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Standard Operating Procedure
XR-002.04

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

Approvals:

Author	1.30.09 Date
Lead Analyst	1/30/09 Date
QA/QC	2/3/09 Date

Effective from: 2.3.09
Effective until: present

REVIEW HISTORY

Review date:	Changes made:	Changes made by:
1/30/09	Updated replicate score calculations to reflect current practices.	Sheri Heldstab
2/1/08	Minor changes to text for clarification, replaced outdated figures (1 & 2) with currently used forms.	Sheri Heldstab
9/22/06	Added section on collimator switching for each instrument.	Sheri Heldstab
9/8/05	Updated to NELAP formatting. Minor typographical corrections. Addition of 772 to list of applicable instrumentation.	Sheri Heldstab
7/1/03	Minor changes to reflect upgrade in computer technology.	Sheri Heldstab
4/22/02	Split into 3 SOPs: Calibration, Operation, and Data Processing for XRF analysis. Polished formatting.	Sheri Heldstab
4/3/02	Updated formatting, revised filter loading procedure, minor changes to include new instrument, "772"	Paul Duda
9/17/98	No changes. Date of origination.	Rick Sarver

ANNUAL REVIEW

The undersigned attests that this standard operating procedure has undergone annual review for adherence to current practices and the latest QA/QC protocols:

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Analysis of Elements in Air Particulates by X-Ray Fluoresence (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: This method is applicable to 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: Atoms in the sample are excited from their ground state to higher energy levels by X-radiation from an X-ray tube. These excited atoms 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 the excited 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 atoms, 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, quarternary 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 The Chester LabNet Chemical Hygiene plan should be followed. Samples of unknown origin and/or constitution should always be treated 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 dosimetry 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.

4.3.1 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 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 real or arbitrary expiration date are neutralized prior to being disposed of via the sanitary sewer system.

4.5.3 Organic liquids beyond their 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 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 (eg 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. Filters with loose deposits should not be analyzed.

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 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.

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 that 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 xray 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 xray 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 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.

8.2.6.1 For 770: the Ta collimator with prefilter is used for exitation conditions 1 and 4. The Ag collimator is used for excitation conditions 0, 2 and 3.

8.2.6.2 For 772: the Ta collimator is used for excitation condition 4. The Ag collimator is used for excitation conditions 0, 1, 2 and 3.

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 discreet 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, 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 your 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 setting to "atm".

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 at the next lower protocol. For example, if the sample was analyzed using Protocol 6, analyze the replicate using Protocol 5.

8.4 After ensuring that the QS sample has passed for this 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 shipping 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 at a low 'standby' power setting which acts to prolong the life of the X-ray tube.

8.6.2 Set the tube power to 10 kV and 0.1 mA.

8.6.3 Set the tube to the secondary target position

8.6.4 Set the target wheel to position zero.

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 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 (δ_{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.

9.2.5 Note: The replicate is usually run at the next lowest protocol so that the detection limits are approximately 1.414x higher than the original analysis.

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 multielement thin film standard is analyzed several times during calibration, and the gross counts for elements Si, Ti, Fe, Se, and Cd in their Kα windows, and Pb in its Lβ 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 is 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:

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

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:

$$\delta_{RPU} = [((\delta_o^2 + \delta_r^2)^{1/2}) / ((X1 + X2) / 2)] \times 100$$

where: δ_{RPU} = the relative percent uncertainty of each analyte
δ_o = the uncertainty for a particular analyte for the original analysis
δ_r = the uncertainty for a particular analyte for the replicate analysis
X1 = the original sample concentration
X2 = 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

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

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.

11.6Round 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.

11.7US 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.

12.3.2 Preparation Batch: a group of one to 20 samples of the same matrix which are prepared together as a group, and which share common QC samples.

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% HNO3 etc) used to establish the zero intercept of the calibration curve.

12.4.2 Method Blank: An unspiked clean sampling media aliquot, taken through the entire preparation and analytical processes associated with a method. This blank determines if the sampling media may be contributing any analyte of interest in the samples.

12.4.3 Preparation Blank: All reagents involved in the preparation, without sampling media (if any), taken through the entire preparation and analytical processes associated with a method. This blank demonstrates cleanliness of reagents and of the preparation process itself.

12.4.4 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.

12.9Control 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.

12.19.2 Secondary standard: any standard created when mixing, diluting or otherwise manipulating aliquots of primary standards. May be called "working standards" or "intermediate standards".

13.0 Analysts' Notes

13.1QS 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 (eg 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:	**Initial/Date:**
Date Results Required:	Load:
Client Name:	
Run Number:	Ag Collimator:
Protocol:	
Sample Description:	Ta collimator:
Total # of Samples:	
Report Number:	Resume:
Date Data Processed:	
Date Worklist Released:	QA:
Comments:	
	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						
15						
16	***QS001***					

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 cm²
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(µg/cm²)	Measured Value (µg/cm²)					% 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

Appendix A:

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	