Designation: D8064 – 16

Standard Test Method for Elemental Analysis of Soil and Solid Waste by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry Using Multiple Monochromatic Excitation Beams[1]

1. Scope

1.1 This test method is based upon energy-dispersive X-ray Fluorescence (EDXRF) spectrometry using multiple monochromatic excitation beams for detection and quantification of selected heavy metal elements in soil and related solid waste.

1.2 This test method is also known as High Definition X-ray Fluorescence (HDXRF) or Multiple Monochromatic Beam EDXRF (MMB-EDXRF).

1.3 This test method is applicable to various soil matrices for the determination of Cr, Ni, As, Cd, Hg, and Pb in the range of 1 to 5000 mg/kg, as specified in Table 1 and determined by a ruggedness study using representative samples. The limit of detection (LOD) for each element is listed in Table 1. The LOD is estimated by measuring a SiO_2 blank sample (see Table X1.1 in Appendix X1).

1.4 This test method is applicable to other elements: Sb, Cu, Se, Ag, Tl, Zn, Ba, Au, Co, V, Fe, Mn, Mo, K, Rb, Sn, Sr, and Ti.

1.5 *X-ray Nomenclature*—This standard names X-ray lines using the Siegbahn convention.[2]

1.6 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D4944 Test Method for Field Determination of Water (Moisture) Content of Soil by the Calcium Carbide Gas Pressure Tester

D5283 Practice for Generation of Environmental Data Related to Waste Management Activities: Quality Assurance and Quality Control Planning and Implementation

D5681 Terminology for Waste and Waste Management

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E1169 Practice for Conducting Ruggedness Tests

E1727 Practice for Field Collection of Soil Samples for Subsequent Lead Determination

E2554 Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques

2.2 *Other Documents:*

ASTM DS46 X-Ray Emission Wavelengths and Kev Tables for Nondiffractive Analysis[4]

ASTM MNL 7 Manual on Presentation of Data and Control Chart Analysis, 8th ed.[4]

US EPA Method, Method 6200 Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment[5]

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[1] This test method is under the jurisdiction of ASTM Committee D34 on Waste Management and is the direct responsibility of Subcommittee D34.01.06 on Analytical Methods.

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[2] Jenkins, R., Manne, R., Robin, R., and Senemaud, C., "Nomenclature System for X-ray Spectroscopy," *Pure & Appl Chem.*, Vol 63, No. 5, pp. 735–746, 1991.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[4] Available from ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959, www.astm.org.

[5] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, https://www.epa.gov/hw-sw846/sw-846–test-method-6200-field-portable-x-ray-fluorescence-spectrometry-determination..

TABLE 1 Limit of Detection (LOD) and Method Range

Element	LOD (mg/kg)	Method Range (mg/kg)
Cr	2.3	11 to 500
Ni	1.1	5 to 500
As	0.2	1 to 2000
Cd	0.4	2 to 100
Hg	0.4	2 to 100
Pb	0.6	3 to 5000

3. Terminology

3.1 *Definitions*—Definitions of terms applying to XRF, soil, and waste management appear in Terminologies D653 and D5681.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *fundamental parameters (FP) model, n*—a model for calibration of X-ray fluorescence response, including the correction of matrix effects, based on the theory describing the physical processes of the interactions of X rays with matter.

3.2.2 *high energy monochromatic beam, n*—a focused monochromatic beam having its selected photon energy between 32 and 40 keV.

3.2.3 *medium energy monochromatic beam, n*—a focused monochromatic beam having its selected photon energy between 15 and 23 keV.

3.2.4 *monochromatic beam, n*—an incident monochromatic beam on a sample having a selected photon energy with a narrow energy bandwidth relative to the selected energy; method precision is achieved with a monochromatic beam having an energy bandwidth (Full Width Half Maximum) less than 15 % relative to the selected energy and containing more than 95 % flux of the spectrum of the excitation beam which is incident on the sample.

3.2.5 *multiple monochromatic excitation beams, n*—two or more monochromatic beams.

3.2.6 *Rayleigh scattering, n*—the elastic scattering of an X-ray photon through its interaction with the bound electrons of an atom; this process is also referred to as coherent scattering.

3.3 *Acronyms:*

3.3.1 *ARV*—accepted reference values

3.3.2 *EDXRF*—energy dispersive X-ray fluorescence

3.3.3 *FP*—fundamental parameters

3.3.4 *HDXRF*—high definition X-ray fluorescence

3.3.5 *LOD*—limits of detection

3.3.6 *MMB*—multiple monochromatic beams

3.3.7 *ND*—non-detected

3.3.8 *RSD*—relative standard deviation

4. Summary of Test Method

4.1 The operating conditions presented in this test method have been successfully used in the determination of Cd, As, Cr, Pb, Hg, Sb, Cu, Ni, Se, Ag, Tl, Zn, Ba, Sn, and Au in soil and related solid waste.

4.2 This technique uses one or more monochromatic excitation beams to quantify elemental concentrations in soil and solid waste samples. The sample is homogenized to a reasonable degree and positioned in front of an aperture where it is exposed to one or more monochromatic X-ray beams that are focused by X-ray optics from an X-ray source. A nearby detector is positioned to collect fluorescent and backscattered X rays. The X rays collected by the detector are converted to electric pulses by a digital pulse processor. A multi-channel analyzer separates the pulses by X-ray energy, forming the measurement spectrum. The spectrum is processed by an FP method to obtain the analysis result.

4.3 The apparatus is calibrated for each monochromatic beam and the detector. The calibration may be performed by the manufacturer or by the user.

5. Significance and Use

5.1 Elemental species such as Cr, Ni, As, Cd, Hg, and Pb are widely used in many industrial processes. These elements have been identified in many former industrial sites driving the need for a quick, easy method for testing on-site at trace levels in soil and solid waste matrices.

5.2 This method may be used for quantitative determinations of Cr, Ni, As, Cd, Hg, and Pb in soil matrices and solid waste. Typical test time is 90 seconds to 15 minutes.

6. Interferences

6.1 *Spectral Interference*—Spectral interferences result from spectral overlaps among the X-ray lines that remain unresolved due to limited energy resolution of the detector. For instance, the arsenic (As) Kα peak directly overlaps the lead (Pb) Lα peak. The Pb Lβ line can be used to account for this overlap and the As K lines can then be resolved from the Pb Lα overlap. The actual lines used for any particular element should be such that overlaps are minimized. Reference ASTM Data Series DS46 for detailed information on potential line overlaps. Interactions of photons and electrons inside the detector result in additional peaks in the spectrum known as escape peaks and sum peaks. These peaks can overlap with X-ray lines of interest, for example, the sum peak of iron (Fe) Kα can overlap with the Pb Lβ peak.

6.2 *Matrix Effects*—Matrix effects, also called interelement effects, exist among all elements as the result of absorption of fluorescent X rays (secondary X rays) by atoms in the specimen. Absorption reduces the apparent sensitivity for the element. In contrast, the atom that absorbs the X rays may in turn emit a fluorescent X ray, increasing apparent sensitivity for the second element. Mathematical methods may be used to compensate for matrix effects. A number of mathematical correction procedures are commonly utilized including full FP treatments and mathematical models based on influence coefficient algorithms.

6.3 *Physical Matrix Effects*—Physical characteristics of the sample such as particle size and homogeneity. Effects can be minimized by mixing samples, grinding and sieving them to a uniform particle size prior to analysis, or by increasing the area exposed to the X-ray beam path by rotating the sample during analysis.

6.4 *Moisture Effects*—Soil samples that are in excess of 15 % moisture content may introduce error to the analysis. Samples with high moisture content can be dried in an oven prior to analysis at less than 150°C. If mercury is a target analyte, a separate portion of the sample should be dried without heating and analyzed on its own. Another option is to use the manufacturer's auto-moisture correction for moisture content using FP modeling.

7. Apparatus

7.1 *EDXRF Spectrometer*[6], designed for X-ray fluorescence analysis using multiple monochromatic excitation beams with an energy dispersive detector and with a design that incorporates at a minimum the following features (unless otherwise specified):

7.1.1 *Source of X-ray Excitation*—An X-ray tube with a zirconium, molybdenum, rhodium, palladium, silver target or other suitable target can be used.

7.1.2 *X-ray Optics*—X-ray optical elements capable of accepting X rays from a tube and directing monochromatic beams on the sample. Two or more X-ray optical elements are necessary to provide multiple monochromatic beams. At least one optical element provides a medium energy monochromatic beam, and at least one optical element provides a high energy monochromatic beam.

7.1.3 *Beam Shutter,* used to select a monochromatic beam or select a combination of monochromatic beams.

7.1.4 *X-ray Detector,* with energy resolution ≤140 eV full width at half maximum of the manganese (Mn) Kα line.

7.1.5 *Digital Pulse Processor and Multi-channel Analyzer*—A digital pulse processor for pulse shaping and conditioning, and a multi-channel analyzer for binning the pulses according to X-ray energy.

7.1.6 *Detector Aperture*—An aperture in the beam path between the sample and the detector to limit the field of view of the detector.

7.2 *Analyzer Test Stand,* may have the following accessories:

7.2.1 *Sample Cell Rotator (optional),* designed to hold a removable sample cell.

7.2.2 *Removable Sample Cell*—An open ended specimen holder compatible with the geometry of the MMB-EDXRF spectrometer and is designed to use replaceable X-ray transparent film to hold a soil specimen with a minimum depth of 1 cm.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Calibration Standard(s)*—At least three homogenous reference materials are required for calibration (see Note 1). The calibration standards should provide (*a*) concentrations of Cr, Ni, As, Cd, Hg, and Pb at or near background soil level, (*b*) some or all of concentrations of Cr, Ni, As, Cd, Hg, and Pb are at low range levels, and (*c*) some or all of concentrations of Cr, Ni, As, Cd, Hg, and Pb are at high range levels. It is recommended to use calibration standards that are traceable to standard reference materials when such materials are available.

NOTE 1—Additional calibration standards may be used for improved accuracy.

8.3 *Calibration Verification Sample(s)*—At least one homogenous reference material containing Cr, Ni, As, Cd, Hg, and Pb is required for calibration.

8.4 *Drift Correction Monitors (optional)*—Due to instability of the measurement system, the sensitivity and background of the spectrometer may drift with time. Drift correction monitors may be used to compensate for this drift. The optimum drift correction monitor samples are permanent materials that are stable with repeated exposure to X rays.

8.5 *Gloves*—Disposable gloves are recommended for handling reference materials and other samples.

8.6 *Quality Control Sample(s)*—To ensure the quality of the results, a quality control (QC) sample is used for establishing and monitoring the stability and precision of an analytical measurement system (see 17.4). If possible, the QC sample shall be reference material representative of samples typically analyzed. The materials shall be stable under the anticipated storage conditions. The QC sample can be a calibration validation sample.

8.7 *Reference Materials*—Homogenous material with a known elemental composition. Reference materials are available from commercial sources or may be prepared gravimetrically. For purposes of this method, homogenous reference materials in this test method are soils or sludge, unless otherwise specified.

8.8 *Independent Reference Material (IRM)*—A material of known purity and concentration obtained either from the National Institute of Standards and Technology (NIST) or other reputable supplier.

8.9 *Silicon Dioxide Powder (SiO_2)*—For preparing gravimetric empirical calibration standards (if using calibration method B, see 12.5) and for use as a blank sample to monitor instrument contamination and sample preparation contamination (see 17.3).

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[6] The sole source of supply of the apparatus known to the committee at this time is XOS, Inc., 15 Tech Valley Drive, East Greenbush, NY 12061. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8.10 *Single/Multi-Element Aqueous Standards*—Aqueous reference material with known elemental composition for preparing gravimetric empirical calibration standards (if using calibration method B or matrix spiked).

8.11 *X-ray Transparent Thin-Film*—Used as a protective barrier between the sample and the analyzer. See Note 2.

NOTE 2—The user should select a thin film that provides for maximum transmittance. The thin-film used in the development of this test method was high-purity 12 µm polypropylene film.

9. Hazards

9.1 Occupational Health and Safety standards for X rays and ionizing radiation shall be observed. Guidelines for safe operating procedures are also given in current handbooks and publications from original equipment manufacturers. For more information see similar handbooks on radiation safety.

9.2 Use proper personal protective equipment (PPE) when handling contaminated soil and solid waste. Consult chemical safety data sheets for recommended PPE.

10. Sampling and Test Specimen Preparation

10.1 *Sampling*—Collected samples in accordance with Practice E1727 or similar procedure.

10.2 *Preparation for Measurement:*

10.2.1 To ensure a representative sample is used, thoroughly mix the sample in the collection container by stirring, mixing, or kneading. Large agglomerations of soil or solid waste should be broken up. If mixing is not possible, take at least five portions of the sample when transferring.

10.2.2 If sample exceeds 15 % moisture content by wet weight it should be dried. Samples that require drying will appear muddy or have visible excess water. If unable to determine visibly, use Test Method D4944 or other method to determine moisture content. If drying is needed, place sample in drying container. Place drying container in oven until mass is constant. Sample can also be air dried or sun dried at the site alternatively.

10.2.3 Exclude non-representative material such as twigs, leaves, roots, insects, asphalt, and rocks. Completely grind the sample until it will pass through a number 50 sieve or higher (<275 µm particle size). Transfer enough material to fill the sample cell and cover with an X-ray film.

11. Preparation of Apparatus

11.1 Follow the manufacturer's instructions for set-up, conditioning, preparation, and maintenance of the spectrometer.

11.2 Allow the apparatus to stabilize for operation according to the manufacturer's guidelines.

11.3 Ensure that the spectral processing operates correctly according to the manufacturer's guidelines addressing spectral and matrix interferences as listed in the interferences section.

11.4 When required, reference spectra should be obtained from pure element standards for all deconvoluted elements.

12. Calibration

12.1 Calibration should, at a minimum, be conducted when a QC sample is out of range or as recommended by the manufacturer. For some applications including regulatory compliance, more frequent calibration may be required.

12.2 *Calibration of the X-ray Detector and Digital Pulse Processor*—Using calibration standards, identify one or more elemental emission line peaks from the spectrum of each monochromatic excitation beam to calibrate the energy to channel relationship of the X-ray Detector and Digital Pulse Processor (see 7.1.4 and 7.1.5). Chosen emission lines should be free from major interferences and should have a statistically significant peak counting area.

12.3 Two methods of calibrations are available:

12.4 *Calibration Method A – Fundamental Parameters Method:*

12.4.1 Fundamental Parameters calibration should be performed using multiple soil calibration standards, consisting of background soil level, low contamination levels and high contamination levels for selected elements to determine the initial sensitivity factors from each monochromatic beam. If appropriate reference soil standards are difficult to be obtained for some elements of interested, a reference standards with adjacent or nearby elements in the periodic table can be used in FP calibration. Soil reference materials may be NIST Soil Standard Reference Materials or similar. Soil reference materials may also be a soil surrogate like SiO_2 powder spiked with known metal contents; see 12.5.2 for spike process. By measuring the X-ray net intensity (cps) for each element and using the determined sensitivity factor for each beam plus a set of equations to account for the X-ray production, the X-ray absorption and enhancement effect, the concentration of all elements present can be determined. Due to the use of monochromatic beams for excitation, the FP calculation is much more accurate compared to the polychromatic excitation.

12.4.2 Solid waste samples may have a matrix quite different from a soil matrix. At least two reference materials with lighter matrix and heavier matrix shall be used to refine the FP model to account for significant matrix variation other than soil matrix. A solid waste sample that has organic type of matrix is considered to be a light matrix. A solid waste sample that contains more than 10 % of metals, like Fe, is considered as a heavy matrix. This step is not needed if only soil samples are tested in an application.

12.4.3 Most manufacturers provide FP calibration software to perform FP calibration and FP refinement. Follow the manufacturer's FP set-up recommendations. The manufacturer may have an optional setup to use a standard that has similar matrix to the testing sample that can be used to refine FP parameters for the best accuracy.

12.5 *Method B – Empirical Calibration Method:*

12.5.1 Empirical calibration for soil matrix is performed using the following calibration standards: a blank and at least four or more concentration levels that bracket between the low range and the high range defined in Table 2. The calibration standards should provide a linear response of element intensity

TABLE 2 Empirical Calibration Standard Ranges

Element	Low Concentration Range (ppm)	High Concentration Range (ppm)	Extended Range (ppm)
Cr	5	500	5000
Ni	5	500	5000
As	1	1000	5000
Cd	1	500	5000
Hg	1	500	5000
Pb	1	1000	5000

to concentration. If extended range is needed, then an additional calibration shall be performed to cover between the high range and extended range. For the additional calibration, use four or more concentration levels that bracket between the high concentration range and the extended range.

12.5.2 Calibration standards may be prepared by gravimetrically mixing SiO_2 powder with single/multi-element in aqueous standard. The mixing weight ratio for aqueous standard and SiO_2 is about 1:1. For example, prepare a 200 mg/kg Pb in SiO_2 standard by mixing 5 g of 100 mg/kg Pb aqueous standard solution, and 5 g of SiO_2. Dry the standard in a 60°C to 100°C oven or allow to air dry.

12.5.3 The matrix effect between the SiO_2 calibrants and soil samples should be corrected for by using a correction factor that is determined by measuring a spiked uncontaminated soil sample. An uncontaminated soil sample should be prepared and spiked (see 12.5.2 and use the uncontaminated soil in the place of the SiO_2 powder) to a known high range concentration to obtain a matrix correction factor between the calibrant and the real soil sample. The correction factor is typically recorded in a software tool provided by the manufacturer.

12.5.4 Empirical calibration for a specific solid waste matrix is performed using the following calibration standards: a blank and at least four or more concentration levels that bracket between the low range and the high range defined in Table 2. The calibration standards should provide a linear response of element intensity to concentration. If extended range is needed, then an additional calibration shall be performed. For the additional calibration, use four or more concentration levels to cover between the high range and extended range. The calibration standards shall have similar matrix to the solid waste matrix. If a matrix match between the calibrants and solid waste batch samples cannot be found, FP calibration method shall be used. This step is not needed if only soil samples are tested in an application.

12.5.5 For elements such as Hg, empirical calibration may produce measurement results which are biased due to its high volatility. Suitability of the empirical calibration for a volatile element can be verified using a commercially available reference material (see 12.4) that has been stored as recommended by the manufacturer and is within expiration date. In this case, a FP calibration method may be preferred over empirical calibration.

12.6 After calibrating, verify analyzer calibration by using one or more calibration validation samples (see 8.4). Results shall have a percent deviation less than 20 % from the known concentration for the target elements. If results for elements of interest are not within acceptable limits, the analyzer must be recalibrated.

12.7 Calibration should be verified periodically per 12.6. The initial validation frequency shall be weekly. If there is sufficient data to demonstrate that the calibration is stable, the calibration validation frequency can be reduced to monthly or longer period.

13. Procedure

13.1 *Measurement of Unknown Sample:*

13.1.1 Prepare the sample according to Section 10, and prepare the instrument according to Section 11. Place the sample in the X-ray beam path and perform the measurement as directed by the manufacturer.

13.1.2 Process the spectrum using the same procedure as outlined in Sections 11 and 12.

13.2 *Measurement of Reference Materials:*

13.2.1 When using reference materials, measure them in the same manner as an unknown sample (13.1) and before measuring any unknowns.

13.2.2 Analysis of result(s) from these samples must be carried out following Section 17. When the sample results exceed the laboratory's control limits, drift correction or instrument calibration may be required.

13.3 *Drift Correction:*

13.3.1 Drift is corrected by normalizing or standardizing the new measured count rates to make them comparable to count rates obtained at the time of calibration. Use the manufacturer's tools, if provided, or another suitable procedure.

14. Interpretation of Results

14.1 Using the net count rates for a sample and the calibration from Section 12, the result is calculated by the instrument software in units of mg/kg for each element that is reported.

14.2 For samples measured on a SiO_2 empirical calibration curve, apply the matrix correction by multiplying the measurement results by the matrix correction factor. Typically a software tool provided by the manufacturer can do the matrix correction automatically.

15. Report

15.1 Report the mass content of each element of the test sample calculated from Section 14 using units of mg/kg, rounded to the nearest 0.01 mg/kg for mass fractions ≤100 mg/kg, and rounded to the nearest 0.1 mg/kg for mass fractions >100 mg/kg. Include a description of the sample type, and indicate that the test results were obtained using Test Method D8064.

16. Precision and Bias

16.1 *Precision*—The precision of this test method was determined from data from a single site study in accordance with Practice E1169. Five NIST SRM soil samples and two NIST SRM sludge samples (see Table X1.2 in Appendix X1) were measured ten times each to determine the relative standard deviation (RSD) and bias. The results obtained for the study are summarized in Table 3. Appendix X1 provides the detailed results for single site blank, and precision and bias study from each NIST SRM.

16.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the repeatability values only in one case in twenty. The final repeatability of this test method will be available following the completion of the interlaboratory or intersite study. A preliminary repeatability is indicated by the single site RSD given in Table 3 and Appendix X1.

16.1.2 *Reproducibility*—The reproducibility of this test method is not currently available. The reproducibility of this test method will be available following the completion of the interlaboratory or intersite study.

16.2 *Bias*—Between-lab bias will not be available until the interlaboratory or intersite study is complete. Single laboratory bias has been determined as shown in Table 3. No significant bias was exhibited for all seven NIST samples in the reporting ranges.

17. Quality Control

17.1 The following quality control requirements shall be performed to ensure the analyzer is within control:

17.1.1 Verify analyzer calibration by using one or more reference materials (see 8.4). Calibration verification shall be performed after calibrating the analyzer and at least once weekly initially. If the calibration is stable for a longer period of time, the calibration validation frequency can be reduced to monthly or a longer period. See 12.4 for calibration verification acceptance criteria.

17.1.2 An initial demonstration of site capability is necessary to prevent errors as a result of unfamiliarity with the test method. See 17.2.

17.1.3 Analysis of a blank is performed to ensure measurement results are not due to contamination. Analysis should be performed at least once daily or for each batch analysis. See 17.3.

17.1.4 Analysis of a Quality Control (QC) sample is performed to ensure that the measurement system is in control at the time samples are being analyzed. Analysis should be performed at least once weekly or for each batch analysis. See 17.4.

17.1.5 A duplicate analysis of a sample or a control sample is performed periodically to ensure precision of the sample analysis within the repeatability of the method. See 17.5.

17.1.6 Analysis of a Matrix Spiked (MS) sample is performed to ensure no significant matrix interference for each batch analysis. Alternatively, an IRM sample can be measured. See 17.6.

17.2 *Initial Demonstration of Site Capability*—If a site has not performed the test method before or if there is a change in the measurement system, for example new analyst, new instrument, etc., a demonstration of laboratory capability shall be performed. Analyze an IRM sample or reference material sample seven times. Calculate the mean, standard deviation, and relative standard deviation for each element measured and compare to the acceptable ranges of the QC acceptance criteria for the Initial Demonstration of Performance in Table 4.

17.2.1 This study should be repeated until the single operator precision and mean are within the limits in Table 4. If a concentration outside of the recommended range is used, refer

TABLE 3 Repeatability and Bias Results for Single Site Study (mg/kg)

NIST SRM		Cr	Ni	As	Cd	Hg	Pb
1646a	Mean	41.66	22.07	6.66	...	...	11.83
	ARV	40.9	23	6.23	0.148	0.04	11.7
	RSD	4.39 %	8.33 %	2.05 %	...	...	1.58 %
	Bias	1.86 %	-4.04 %	6.90 %	...	...	1.11 %
2586	Mean	313.2	72.91	8.16	2.89	0.63	422.80
	ARV	301	75	8.7	2.71	0.367	432
	RSD	2.56 %	0.78 %	9.49 %	12.31 %	37.7 %	0.65 %
	Bias	4.06 %	-2.79 %	-6.21 %	6.64 %	71.66 %	-2.13 %
2709a	Mean	133.70	87.01	11.63	...	0.96	18.07
	ARV	130	85	10.5	0.37	0.9	17.3
	RSD	2.18 %	0.78 %	5.10 %	...	27.47 %	1.02 %
	Bias	2.82 %	2.36 %	10.76 %	...	6.67 %	4.45 %
2710a	Mean	23.25	8.85	1506.5	11.68	9.44	5422.5
	ARV	23	8	1540	12.3	9.88	5520
	RSD	11.44 %	6.12 %	0.79 %	3.27 %	11.49 %	0.15 %
	Bias	1.09 %	10.63 %	-2.17 %	-5.04 %	-4.45 %	-1.77 %
2711a	Mean	54.30	18.76	104.54	55.04	7.49	1404.6
	ARV	52.3	21.7	107	54.1	7.42	1400
	RSD	5.06 %	2.32 %	2.27 %	1.50 %	4.37 %	0.11 %
	Bias	3.82 %	13.55 %	-2.30 %	1.74 %	0.94 %	0.33 %
2782	Mean	109.0	153.4	159.8	4.31	...	594.7
	ARV	109	154.1	166	4.17	1.1	574
	RSD	10.58 %	2.43 %	1.23 %	14.58 %	...	0.59 %
	Bias	0.00 %	-0.47 %	-3.76 %	3.43 %	...	3.61 %
2781	Mean	202.3	80.29	8.14	12.69	3.78	201.6
	ARV	202	80.2	7.82	12.78	3.64	202.1
	RSD	1.95 %	1.27 %	3.78 %	14.36 %	13.78 %	0.36 %
	Bias	0.15 %	0.11 %	4.10 %	-0.72 %	3.83 %	-0.25 %

TABLE 4 QC Acceptance Criteria

NOTE 1—Data is preliminary until a multi-lab validation study is completed.

Element	ARV Range (mg/kg)	Initial Demonstration of Performance			Laboratory/Site Control Sample	
		Bias (%)		Precision Max	Bias (%)	
		Lower Limit	Upper Limit	RSD (%)	LCL (%)	UCL (%)
Pb	300 to 4000	-20	20	20	80	120
As	100 to 1500	-20	20	20	80	120
Cr	100 to 400	-20	20	20	80	120
Ni	100 to 400	-20	20	20	80	120
Cd	10 to 80	-20	20	20	80	120
Hg	5 to 40	-20	20	20	80	120

to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

17.2.2 The QC acceptance criteria for the initial demonstration of laboratory capability in Table 4 were generated from the single-laboratory data shown in Section 16. It is recommended that each laboratory or site determine in-house QC acceptance criteria which meet or exceed the criteria in this test method.

17.3 *Blank Analysis:*

17.3.1 *Instrument Blank Analysis*—A blank sample shall be measured at least once daily to investigate for instrument contamination. The concentration of the target element(s) shall be at less than half of the reporting limits. If the result is not within these limits, replace the sample cell film, any secondary window film(s) (if applicable), and follow manufacturer cleaning processes to remove contamination. Perform these processes until the blank measurement is within acceptable limits. Impacted samples should be reanalyzed. Reagent grade SiO_2 has been found to be an acceptable blank sample, although other reference materials may be used as long as the measurement results are within acceptable limits.

17.3.2 *Sample Preparation Blank Analysis*—A blank sample shall be prepared at least once daily when samples are prepared for analysis. The blank sample shall go through the same sample preparation process as the samples in the batch and be analyzed with the samples in the batch. Reagent grade SiO_2 has been found to be an acceptable material for blank sample preparation, although other materials may be used as long as the measurement results are within acceptable limits. If a sample preparation blank result exceeds the reporting limit for a specific analyte then the sample results for that specific analyte in the sample batch must be properly coded in the analytical report. If a sample preparation blank exceeds three times the reporting limit for any specific analyte, then all potentially impacted samples must be prepared again with a new sample preparation blank and reanalyzed to verify sources of cross contamination have been removed from the sample preparation process. Properly cleaning or replacing devices or materials used in the sample preparation process must be done to remove sources of contamination.

17.4 *Quality Control (QC) Sample*—Analyze at least one QC sample containing mid-range level elements weekly and use control charting techniques to monitor and control the stability of the measurement system. Results obtained for the QC sample shall fall within the limits in Table 4. It is recommended that each site determine in-house QC acceptance criteria meeting or exceeding the criteria stated in this test method. Calibration validation samples may be used as QC samples.

17.4.1 Each laboratory or site should generate its own in-house QC acceptance criteria after 15 to 20 analyses of the QC sample. For further guidance on QC and control charting techniques, see Practice E2554 or MNL-7A.

17.4.2 It is recommended that a QC analysis should be performed prior to each batch analysis. Multiple QC analysis may be needed in between for a large batch analysis.

17.5 *Duplicate Analysis*—To check the precision of sample analyses, analyze a sample in duplicate periodically. Duplicate analysis frequency shall be similar to the frequency of calibration check in 17.1. The duplicate samples shall contain elements within the range of this method, and the precision of the duplicates shall not exceed the repeatability of this method. If the result is not within these limits, sample analysis is halted until corrective action resolving the problem has been performed. Impacted samples in the batch should be reanalyzed.

17.6 *Matrix Spike (MS):*

17.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from a batch samples in a site by spiking the sample with a spiking solution. The spiking solution can be a 2 to 5 g Single/Multi-Element Aqueous Standards with appropriate elemental concentrations. Spike the standards solution into a site sample with 1:1 weight ratio, mix well and allow the mixed sample to dry at room temperature or in a 60 to 100°C oven. The spiked sample shall have a concentration of two to five times the unspiked sample.

17.6.2 The site sample shall be selected from the batch in such a way that the concentrations of the interested elements are in the lower half of the range of method. The final concentration of the spiked sample shall not exceed the upper range of the method.

17.6.3 Calculate the percent recovery of the spike (P) using Eq 1:

$$P = 100\frac{|AW - BW|}{Cw} \qquad (1)$$

where:

A = concentration by weight found in spiked sample,
B = concentration by weight found in unspiked sample,
C = concentration by weight of analyte in Single/Multi-Element Aqueous Standards,
W = weight of sample used,

w = weight of spiking aqueous solution added, and
P = percent recovery.

17.6.4 The percent recovery of the spike shall fall within the limits in Table 5. The limits in Table 5 were generated by a single site data listed in Table 6. The detail study and results are shown in Table X1.9 in Appendix X1. The limits in Table 5 are preliminary until a multi-site validation study is completed.

17.6.5 Alternatively, the interference of matrix can also be checked by using an IRM sample with matrix similar to the batch samples. The bias and precision of the IRM sample shall fall within the limits in Table 4.

17.6.6 Matrix similarity between the IRM sample and the batch samples is defined as the major elemental compositions are within 30 % between the two matrixes. Major elemental compositions are any elemental composition greater than 5 % in the matrix.

18. Keywords

18.1 arsenic; As; cadmium; Cd; chromium; Cd; EDXRF; fundamental parameters; FP; HDXRF; heavy metals; Hg; lead; mercury; MMB-EDXRF; Multiple Monochromatic Beam EDXRF; Ni; nickel; Pb; soil; solid waste

TABLE 6 Single-Site Recovery Data of a Soil Sample in Geneva, New York

	Pb	As	Ni	Cr	Cd
Mean (unspiked)	323.3	11.97	36.70	82.44	ND ± 0.8
Mean (spiked)	682.2	74.54	81.64	185.3	39.28
Recovery	103 %	107 %	96 %	106 %	101 %

TABLE 5 MS QC Acceptance Criteria

Element	Spiked Conc. (mg/kg)	MS		
		Recovery		Precision Max
		Lower Limit	Upper Limit	RSD (%)
Pb	2-5 times of unspiked conc.	70	130	20
As	2-5 times of unspiked conc.	70	130	20
Cr	2-5 times of unspiked conc.	70	130	20
Ni	2-5 times of unspiked conc.	70	130	20
Cd	2-5 times of unspiked conc.	70	130	20
Hg	2-5 times of unspiked conc.	70	130	20

APPENDIX

(Nonmandatory Information)

X1. BLANK, SITE PRECISION, BIAS, AND MATRIX SPIKED RESULTS

X1.1 Table X1.1 provide the results for single site blank measurement using a SiO_2 powder sample. The errors given are nominally ±2 sigma for none detected elements. All listed elements are less than half of the reporting low limits or non-detected. The LOD is estimated as three times of the standard deviation of the blank.

X1.2 Detail information of five NIST soil standards and two solid waste standards used in the single data collection is listed in Table X1.2. Sample 1646a is a soil standard that contains metals at or near background levels.

X1.3 In the single site study, each sample in Table X1.2 were tested ten times according to the method. Each tested results, mean, standard deviation and RSD for the ten repeats were given in Tables X1.3-X1.9 for each sample type. A bias is calculated as the percentage discrepancy respect to the accepted reference value.

X1.4 Matrix Spike Recoveries

X1.4.1 Soil samples collected from a site in Geneva, New York were tested using this method. The five tested results are listed in Table X1.10 as unspiked samples.

X1.4.2 A matrix spike was performed according to 17.6 with a gravimetrically prepared multi-element water standard containing the following elements: Pb, As, Ni, Cr, and Cd. The weight of the unspiked soil sample, weight of the multi-element water solution, and the elemental concentrations in the water solution are listed in Table X1.11. The spiked sample was dried at room temperature.

X1.4.3 The dried spiked soil was measured five times and the recovery percentage was calculated using Eq 1. The results are listed in Table X1.10.

TABLE X1.1 Blank Sample (SiO_2) Results for Single Site Repeatability Study (mg/kg)

NOTE 1—For non-detect elements, the 1 sigma error is used for the standard deviation.

SiO_2	Cr	Ni	As	Cd	Hg	Pb
1	2.50	1.38	ND ± 0.15	0.33	0.31	0.86
2	0.94	1.33	ND ± 0.15	0.24	0.41	0.97
3	2.84	2.12	ND ± 0.15	0.53	0.33	0.85
4	2.57	1.96	ND ± 0.15	0.39	0.13	0.55
5	2.49	1.91	ND ± 0.15	0.25	0.37	0.58
Stan. Dev.	0.76	0.36	0.08	0.12	0.11	0.18
LOD	2.27	1.08	0.23	0.36	0.32	0.55

TABLE X1.2 Accepted Reference Values (ARV) (mg/kg) for NIST SRMs Used in Method Precision

Part #	Description	Cr	Ni	As	Cd	Hg	Pb
1646a	Estuarine Sediment	40.9	23	6.23	0.148	0.04	11.7
2586	Trace Elements in Soil Containing Pb from Paint	301	75	8.7	2.71	0.367	432
2709a	San Joaquin Soil	130	85	10.5	0.371	0.9	17.3
2710a	Montana I Soil	23	8	1540	12.3	9.88	5520
2711a	Montana II Soil	52.3	21.7	107	54.1	7.42	1400
2782	Industry Sludge, Solid Waste	109	154.1	166	4.17	1.1	574
2781	Domestic Sludge, Solid Waste	202	80.2	7.82	12.78	3.64	202

TABLE X1.3 NIST SRM 1646a Results for Single Site Repeatability Study (mg/kg)

SRM 1646a	Cr	Ni	As	Cd	Hg	Pb
1	41.57	24.34	6.70	<1.12	<0.36	11.98
2	39.91	23.91	6.86	<1.16	<0.37	11.68
3	38.20	21.99	6.67	<1.15	<0.37	11.49
4	42.73	22.27	6.53	<1.16	<0.39	11.89
5	41.66	23.30	6.63	<1.14	<0.37	11.81
6	41.95	18.90	6.42	<1.16	<0.39	12.01
7	41.93	21.70	6.63	<1.01	<0.39	11.99
8	40.71	21.72	6.81	<1.16	<0.37	11.58
9	42.93	23.38	6.58	<1.18	<0.36	11.87
10	45.01	19.19	6.79	<1.17	<0.39	12.01
Mean	41.66	22.07	6.66	...	...	11.83
Stand. Dev.	1.83	1.84	0.14	...	...	0.19
RSD	4.39 %	8.33 %	2.05 %	...	...	1.58 %
ARV	40.9	23	6.23	0.148	0.04	11.7
Bias	1.86 %	-4.04 %	6.90 %	...	...	1.11 %

TABLE X1.4 NIST SRM 2586 Results for Single Site Repeatability Study (mg/kg)

SRM 2586	Cr	Ni	As	Cd	Hg	Pb
1	311.7	72.09	7.38	2.89	<0.35	422.6
2	319.8	72.52	6.92	2.95	0.62	416.3
3	318.2	73.51	8.52	2.97	0.36	426.8
4	310.2	72.51	8.33	2.37	0.39	424.5
5	311.0	73.01	8.70	2.87	1.00	423.1
6	331.4	72.89	7.79	2.75	<0.75	421.8
7	310.4	72.39	9.44	2.29	0.68	424.0
8	310.2	73.73	8.73	3.34	0.71	421.3
9	303.3	72.81	8.42	3.34	0.42	424.2
10	306.1	73.66	7.36	3.18	0.92	423.2
Mean	313.2	72.91	8.16	2.89	0.63	422.8
Stand. Dev.	8.02	0.57	0.77	0.36	0.24	2.75
RSD	2.56 %	0.78 %	9.49 %	12.31 %	37.70 %	0.65 %
ARV	301	75	8.7	2.71	0.367	432
Bias	4.06 %	-2.79 %	-6.21 %	6.64 %	71.66 %	-2.13 %

TABLE X1.5 NIST SRM 2709a Results for Single Site Repeatability Study (mg/kg)

SRM 2709a	Cr	Ni	As	Cd	Hg	Pb
1	137.3	88.50	12.23	<1.36	1	18.09
2	135.3	87.03	12.24	<1.34	0.72	18.35
3	130.1	86.37	10.73	<1.33	0.90	18.08
4	134.2	86.30	10.90	<1.32	1.05	18.03
5	133.7	86.57	11.93	<1.34	1.20	18.02
6	132.3	87.37	11.44	<1.32	1.11	18.36
7	130.3	87.66	11.27	<1.35	0.86	17.99
8	130.5	86.67	11.90	<1.35	1.27	18.17
9	134.5	86.95	11.21	<1.37	1.09	17.91
10	138.5	86.66	12.40	<1.36	0.37	17.77
Mean	133.7	87.01	11.63	...	0.96	18.07
Stand. Dev.	2.91	0.68	0.59	...	0.26	0.18
RSD	2.18 %	0.78 %	5.10 %	...	27.47 %	1.02 %
ARV	130	85	10.5	0.37	0.9	17.3
Bias	2.82 %	2.36 %	10.76 %	...	6.67 %	4.45 %

TABLE X1.6 NIST SRM 2710a Results for Single Site Repeatability Study (mg/kg)

SRM 2710a	Cr	Ni	As	Cd	Hg	Pb
1	27.12	8.51	1495.2	11.53	8.43	5429.3
2	20.93	8.64	1498.3	11.83	8.75	5438.0
3	21.55	9.3	1507.9	11.17	10.33	5422.0
4	27.88	9.57	1513.3	11.95	8.24	5414.4
5	20.66	8.28	1503.0	12.05	10.10	5411.5
6	25.26	8.58	1517.2	11.48	9.91	5425.1
7	22.69	7.98	1510.1	11.74	10.87	5424.5
8	21.19	8.89	1482.8	11.29	10.83	5413.4
9	23.81	9.43	1522.4	12.38	8.75	5420.0
10	21.43	9.34	1515.2	11.35	8.11	5427.3
Mean	23.25	8.85	1506.5	11.68	9.44	5422.5
Stand. Dev.	2.6	0.54	11.9	0.38	1.08	8.14
RSD	11.44 %	6.12 %	0.79 %	3.27 %	11.49 %	0.15 %
ARV	23	8	1540	12.3	9.88	5520
Bias	1.09 %	10.63 %	-2.17 %	-5.04 %	-4.45 %	-1.77 %

TABLE X1.7 NIST SRM 2711a Results for Single Site Repeatability Study (mg/kg)

SRM 2711a	Cr	Ni	As	Cd	Hg	Pb
1	57.57	18.67	100.9	56.35	7.49	1404.0
2	56.97	18.69	107.2	55.54	7.01	1407.3
3	49.53	19.13	105.8	55.05	7.27	1403.9
4	53.98	17.97	107.5	55.21	8.00	1404.8
5	54.38	18.29	103.7	55.03	7.32	1405.0
6	54.78	19.00	102.6	55.63	7.61	1402.0
7	52.26	19.47	105.0	54.21	7.30	1403.8
8	54.6	18.65	106.6	53.44	7.21	1406.6
9	57.85	18.65	104.9	54.44	7.74	1404.1
10	51.09	19.12	101.2	55.48	7.93	1404.7
Mean	54.3	18.76	104.5	55.04	7.49	1404.6
Stand. Dev.	2.75	0.43	2.37	0.83	0.33	1.49
RSD	5.06 %	2.32 %	2.27 %	1.50 %	4.37 %	0.11 %
ARV	52.3	21.7	107	54.1	7.42	1400
Bias	3.82 %	-13.55 %	-2.30 %	1.74 %	0.94 %	0.33 %

TABLE X1.8 NIST SRM 2782 Results for Single Site Repeatability Study (mg/kg)

SRM 2782	Cr	Ni	As	Cd	Hg	Pb
1	113.3	159.1	162.6	4.62	<2.13	589.9
2	100.3	154.5	159.9	4.13	<2.15	598.6
3	94.7	149.8	159.1	4.46	<2.14	596.8
4	130.3	158.0	161.3	4.03	<2.13	591.7
5	112.0	155.0	158.8	4.22	<2.12	594.6
6	98.0	149.9	161.9	5.68	<2.14	595.0
7	111.8	152.2	158.2	3.93	<2.14	600.1
8	124.2	147.2	156.8	3.27	<2.16	592.6
9	102.6	153.1	157.6	4.72	<2.13	597.2
10	103.0	155.0	161.3	4.07	<2.14	590.6
Mean	109.0	153.4	159.8	4.31	...	594.7
Stand. Dev.	11.54	3.73	1.96	0.63	...	3.48
RSD	10.58 %	2.43 %	1.23 %	14.58 %	...	0.59 %
ARV	109	154.1	166	4.17	1.1	574
Bias	0.00 %	-0.47 %	-3.76 %	3.43 %	...	3.61 %

TABLE X1.9 NIST SRM 2781 Results for Single Site Repeatability Study (mg/kg)

SRM 2781	Cr	Ni	As	Cd	Hg	Pb
1	209.0	80.39	8.67	10.17	3.21	202.6
2	204.3	79.96	8.39	10.92	4.65	201.3
3	199.9	78.09	7.71	15.90	3.83	200.1
4	203.1	81.37	7.86	14.20	3.67	201.1
5	202.1	80.22	7.78	12.28	4.29	201.7
6	199.3	80.64	7.94	13.25	3.20	201.8
7	200.0	81.02	8.26	11.32	3.25	202.5
8	207..9	79.29	8.32	14.29	3.98	201.6
9	201.4	80.31	8.13	13.40	3.40	201.2
10	196.1	81.57	8.34	11.15	4.31	202.0
Mean	202.3	80.29	8.14	12.69	3.78	201.6
Stand. Dev.	3.95	1.02	0.31	1.82	0.52	0.73
RSD	1.95 %	1.27 %	3.78 %	14.36 %	13.78 %	0.36 %
ARV	202	80.2	7.82	12.78	3.64	202.1
Bias	0.15 %	0.11 %	4.10 %	-0.72 %	3.83 %	-0.25 %

TABLE X1.10 Single-Site Recovery Data of a Soil Sample in Geneva, New York (mg/kg)

	Pb	As	Ni	Cr	Cd
unspiked					
1	324.3	10.87	36.83	80.89	ND ± 0.8
2	326.3	11.48	35.23	83.86	ND ± 0.8
3	323.3	11.82	37.83	88.02	ND ± 0.8
4	321.7	12.52	37.43	80.42	ND ± 0.8
5	321.1	13.16	36.18	79.03	ND ± 0.8
Mean B	323.3	11.97	36.70	82.44	ND ± 0.8
RSD	0.65 %	7.46 %	2.81 %	4.34 %	
spiked					
1	685.3	74.59	80.35	178.2	42.03
2	683.8	71.41	82.91	182.9	42.35
3	681.3	72.06	83.68	191	36.41
4	684.2	74.72	77.92	189.7	34.97
5	676.2	79.92	83.32	184.7	40.63
Mean A	682.2	74.54	81.64	185.3	39.28
RSD	0.53 %	4.5 %	3.0 %	2.81 %	8.6 %
Recovery	103 %	107 %	96 %	106 %	101 %

TABLE X1.11 Data for Weight of Unspiked Geneva Soil W, Weight of Multi-Element Water Standard w, and Elemental Concentration in the Water Standard C

W g	w g	C_{Pb} mg/kg	C_{As} mg/kg	C_{Ni} mg/kg	C_{Cr} mg/kg	C_{Cd} mg/kg
2.57	2.57	348.86	58.28	46.69	97.02	39.01

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