647				
Hg	0.0000	+/-	0.0017	0.0000	+/-	0.0023	0.0000	+/-	0.0029				
Pb	0.0005	+/-	0.0022	0.0006	+/-	0.0030	-0.0001	+/-	0.0038				

RPD: Relative Percent Difference  $(X1-X2)/[(X1+X2)/2]*100$ . RPD is calculated when original value is greater than three times its uncertainty.

C:\IXRF\QS024.sp0						sp0
Livetime	Target	Filter	kV	mA		
50	Direct	CeI	7.5	0.1	5	
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery			
Si 9004	1801	1706	1.056	PASS		

C:\IXRF\QS024.sp1						sp1
Livetime	Target	Filter	kV	mA		
50	Direct	Cu	20	0.2	2	
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery			
Si 416	41.6					
Ti 8621	862.1	871.9261	0.989	PASS		
Fe 17790	1779.0	1822.317	0.976	PASS		

C:\IXRF\QS024.sp2						sp2
Livetime	Target	Filter	kV	mA		
50	Ge	0	30	1	2	
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery			
Ti 10138	202.76	205.4454	0.987	PASS		
Fe 24524	490.48	493.9854	0.993	PASS		

C:\IXRF\QS024.sp3						sp3
Livetime	Target	Filter	kV	mA		
50	8	Rh	35	1	1	
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery			
Ti 3566	71.32	68.11	1.047	PASS		
Fe 8901	178.0	176.8	1.007	PASS		
Se 10624	212.5	206.8	1.027	PASS		
Pb 13075	261.5	260.8	1.003	PASS		

C:\IXRF\QS024.sp4						sp4
Livetime	Target	Filter	kV	mA		
50	Direct	W	55	0.6	0	
Gross Counts	Normalized (gross/sec)	Avg cts/sec	Recovery			
Cd 5561	185.4	187.7	0.987	PASS		

Figure 4. Example QS data report.

## APPENDIX A: Differences from Promulgated methods

There is no promulgated method for the processing of data generated by Kevex model XRF's. This method was developed in-house to meet a need which has not yet been met by any promulgating authority that *CHESTER LabNet* is aware of.

The QC controls in this method were developed in house based on direction from the XRF Technical Director.

# CHESTER LabNet

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## Standard Operating Procedure XR-007.02

Analysis of Elements in Air Particulates  
by X-Ray Fluorescence (Thermo Scientific ARL QUANT'X )  
US EPA IO 3.3

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### Approvals:

 _____ Author	<u>3-1-16</u> Date
 _____ Lead Analyst	<u>3-1-16</u> Date
 _____ QA/QC	<u>3-1-16</u> Date

Effective from: 3-1-16  
Effective until: present



Analysis of Elements in Air Particulates  
by X-Ray Fluorescence (Thermo Scientific ARL QUANT'X)  
US EPA IO 3.3

**1.0 Introduction**

1.1 Test Method Reference ID: US EPA Inorganics Compendium Method 3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectrometry.

1.2 Applicability: This method is applicable to the quantitative analysis of aerosols deposited on a variety of filter types for the elements Na through U.

1.3 Detection Limit: XRF does not utilize detection limits as commonly defined, rather all results are reported with an associated uncertainty which varies based upon filter matrices and interferences present in the deposit.

1.4 Method Performance: Refer to referenced method.

**2.0 Summary**

2.1 Scope and Application: The intended use of this method is for the quantitative analysis of aerosols deposited on a variety of filter types for the elements Na through U. This method is also applicable to the quantitative analysis of resuspended solids deposited on a variety of filter types for the elements Na through U, when first resuspended onto a variety of filter media following SOP XR-001. This method meets its intended use.

2.2 Summary of Method: Electrons in the sample are excited from their ground state to higher energy levels by X-ray irradiation from an X-ray tube. These excited electrons emit discrete energy X-rays as they return to their normal ground state energy level. The energy of these emitted X-rays is characteristic of each element and is used to identify the element in the spectrum.

A silicon-lithium crystal detector measures the change in the electronic field generated by the release of the eV charge during elemental excitation. This change in the field is proportional to the energy of excited electrons, and is used to identify specific elements in the deposit.

Selectivity is by the frequency of any given energy level ("KeV lines") used to quantify that element through direct comparison with thin film standards.

This method is not designed as a training manual for new users, and does not contain all of the fine details a trained analyst would know.

- 2.3 Interferences: As with all emissions spectrophotometry, secondary, tertiary, quaternary emission lines may overlap primary lines depending on the amount of interferent present.
- 2.4 Sample collection/preservation/shipment/storage: Collection, field preservation and shipment of samples is performed by the client. Chester LabNet has no control over the actions of the client in the field. Upon receipt, samples are stored either at room temperature, or in refrigerators.

### **3.0 Safety**

- 3.1 Follow the Chester LabNet Chemical Hygiene Plan. Always treat samples of unknown origin and/or constitution as hazardous.
- 3.2 This method presents no safety risk beyond typical laboratory safety hazards.
- 3.3 No carcinogenic reagents are used in this method.
- 3.4 Although X-rays are produced by the instrument at dangerous levels, the X-rays will not turn on unless all interlocks are fully locked, thus ensuring the user is shielded from the X-rays. All users must wear dosimeter badges. To date, Chester LabNet has not had a dosimeter badge showing any radiological exposure of any XRF technician. Normal operation of the instrument will not expose the user to X-rays generated by the instrument. Radiation shielding should only be removed by qualified personnel while servicing the instrument, and must always be in place during routine analysis. Removal of DiLithium crystals may only be performed by Mr. Scott or one of his staff.

### **4.0 Pollution Prevention and Waste Management**

- 4.1 The smallest quantity of chemical feasible is removed from its primary container for use.

4.2 Chemicals are used in amounts needed by the method, and excess reagents are not made.

4.3 Chester LabNet is a conditionally exempt small quantity generator and as such does not require formal chemical waste processing.

4.4 Larger quantities of known hazards are returned to the client for disposal.

## **5.0 Apparati, Equipment and Supplies**

5.1 Instrument. Thermo Scientific ARL QUANT'X energy dispersive XRF (EDXRF) equipped with a thermoelectric (Peltier) cooled Si(Li) detector, and an air cooled X-ray tube with a rhodium anode and a peak operating power of 50W. Ethernet connection transfer the data files to the processing computer.

### 5.2 Accessories

- 5.2.1 Sample analysis holders
- 5.2.2 Petri dishes & slides of varying sizes
- 5.2.3 Petri dish rack
- 5.2.4 46mm diameter punch for sampling larger media
- 5.2.5 Forceps
- 5.2.6 25mm filter holder adapters
- 5.2.7 Kimwipes

### 5.3 Thin Film Calibration Standards

- 5.3.1 Micromatter Inc. vapor deposit of single or two non-interfering elements onto thin Mylar film.
- 5.3.2 EPA organo-metallic acetate film, usually with two non-interfering elements.
- 5.3.3 NIST SRM's 1832 and 1833 multi-element vapor deposits on glass films.

## 6.0 Reagents and Standards

6.1 95% ethanol

## 7.0 Preparation, Calibration and Standardization

### 7.1 Sample loading

7.1.1 Obtain an XRF Analysis Request Form (Figure 1.).

7.1.2 Retrieve the samples indicated in the LIMS ID column of the request form.

7.1.3 Prepare the work area: Filter loading is done in the laminar flow hood in the Weighroom.

7.1.3.1 Turn the hood blower and lights on

7.1.3.2 Clean the work surface with a Kimwipe and ethanol

7.1.3.3 Clean a pair of forceps with Kimwipes and ethanol.

7.1.3.4 Place the filters to be analyzed, the sample analysis holders, the Analysis Request Form and a pen in the hood.

7.1.4 Load the filters:

7.1.4.1 Clean all sample analysis holders with ethanol-soaked Kimwipes. Do not erase the hand-written number that identifies each holder.

7.1.4.2 Remove the filter from its container and place deposit side down in the sample analysis holder with the filter ID aligned with the slit in the cassette then return loaded cassette to petri dish.

- 7.1.4.3 Use forceps and handle the filter only around its perimeter. If the forceps touch the deposit, clean forceps before proceeding.
- 7.1.4.4 Ensure that deposit area is within the analysis area (e.g. near the center of the filter).
- 7.1.4.5 Note the condition of the filter and record any comments on the Analysis Request Form that may apply to the XRF analysis, such as non-uniform deposit, wrinkled filter, etc. Do NOT analyze filters with loose deposits.
- 7.1.4.6 Place the numbered sample analysis holder in sequence with the other cassettes in petri dishes and return to the rack. **IT IS EXTREMELY IMPORTANT TO MATCH FILTER NUMBER TO LOCATION NUMBER ON XRF REQUEST FORM.**
- 7.1.4.7 Continue steps 7.1.4.1 through 7.1.4.6 for the remaining filters (maximum of ten).
- 7.1.4.8 Write the cassette batch letter/character (A, B, etc.) in the upper left-hand corner of the Analysis Request Form and initial and date the line labeled "Load" on the upper-right-hand section of the Analysis Request Form.
- 7.1.5 Queue samples:
  - 7.1.5.1 Place the cassette rack containing sample analysis holders in the appropriate staging area (active sample refrigerator or on the counter in the XRF area) awaiting XRF analysis.
  - 7.1.5.2 Place the Analysis Request Form(s) in the associated instrument specific queue.
  - 7.1.5.3 Place the client's filter containers in the staging area to be reloaded with the filters post-analysis.

## 8.0 Procedure

8.1 QUANT'X Operating Procedure - the QUANT'X operating manual should be reviewed before operating the instrument. One should be familiar with the hazards of incorrect operation and the safety systems of the instrument.

8.2 QUANT'X Start Up – performed at the beginning of each work week.

8.2.1 Update DPP Code:

8.2.1.1 Under Start → Programs/WinTrace/Service/Update DPP Code. Allow the instrument to perform DPP update; do not open lid until initiating click is heard.

8.2.2 Energy Calibration Adjustment

8.2.2.1 Place the copper standard in position 10.

8.2.2.2 Open the "Acquisition Manager" on the desktop.

8.2.2.3 Under Analyze, choose the "Energy Adjustment" option.

8.2.2.4 Check box to Acquire for all count rates, then click OK.

8.2.2.5 Upon completion, print the report and enter the FWHM, Zero Width data, and detector temperature (°K) into the energy cal spreadsheet in the QUANT'X directory on the processing computer. Manually write the detector temperature (°K) on the report page and archive into the designated folder.

8.2.2.6 Unload the Cu standard from instrument.

8.2.3 Analyze Weekly QS standard:

8.2.3.1 Place QS standard in position 1.

8.2.3.2 Open the QS protocol in the "Method Explorer" and create a new sample list. For weekly NIST check, label the sample list with QSYMMDD (where YY = year, MM = month and DD = date).

8.2.3.3 Click the sample list icon and enter the list name from Section 8.2.3.2 into position 1.

8.2.3.4 Click the "Analyze" icon.

8.2.3.5 When Spectrum Collection Dialog box appears, click "Collect All."

8.2.3.6 When the "Acquisition Manager" dialog box appears, review the list for accuracy, then click "OK" to continue.

8.2.3.7 Click the green "GO" icon to start the analysis.

8.2.3.8 In the QUANT'X Logbook enter the date, time, analyst's initials, and QS sample name.

8.2.3.9 When the QS run is complete and the "Spectrum Collection" dialog box appears, click "Continue."

8.2.3.10 Click "OK" to acknowledge Analysis status.

8.2.3.11 Save the method.

8.2.3.12 In the File dropdown menu in the browser, chose "Save Report File."  
Name the report file as the list name (i.e. QS001) and save it as a ".csv" file in the appropriate client subdirectory on the processing computer.

8.2.3.13 Print the Analysis Report ".csv" file from WinTrace.

8.2.3.14 Process the QS per section 8.5.1. If the QS passes acceptable criteria, proceed to section 8.2.4.

8.2.3.15 Unload the QS filter from instrument.

8.2.4 Analyze SRM particle standard.

8.2.4.1 Place SRM 2783 standard in position 1.

8.2.4.2 Open the current SRM 2783 protocol in Method Explorer and create a new sample list. Name the list the date (YYMMDD).

8.2.4.3 Open the sample list and enter SRM 2783 standard name in position 1.

8.2.4.4 Run the SRM 2783 standard as a normal sample (section 8.3).

8.2.4.5 Once the run is finished, save the method and also open the file dropdown menu in the browser, chose "Save Report File" as the run number in the current NIST subdirectory on the processing computer. Save the Analysis Report as a ".csv" file type with the date as well as the SRM ID (e.g. YYMMDD\_SRM2783, where YY = year, MM = month and DD = date) into the current NIST subdirectory on the XRF data processing computer.

8.2.4.6 On the processing computer, open the SRM file saved in Excel.

8.2.4.7 Remove measurement units in column C.

8.2.4.8 Copy/paste concentrations from column C from processing program into the indicated section of the current quantx\_NIST file tab Report (2783).

8.2.4.9 Confirm passing results before printing report and removing SRM 2783 standard from the XRF sample chamber.

8.2.4.10 Copy/paste row 30 of SRM (2783) to QuantX QA tab. Add date before copy/paste the QuantX QA newly made line to the master tab in the current QuantX\_NIST file.

8.2.4.11 Copy/paste row 27 of the SRM (2783) tab to the archive tab in the QuantX\_NIST file. Enter the date in column A, to the left of the SRM (2783) data.

#### 8.2.5 Analyze Audit Standards

8.2.5.1 Place the micromatter audit standards in the correct positions in the instrument.

8.2.5.2 Open the current audit standards protocol in Method Explorer and create a new sample list. Name the list "YYMMDD" (where YY = year, MM = month and DD = date).

8.2.5.3 Open the sample list and enter the audit standards names in the correct positions.

8.2.5.4 Analyze the audit standards in the same manner as unknowns (section 8.3)

8.2.5.5 Once the run is finished, save the method. In the "File" dropdown menu, chose "Save Report File." Name the report as the run number and save in the current NIST subdirectory on the processing computer. Save the Analysis Report as a ".csv" file with the date. Indicate that they are micromatter standards. (e.g. "YYMMDD\_MICROMATTER" where YY = year, MM = month and DD = date).

8.2.5.6 On the processing computer, open the micromatter ".csv" file in Excel.

8.2.5.7 Copy columns A through G from the micromatter ".csv" file, then paste values into the current precise\_processing-pgm file starting in cell "A1." Run the macros to remove measurement units.

- 8.2.5.8 Select all, then copy the results from processing program, then paste into the 25mm tab in the current year's Quant'X NIST file (i.e. quantx\_NIST\_YYYY where YYYY = year).
  - 8.2.5.9 In the Quantx\_NIST\_YYYY file, print the "25mm TFE" tab, the "Sheet1" tab, and the "QuantxQA" tab.
  - 8.2.5.10 Save Quantx\_NIST\_YYYY file.
  - 8.2.5.11 Remove the micromatter standards from the XRF sample chamber.
  - 8.2.5.12 Backup new NIST check by saving the most recent files (Quantx\_NIST-YYYY, Quant'X QS, and YYYY\_energy\_cal) to the dedicated flash drive.
- 8.2.6 Analyze instrument comparison filter
- 8.2.6.1 Place the inter-instrument comparison filter in the sample tray position 1. The inter-instrument comparison filter is currently a 47mm Teflon filter labeled "08T5052."
  - 8.2.6.2 Open the current corresponding analysis protocol in the Method Explorer and create a new sample list. Name the list YYMMDD, where YY = year, MM = month and DD = date.
  - 8.2.6.3 Open the sample list and enter inter-instrument comparison filter ID in correct tray position.
  - 8.2.6.4 Run the filter as an unknown (section 8.3)
  - 8.2.6.5 Once the run is finished, save the method. In the file dropdown menu, chose "Save Report File." Name the Report file as the run number and save in the current Quant'X NIST folder on the processing computer. Save the Analysis Report as a ".csv" file. Name the Quant'X result file with the date and filter ID. (e.g. YYMMDD\_08T5052) and save in the current NIST subdirectory on the processing computer.

- 8.2.6.6 On the processing computer, use Excel to open the analysis report ".csv" file.
- 8.2.6.7 Copy columns A through G and paste values into the current XRF processing file. Run the macros to remove measurement units.
- 8.2.6.8 Select all, then copy the results from the processing file and paste into the appropriate inter-instrument processing files: "770-Quant\X\_replicate\_xrf" and "772-Quant\S\_replicate\_xrf." Save both files before closing.
- 8.2.6.9 When the inter-instrument comparison filter has been analyzed on all XRF instruments, enter the data in the appropriate instrument specific files, then print the replicate report and archive with NIST Check printed data. Print out extra copies to archive with associated instruments weekly NIST Check data.

### 8.3 Analyze Samples

- 8.3.1 Analyze and process the Quality Assurance Standard ('QS") prior to each analytical run. (See section 8.2.3.2)
- 8.3.2 If a client report subdirectory has not been created by the project manager, create a new subdirectory on the processing computer and name it the report number and, in parentheses, the client name as listed on the Analysis Request Form (e.g. "YY-RRR (Acme)" where YY = year and RRR = report number).
- 8.3.3 Open the appropriate report file template on the processing computer and save it as the run number as listed on the Analysis Request Form within the client report subdirectory from Section 8.3.2. Name the file CNNN-XXX, where CNNN = client number and XXX = chronological run number.
- 8.3.4 If a sample ID ".csv" file was created within the client report subdirectory, copy the information and paste it into the sample log tab of the report file from Section 8.3.2.

- 8.3.5 Transfer each sample analysis holder in sequence to the like numbered position in the QUANT'X sample tray. The number of each sample analysis holder should correspond to the number on the tray, and should be oriented with the slit closest to the tray ID number. The QUANT'X has 10 positions. When properly loaded, the deposit side of the filter should be facing down.
- 8.3.6 Open the Method Explorer using the icon located on the desktop of the Quant'X computer.
- 8.3.7 Use the "open" icon in the Method Explorer to open the proper method needed for analysis. The method templates are located in C:\My Documents.
- 8.3.8 Save the chosen method file as the report number listed on the XRF Analysis Request Form. See 8.3.2.
- 8.3.9 In the Method Contents menu, click on "Sample Lists". Using the "Add Sample List" icon, name the new list the client run number listed on the Analysis Request Form. See 8.3.3.
- 8.3.10 Open the newly created list and enter the sample IDs in the "Sample Name" fields.
- 8.3.11 The analysis is ready to begin. Click the "Analyze" icon. Choose "Collect All" when prompted with the Spectrum Collection Dialog box.
- 8.3.12 When the "Acquisition Manager" dialog box appears, review the list for accuracy, then click "OK" to continue.
- 8.3.13 Click the green "GO" icon to start the analysis. You will hear the instrument initiate.
- 8.3.14 On the Analysis Request Form record the analyst's initials, and the date and the time of analysis.
- 8.3.15 In the QUANT'X Logbook enter the date, time, analyst's initials, run number, analysis protocol, sample analysis holder ID letter, and number of samples.

- 8.3.16 After the analysis is complete, the Spectrum Collection dialog box appears. Click "Continue."
- 8.3.17 Click "OK" to acknowledge Analysis status.
- 8.3.18 Save the method.
- 8.3.19 Open the File drop down menu in the browser, chose "Save Report File" and save as a ".csv" file in the appropriate client subdirectory on the processing computer.
- 8.3.20 Process the run as described in Section 8.5.2.

#### 8.4 Replicate Analysis

- 8.4.1 After a sample for replicate analysis has been chosen as described in section 8.5.2.5, re-analyze the sample using the same Sample List created in section 8.3.7 by adding the replicate ID under the last sample ID in the existing list. Use the letter "R" in place of the year represented in the sample ID. For example, the replicate for 15X1234 would be entered as RX1234.
- 8.4.2 Remove all other samples from the sample tray and place in their corresponding petri dishes. Return the petri dishes to the sample rack.
- 8.4.3 Rotate the chosen sample replicate 90 degrees and place in position 1 of the sample tray.
- 8.4.4 Click the "Analyze" icon. Choose "Collect" when prompted with the Spectrum Collection Dialog box. Analyze ONLY the replicate sample.
- 8.4.5 When the "Acquisition Manager" dialog box appears, review the list for accuracy, then click "OK" to continue.
- 8.4.6 Click the green "GO" icon to start the analysis. You will hear the instrument initiate.

- 8.4.7 After the replicate analysis is complete, the Spectrum Collection dialog box appears. Click "Continue."
- 8.4.8 Click "OK" to acknowledge Analysis status.
- 8.4.9 Save the method.
- 8.4.10 Open the File drop down menu in the browser, chose "Save Report File" and save as a ".csv" file in the appropriate client subdirectory on the processing computer.
- 8.4.11 Process the replicate.
- 8.4.12 After ensuring that the run has passed QC (see Section 9), remove the replicate sample from the sample tray and place in its corresponding petri dish. Return the petri dish to the sample rack.
- 8.4.13 The samples are now ready to be transferred from the sample analysis holders back into their original storage containers, then either archived or returned to the client.
- 8.4.14 Transfer the data into the LIMS as in Section 8.6.

## 8.5 Data Processing

### 8.5.1 Processing QS

- 8.5.1.1 After the QS data has been properly saved onto the processing computer as instructed in Section 8.2.3, reopen the analysis report ".csv" file saved on the processing computer using Excel. Copy the cells of the results only.
- 8.5.1.2 Additionally, open the "QS Template" located at c:\QUANT'X\Processing and the "Quant'X QS" log file located in the current NIST subdirectory.

8.5.1.3 In the "QS Template," paste the cells of the raw data into corresponding cells (A51 through F57), then run macros to remove measurement units.

8.5.1.4 Copy the contents of line 60, and paste into the Quant'X QS log. Enter the time the QS was analyzed as well as the list name. Enter the protocol used and number of samples analyzed with the associated QS.

8.5.1.5 The QS Percent Recovery results are located to the right of the data entered into the Quant'X QS log. Highlight the line with the date. Use find/replace to update the information into the correct line in the Quant'X QS log that corresponds to the most current QS.

8.5.1.6 Print the QS Percent Recovery results on the Quant'X Analysis report.

8.5.1.7 Copy/paste the Micromatter QS analysis results onto the client's QS Analysis Report ".csv" file and copy this page to the corresponding report file.

8.5.1.8 For NIST Check QS, copy/paste the newly created line in the "Quant'X QS" log into the current Quantx\_NISTYYYY file.

## 8.5.2 Processing Data

8.5.2.1 After the run has been properly saved onto the processing computer as described in Section 8.3, reopen the analysis report ".csv" file in Excel using the processing computer. Copy columns A-G.

8.5.2.2 Paste copied values into appropriate processing program and run macros to remove measurement units.

8.5.2.3 Enter sample IDs and information into the "Sample Log" tab in the report file created in section 8.3.2.

8.5.2.4 Copy/paste the sample IDs and information from the "Sample Log" tab to the indicated area in the processing program.

- 8.5.2.5 Choose the replicate. Select the proper LIMS format tab within the processing file (XRF, RTI, Precise, etc). This worksheet will automatically calculate the best candidates for the replicate sample analysis. The number of analytes which are both greater than 3x their uncertainty and greater than the mean value for each analyte in the group of samples analyzed will be displayed in a column at the far right-hand side of the file.
- 8.5.2.6 Copy/Paste the data from the sample chosen to be the replicate from the "printout" tab in the processing file and paste into the "original" tab of the report file.
- 8.5.2.7 Select the "Sample Log" tab in the report file and add a line to reflect the chosen replicate.

### 8.5.3 Processing Replicate

- 8.5.3.1 After the replicate data has been properly saved onto the processing computer, reopen the analysis report ".csv" file using Excel on the processing computer. Copy columns A-G.
- 8.5.3.2 Paste the copied values into the "csv file" tab of the processing file. Run macros to remove measurement units.
- 8.5.3.3 Copy the sample IDs and information from the "Sample Log" tab in the report file, and paste into the indicated area in the "csv file" tab of the processing file.
- 8.5.3.4 Copy the replicate data from the "printout" tab in the processing program, and paste into the report file "replicate" tab.
- 8.5.3.5 Open the "report" tab in the processing program and print.
- 8.5.3.6 Create a copy of the processing file "printout" tab in the report file.

8.5.3.7 In the "printout" tab in the processing program, Edit→Move→Create a Copy→To into the client report file. Select all, copy and paste values to convert the contents of the cells from formulae to numerical values in the client report file. Remove any extra rows that were not utilized.

8.5.3.8 Print both the replicate "report" tab and the "printout" tab data.

8.5.3.9 Paperclip the pages of the report together and place in QC staging area. A complete report should contain the following: XRF Run Sheet, QS Data, Replicate Report and sample data, in that order.

8.5.4 QC data : *Only a qualified XRF spectroscopist should critique the XRF spectra. Data corrections are made in red ink on the XRF printout. The data is then amended with the corrections.*

Check the processed data for anomalies and corrections made in the 'LIMS' worksheet of the run file. Anomalies may include:

- Over-subtraction of very intense peaks. Peaks that exceed 10000x the background counts can become over-corrected for background counts as the background subtraction channels begin to 'ride' up the sides of the analyte peak.
- False positives' for analytes in the 'noisier' background regions of the spectra; most notably Rh through La in the high energy (50 kV) excitation condition, and Y through Mo in the 50 kV direct excitation condition.
- Low Al absorption values <0.95 could indicate "DNCTTFM" (i.e. Does Not Conform to Thin Film Model)

## 8.6 Data reporting

8.6.1 After the data file has been reviewed, corrected, amended, and saved, transfer the data to the LIMS.

8.6.2 Copy/paste the sample results and uncertainties from the "LIMS" tab in the report file into a new excel spreadsheet. Do not include the header.

- 8.6.3 Save the new spreadsheet as the appropriate ".csv" worklist in the worklist subdirectory of the LIMS computer.
- 8.6.4 Transfer the worklist into the LIMS as described in SOP AD-007, "Laboratory Information Management System"
- 8.6.5 Confirm that the data was transferred correctly by checking results from the printed raw data against the results imported into LIMS. Distribute the data.
- 8.6.6 Enter comments into LIMS for each sample, if any.
- 8.6.7 Initial and date the "Date Worklist Released" line on the Run Sheet to indicate that results have been distributed in the LIMS.
- 8.6.8 Print a copy of the replicate report as well as an updated XRF Analytical Quality Assurance Report (i.e. Quant'X QA tab) to be placed in the client's folder. (See figures 3 and 4 at the back of this document).
- 8.6.9 Place the filters, their associated Analysis Request Form(s) and the data packet in the staging area to be archived.

## 9.0 QA/QC

- 9.1 Quality Assurance Standard (QS). The QS is a multi-element thin film vapor-deposited standard on Mylar manufactured by Micromatter Inc. The QS measurements are considered to be a reliable approximation of the precision of the instrument between the time of calibration and the time of analysis.
  - 9.1.1 Frequency: once, at the beginning of each analytical run
  - 9.1.2 QC statistic: percent recovery
  - 9.1.3 Control limits: 90-110 %
  - 9.1.4 Corrective action: terminate analysis, determine cause of QS failure. Failure necessitates re-analysis of any excitation condition(s) falling outside the limit. Repeated failure requires a recalibration of any excitation condition(s) not meeting the required limits and reanalysis of the samples associated with the failed QS. See analyst's notes for possible sources of QS failures.

9.1.5 Note: See section 10 for a description of the QS true value determinations.

9.2 Laboratory Replicate. This is a sample which is analyzed twice.

9.2.1 Frequency: once per analytical batch of ten client samples.

9.2.2 QC Statistic: relative percent difference (RPD) of both the sample results and the uncertainties of the sample results ( $\delta_{\text{RPU}}$ ) for all results greater than three times the uncertainty of that analyte.

9.2.3 Control limits: Average analyte score for the sample should exceed "1.5" for a sample with a uniform deposit. See section 10.2 for the calculations relating to scoring of samples.

9.2.4 Corrective action: Note in Case Narrative. Replicate results represent deposit uniformity and are intended to demonstrate analytical confidence in XRF measurements of each analyte. A replicate score less than 1.5 is indicative of a non-uniform sample deposit on the filter.

9.3 NIST weekly accuracy check (NIST check). These standards are thin film standard prepared and certified by NIST. The frequency of this analysis is limited by the fragile nature of the standards. Elements analyzed are Al, Si, S, K, Ca, Ti, V, Mn, Fe, Cu, Zn, and Pb. Each element is analyzed in each pertinent excitation condition.

9.3.1 Frequency: once per week

9.3.2 QC statistic: analytical result

9.3.3 Control limits: within the NIST certified uncertainty for each analyte

9.3.4 Corrective action: terminate analysis, recalibrate the excitation condition in which the failure occurs.

## 10.0 Calculations

10.1 Calculation of QS standard percent recovery:

The QS multi-element thin film standard is analyzed several times during calibration, and the concentrations for elements Si, Ti, Fe, Se, and Cd in their  $K\alpha$  windows, and Pb in its  $L\alpha$  and  $L\beta$  windows are averaged. These averaged values are entered into the QS data processing program. The QS is then run concurrent with each analytical run of samples and the concentrations for each element in each excitation condition are compared with those

obtained during calibration.

Percent recoveries are calculated as follows:

$$R_{i,j} = U_{i,j} / C_{i,j} * 100$$

where:  $R_{i,j}$  = recovery for element i in excitation condition j.  
 $U_{i,j}$  = concentration for element i in excitation condition j obtained during analysis of samples.  
 $C_{i,j}$  = the averaged concentration for element i in excitation condition j from the calibration runs.

## 10.2 Scoring of Replicate Samples:

For a given sample, all analyte results which exceed three times the uncertainty for that analyte are given both a score and a qualifier. The score is a numerical value assigned to a qualifier to aid in determining the overall score of the replicate sample. The qualifier and score are determined by comparing the relative percent difference of the analyte result to the relative percent *uncertainty* of the analyte result.

10.2.1 The relative percent difference (RPD) of the analyte result is calculated as follows:

$$RPD = [(X_1 - X_2) / ((X_1 + X_2) / 2)] \times 100$$

where:  $X_1$  = original sample concentration  
 $X_2$  = replicate sample concentration

10.2.2 The relative percent uncertainty (RPU) of the uncertainties is calculated as follows:

$$\delta_{RPU} = [((\delta_o^2 + \delta_r^2)^{1/2}) / ((X_1 + X_2) / 2)] \times 100$$

where:  $\delta_{RPU}$  = the relative percent uncertainty of each analyte  
 $\delta_o$  = the uncertainty for a particular analyte for the original analysis  
 $\delta_r$  = the uncertainty for a particular analyte for the replicate analysis  
 $X_1$  = the original sample concentration  
 $X_2$  = the replicate sample concentration

10.2.3 Each replicate analyte is graded and qualified as follows:

Condition	Score	Qualifier
$RPD \leq \delta_{RPU}$	+2	+
$\delta_{RPU} < RPD \leq 2 \times \delta_{RPU}$	+1	0
$2 \times \delta_{RPU} < RPD \leq 3 \times \delta_{RPU}$	-1	-
$RPD > 3 \times \delta_{RPU}$	-2	--

10.2.4 The intermediate score of the replicate is calculated as follows:

$$S_f = \frac{\sum S_i}{n}$$

where:  $S_f$  = the intermediate grade

$S_i$  = each individual analyte score ('+2', '+1', '-1', or '-2')

$n$  = the total number of analytes whose original concentration exceeds 3x its uncertainty

10.2.5 The final determinative sample score is calculated as follows:

$$S_d = S_f / \text{average RPD}$$

where:  $S_d$  = the determinate score

$$\text{average RPD} = \frac{|RPU / RPD|}{n}$$

## 11.0 References

11.1 Quant'X Technical Manual

11.2 WinTrace User's Guide

11.3 Practical X-Ray Spectrometry, R. Jenkins and J.L. De Vries, second edition, Philips Technical Library, Springer-Verlag New York Inc.

- 11.4 X-Ray Fluorescence Analysis of Environmental Samples, Jaklevic, et al, Ed. by T.G. Dzubay, Ann Arbor Sci.
- 11.5 Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, T.G. Dzubay and R.O. Nelson, in Advances in X-Ray Analysis, Vol 18, 619-631.
- 11.6 Quantitative Analysis of Aluminum and Silicon in Air Particulate Deposits on Teflon Membrane Filters by X-Ray Fluorescence Analysis, J.A. Cooper, L.M. Valdovinos, J.R. Sherman, W.L. Pollard, R.H. Sarver, and J.K. Weider, report by NEA, Inc., Beaverton, OR, July 15, 1987.
- 11.7 Round Robin Evaluation: Elemental Analysis of Bulk Samples and PM<sub>10</sub> Loaded Teflon Filters, presented at the 82nd Annual Meeting of AWMA, Anaheim, CA, June 24-30, 1989.
- 11.8 US EPA Inorganics Compendium Method IO 3.3; Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectrometry

## 12.0 Definitions

- 12.1 Analyst: the designated individual who performs the "hands-on" method and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality.
- 12.2 Analysts' Notes: Non-essential aspects of a method, which may help the analyst during some phase of the method. Notes may include, but not be limited to, historical aspects of the method, "tricks" of the method, unexpected issues to be aware of, or other facts or opinions related to the method, but not directly part of the procedure.
- 12.3 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.
  - 12.3.1 Analytical Batch: a group of prepared samples (extracts/digests etc) that are analyzed together as a group, although they may have been prepared separately.
- 12.4 Blank: a clean aliquot of the same matrix as the digested samples. A blank is subjected to the usual analytical and measurement processes.
  - 12.4.1 Calibration Blank: An unspiked clean matrix of similar constitution as the sample extracts or digests (e.g. DI Water, 5% HNO<sub>3</sub> etc) used to establish the zero intercept of the calibration curve.

- 12.4.2 Field Blank: A blank prepared by the client in the field. This blank is treated as a sample by the laboratory.
- 12.5 Calculations (Data Reduction): the mathematical process of transforming raw data into a more useable form.
- 12.6 Calibrate: to determine, by measurement or comparison with a standard, the correct value of each reading of the instrument.
- 12.7 Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements where possible.
- 12.8 Calibration Standard: a substance or reference material used to calibrate and instrument.
- 12.9 Control Limit: A mathematical representation of acceptable limits for a given Quality Control Metric such as percent recovery or percent difference. Limits may be in the form of an absolute number or represented as a percentage.
- 12.10 Corrective Action: the action taken to address and/or eliminate where possible the causes of a nonconformity, such as exceeding a control limit. Actions may include reanalyzing a sample, or noting the non-conformance in the data report.
- 12.11 Correlation Coefficient: the statistical representation of how closely a set of x,y coordinates comes to a true line. A correlation coefficient of 1.000 is considered a perfectly straight line. Correlation coefficients above 0.995 are usually attainable by most instruments.
- 12.12 Duplicate: A second aliquot of a sample, taken through all steps of the method, including digestion/preparatory stages.
- 12.13 Frequency: The number of occurrences of a specified event within a given interval. The number of samples or analytical runs with which a given QC sample or metric must be analyzed or verified.
- 12.14 Laboratory Information Management System (LIMS): a comprehensive computerized database system that a laboratory uses for sample tracking and data management, from sample receipt to reporting and archiving.
- 12.15 Matrix/Matrices: the component or substrate that contains the analyte of interest.
- 12.16 QA/QC: Quality Assurance/Quality Control. A series of samples or metrics designed to show precision, accuracy and bias of the procedure are within acceptable limits.
- 12.17 QC Statistic: any of a number of statistical permutations performed on raw data to generate a metric capable of being subjected to control limits and corrective actions.
- 12.18 Reagent: a single chemical or combination of chemicals or a chemical solution used in the preparation or analysis of samples.
- 12.19 Standard: a solution or matrix of a known amount of analyte(s).

12.19.1 Primary standard: a standard received from a vendor with NIST or equivalent traceability.

### 13.0 Analysts' Notes

13.1 Carefully close the chamber lid. If the lid is suddenly dropped, the resulting pressure may be sufficient to rupture the thin Be windows on the X-ray tube and detector.

13.2 After each analysis, confirm the sample tray is in the last sample position, and the prefilter is in the Cu position. After dpp update, sample tray should be in position 1 and the prefilter should be in the carbon position. This simple check could save the analyst time in processing and finding errors or starting an unsuccessful run.

13.3 QS and NIST failures indicative of XRF system malfunctions may include:

- 13.3.1 Processing of sample through incorrect spreadsheet. Prior to any other troubleshooting, analyst should verify that the QS or NIST standard was processed through the appropriate spreadsheet (e.g. a Teflon QS will fail if processed through the quartz QS spreadsheet).
- 13.3.2 Sample Tray misalignment will cause obvious spectral issues (e.g. high dead time and scatter peaks). When tray malfunction occurs, update the dpp code. If update does not fix issue, reboot spectrometer, QUANT'X computer and update dpp code.
- 13.3.3 Prefilter misalignment will cause spectra issues (e.g. high dead time and scatter peaks). When prefilter malfunction occurs, update the dpp code. If update does not fix issue, reboot spectrometer, QUANT'X computer and update dpp code.
- 13.3.4 Vacuum failure/decay where the lower energy elements Si and Ti are readily absorbed by the Ar in the atmosphere. Si will exhibit the lowest recovery, then Ti < Fe < Se < Pb < Cd.
- 13.3.5 Channel drifting will cause peaks to shift so that recoveries are low for all elements. Check the QS spectra for shifting and correct by recalibrating the channels (see SOP XR-004).

- 13.3.6 Degradation in peak intensity in all excitation conditions can signal a decline in X-ray tube performance.
- 13.3.7 Loss of resolution (peak broadening) is a sign of detector degradation or loss of vacuum behind the Be window.

Filter Holder: \_\_\_\_\_

Instrument: \_\_\_\_\_

### XRF Analysis Request Form

Date of Request: \_\_\_\_\_  
 Date Results Required: \_\_\_\_\_  
 Client Name: \_\_\_\_\_  
 Run Number: \_\_\_\_\_  
 Protocol: \_\_\_\_\_  
 Sample Description: \_\_\_\_\_  
 Total # of Samples: \_\_\_\_\_  
 Report Number: \_\_\_\_\_  
 Date Data Processed: \_\_\_\_\_  
 Date Worklist Released: \_\_\_\_\_  
 Comments: \_\_\_\_\_  
 \_\_\_\_\_

**Initial/Date:**  
 Load: \_\_\_\_\_  
 Ag Collimator: \_\_\_\_\_  
 Ta collimator: \_\_\_\_\_  
 Resume: \_\_\_\_\_  
 QA: \_\_\_\_\_  
 Unload: \_\_\_\_\_

	a	b
Cond	Date/Time	Date/Time

Pos.	LIMS ID	S	Deposit Area	Mass	Client ID	Comments
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						

Figure 1. XRF Analysis Request Form

EDXRF Analysis Report

Thermo Fish Madison Wisconsin USA  
 Sample Li: Analyzed: 07/09/15 16:11:34  
 Analysis T Last Calibrated: 12/26/14 10:34:58  
 Method Fi Software version: 7.1 Service Pack 3 (Build 85)

Conditions

Mid Zb

Voltage 35 kV Current Auto  
 Livetime 50 seconds Counts Limit 0  
 Filter Pd Medium Atmosphere Vacuum  
 Maximum 40 keV Count Rate Medium  
 Warmup ti 0 seconds

Low Za

Voltage 8 kV Current Auto  
 Livetime 50 seconds Counts Limit 0  
 Filter Carbon Atmosphere Vacuum  
 Maximum 40 keV Count Rate Medium  
 Warmup ti 0 seconds

Low Zc

Voltage 20 kV Current Auto  
 Livetime 50 seconds Counts Limit 0  
 Filter Aluminum Atmosphere Vacuum  
 Maximum 40 keV Count Rate Medium  
 Warmup ti 0 seconds

Mid Zc

Voltage 50 kV Current Auto  
 Livetime 50 seconds Counts Limit 0  
 Filter Pd Thick Atmosphere Vacuum  
 Maximum 40 keV Count Rate Medium  
 Warmup ti 0 seconds

High Za

Voltage 50 kV Current Auto  
 Livetime 100 seconds Counts Limit 0  
 Filter Cu Thin Atmosphere Vacuum  
 Maximum 40 keV Count Rate Low  
 Warmup ti 0 seconds

Results

Element	Concentration	Uncertainty	Peak (cps/mA)	Background (cps/mA)				
QS008								
Si	7.990 ug/cm2	0.035	1137	-1				
Ti	10.909 ug/cm2	0.039	2159	-74				
Fe	11.249 ug/cm2	0.048	1126	-32				
Se	5.213 ug/cm2	0.038	753	11				
Cd	6.74 ug/cm2	0.16	98	2				
Pb	12.780 ug/cm2	0.068	925	-9				
	Date	Time	Si	Ti	Fe	Se	Cd	Pb
QS008	07/09/15	16:11:00	7.990	10.909	11.249	5.213	6.74	12.78
% Recovery			99.2	99.8	99.6	98.7	101.4	99.4
s.d.			-1.4	-0.6	-0.8	-2.0	1.3	-1.5

Figure 2. Example QS results page

## QUANT'X 1020 REPLICATE REPORT

3.63

Original ID: 15T1234

Replicate ID: RT1234

Element	Original ug/cm2		Replicate ug/cm2		Difference ug/cm2		RPD	
Na	0.0969	+/- 0.0545	0.1028	+/- 0.0549	-0.0060	+/- 0.0774		
Mg	0.1157	+/- 0.0194	0.0937	+/- 0.0191	0.0220	+/- 0.0272	+	21.0 +/- 26.0
Al	0.2649	+/- 0.0168	0.2465	+/- 0.0160	0.0184	+/- 0.0232	+	7.2 +/- 9.1
Si	0.6673	+/- 0.0342	0.6549	+/- 0.0337	0.0124	+/- 0.0480	+	1.9 +/- 7.3
P	0.0119	+/- 0.0020	0.0128	+/- 0.0020	-0.0009	+/- 0.0029	+	-7.3 +/- 23.1
S	0.0957	+/- 0.0058	0.0980	+/- 0.0059	-0.0023	+/- 0.0083	+	-2.4 +/- 8.6
Cl	0.0383	+/- 0.0041	0.0474	+/- 0.0044	-0.0091	+/- 0.0061	0	-21.2 +/- 14.1
K	0.1059	+/- 0.0060	0.1130	+/- 0.0063	-0.0071	+/- 0.0087	+	-6.5 +/- 8.0
Ca	1.2176	+/- 0.0613	1.2136	+/- 0.0612	0.0040	+/- 0.0866	+	0.3 +/- 7.1
Ti	0.0212	+/- 0.0017	0.0194	+/- 0.0017	0.0018	+/- 0.0024	+	8.9 +/- 11.6
V	0.0000	+/- 0.0008	0.0000	+/- 0.0008	0.0000	+/- 0.0012		
Cr	0.0000	+/- 0.0014	0.0000	+/- 0.0008	0.0000	+/- 0.0016		
Mn	0.0127	+/- 0.0015	0.0124	+/- 0.0015	0.0003	+/- 0.0021	+	2.4 +/- 17.1
Fe	0.2780	+/- 0.0142	0.2691	+/- 0.0138	0.0089	+/- 0.0198	+	3.3 +/- 7.2
Co	0.0000	+/- 0.0006	0.0000	+/- 0.0006	0.0000	+/- 0.0008		
Ni	0.0000	+/- 0.0006	0.0014	+/- 0.0007	-0.0014	+/- 0.0009		
Cu	0.0053	+/- 0.0009	0.0049	+/- 0.0009	0.0003	+/- 0.0013	+	6.6 +/- 25.3
Zn	0.0194	+/- 0.0013	0.0199	+/- 0.0014	-0.0005	+/- 0.0019	+	-2.7 +/- 9.7
Ga	0.0000	+/- 0.0004	0.0001	+/- 0.0006	-0.0001	+/- 0.0007		
Ge	0.0000	+/- 0.0006	0.0003	+/- 0.0007	-0.0003	+/- 0.0009		
As	0.0025	+/- 0.0016	0.0023	+/- 0.0016	0.0002	+/- 0.0023		
Se	0.0000	+/- 0.0007	0.0000	+/- 0.0003	0.0000	+/- 0.0008		
Br	0.0000	+/- 0.0006	0.0002	+/- 0.0009	-0.0002	+/- 0.0010		
Rb	0.0017	+/- 0.0008	0.0002	+/- 0.0008	0.0014	+/- 0.0011		
Sr	0.0028	+/- 0.0013	0.0006	+/- 0.0013	0.0022	+/- 0.0018		
Y	0.0000	+/- 0.0009	0.0002	+/- 0.0016	-0.0002	+/- 0.0018		
Zr	0.0001	+/- 0.0021	0.0006	+/- 0.0021	-0.0005	+/- 0.0029		
Mo	0.0021	+/- 0.0021	0.0000	+/- 0.0021	0.0021	+/- 0.0029		
Pd	0.0007	+/- 0.0021	0.0034	+/- 0.0021	-0.0027	+/- 0.0029		
Ag	0.0000	+/- 0.0021	0.0000	+/- 0.0021	0.0000	+/- 0.0029		
Cd	0.0000	+/- 0.0029	0.0000	+/- 0.0029	0.0000	+/- 0.0041		
In	0.0025	+/- 0.0032	0.0000	+/- 0.0032	0.0025	+/- 0.0045		
Sn	0.0000	+/- 0.0037	0.0000	+/- 0.0037	0.0000	+/- 0.0052		
Sb	0.0040	+/- 0.0047	0.0210	+/- 0.0048	-0.0170	+/- 0.0068		
Ba	0.0000	+/- 0.0038	0.0070	+/- 0.0038	-0.0070	+/- 0.0054		
La	0.0000	+/- 0.0015	0.0000	+/- 0.0015	0.0000	+/- 0.0022		
Hg	0.0064	+/- 0.0075	0.0000	+/- 0.0006	0.0064	+/- 0.0076		
Pb	0.0078	+/- 0.0023	0.0102	+/- 0.0023	-0.0024	+/- 0.0032	+	-26.6 +/- 35.7

RPD: Relative Percent Difference  $(X1-X2)/[(X1+X2)/2]*100$ . RPD is calculated when original value is greater than three times its uncertainty.

Figure 3. Replicate Report.

**CHESTER LabNet****Quant'X 1020 XRF Analytical Quality Assurance Report**

Client: Weekly NIST Check cal001 (3/19/13)

Report:

Analysis Period: through July 20, 2015

Number of Samples: 0

**1. Precision Data**

Micromatter Multi-elemental Quality Control Standard: QS285

**QC Standard Results**

Analyte	n	micrograms per square centimeter			c.v.	%E
		Calib.	Meas.	S.D.		
Si	1	8.06	8.13	na	na	0.84
Ti	1	10.93	10.92	na	na	-0.13
Fe	1	11.29	11.21	na	na	-0.76
Se	1	5.28	5.22	na	na	-1.09
Cd	1	6.65	6.71	na	na	0.96
Pb	1	12.85	12.77	na	na	-0.64

**2. Accuracy Data**

NIST Standard Reference Materials: SRM 1832, SRM 1833, SRM 2783

Analyte/ SRM	n	Certified Value( $\mu\text{g}/\text{cm}^2$ )	Measured Value ( $\mu\text{g}/\text{cm}^2$ )			% Rec.
			High	Low	Average	
Al 2783	47	2.3303	2.4740	2.0640	2.2858 +/- 0.1117	98.1
K 2783	47	0.5301	0.5786	0.5426	0.5597 +/- 0.0083	105.6
Ca 2783	47	1.3253	1.3443	1.2822	1.3136 +/- 0.0138	99.1
Ti 2783	47	0.1496	0.1682	0.1502	0.1603 +/- 0.0044	107.2
Mn 2783	47	0.0321	0.0386	0.0247	0.0306 +/- 0.0027	95.4
Fe 2783	47	2.6606	2.7265	2.6375	2.6892 +/- 0.0218	101.1
Cu 2783	47	0.0406	0.0423	0.0358	0.0395 +/- 0.0014	97.4
Zn 2783	47	0.1797	0.1843	0.1754	0.1790 +/- 0.0020	99.6
Pb 2783	47	0.0318	0.0350	0.0257	0.0318 +/- 0.0019	100.0

*NIST: National Institute of Standards and Technology**% Rec: Percent Recovery = (Experimental/Given) x 100**n: Number of Observations**S.D.: Standard Deviation**c.v.: Coefficient of Variation = (S.D./Measured) x 100**% E: Percent Error = [(Measured-Calibrated)/Calibrated] x 100***Figure 4. XRF Analytical Quality Assurance Report.**

Appendix A: Deviations from Promulgated Method  
(Inorganics Air Compendium Method IO3.3)

Item	Promulgated requirement	CLN	Justification
1	Section 3: The instrument is a commercially available Kevex EDX-771 energy dispersive x-ray spectrometer which utilizes secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements.	New instrument is the Thermo Scientific ARL QUANT'X that utilizes direct excitation and uses five direct excitation conditions with filtered X-rays.	Most secondary targets give inferior count rates requiring longer counting times.
2	Section 6: To minimize radiation damage to delicate aerosol samples only the secondary mode is used.	Use five direct excitation with filtered X-rays.	Most secondary targets give inferior count rates requiring longer counting times.
3	Section 6: Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background.	Use Vacuum.	Helium purge presents problems with degradation of vacuum behind the Beryllium windows of the X-ray tube and detector.

Item	Promulgated requirement	CLN	Justification
4	<p>7.3 In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.</p>	<p>Use direct Cu-filtered excitation.</p>	<p>This delivers higher count rates for the analytes of interest (Rh through Ce) which reduces signal to noise ratio and yields lower detection limits as well as lower overlap uncertainties for K, Ca, Sc, Ti, V, and Cr.</p>
5	<p>9.1 Spectra are acquired in sets of 15 samples each. Up to 7 spectra are acquired for each sample depending on how many secondary excitation targets are selected. Utilizing all seven fluorescers requires approximately 4 hours machine time for 44 elements analyzed plus atmospheric argon.</p>	<p>Use five direct excitation with filtered X-rays.</p>	<p>Most secondary targets give inferior count rates requiring longer counting times. Analysis times are on the order of 1 hour per sample.</p>
6	<p>9.3 X-ray attenuation corrections are performed as described in Section 15, Citation 10 and are briefly described here.</p>	<p>Use mass absorption (thickness) attenuation correction.</p>	<p>Mass absorption corrections performed as described in IO-3.3, Section 15, Citation 13.</p>

Item	Promulgated requirement	CLN	Justification
7	<p>9.5 When samples are collected by the dichotomous or other samplers using virtual impaction, an additional correction must be employed because these types of samplers do not perfectly separate the fine and coarse particles. Due to virtual impaction requirements, about 10% of the fine particle mass is deposited on the coarse filter. Therefore, the attenuation corrections used for the particles on the coarse filter "over-correct" the attenuation because of these residual fines on the coarse filter. These effects are compensated for by the flow fraction correction.</p>	<p>Use mass absorption (thickness) attenuation correction</p>	<p>Mass absorption corrections performed as described in IO-3.3, Section 15, Citation 13.</p>
8	<p>10. Data Reporting Elements with concentrations below 3 times the uncertainty are flagged with an asterisk (*) on the printed record.</p>	<p>Elemental concentrations less than 3 times the uncertainty are not routinely flagged.</p>	<p>Clients may request a report format to flag data as MDL when concentrations fall below a specified threshold.</p>

Item	Promulgated requirement	CLN	Justification
9	<p>11.3 The background files which are used for background fitting are created at calibration time. Thirty clean Teflon® and Nuclepore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.</p>	<p>Ten Teflon blanks are used to determine concentrations of elements thought to be artifact to the analysis chamber. These concentrations are averaged, then subtracted from elemental concentrations during analysis. All concentrations are derived using least squares background subtraction.</p>	<p>Teflon blanks do not present a uniform background. Significant background subtraction errors can arise when the thickness of the deposit or of the Teflon membrane itself causes X-ray scatter to increase.</p>
10	<p>12. Detection Limits The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty (<math>\pm 5\%</math>); long term system stability (<math>\pm 5\%</math>);</p>	<p>No long term system stability uncertainty calculation is performed.</p>	<p>Peak and background subtraction uncertainties are considered sufficient in approximating long term stability uncertainty. Quality Assurance Standard analysis is an adequate monitor of long term stability.</p>