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Standard Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry¹

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1. Scope

1.1 This standard provides guidelines for developing and describing analytical procedures using a wavelength dispersive X-ray spectrometer for elemental analysis of solid metals, ores, and related materials. Material forms discussed herein include solids, powders, and solid forms prepared by chemical and physical processes such as borate fusion and pressing of briquettes.

1.2 Liquids are not discussed in this guide because they are much less frequently encountered in metals and mining laboratories. However, aqueous liquids can be processed by borate fusion to create solid specimens, and X-ray spectrometers can be equipped to handle liquids directly.

1.3 Some provisions of this guide may be applicable to the use of an energy dispersive X-ray spectrometer.

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

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This guide is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.20 on Fundamental Practices.

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2. Referenced Documents

2.1 ASTM Standards:²

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E1257 Guide for Evaluating Grinding Materials Used for Surface Preparation in Spectrochemical Analysis

E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)³

E1361 Guide for Correction of Inter-element Effects in X-Ray Spectrometric Analysis

E2857 Guide for Validating Analytical Methods

E2972 Guide for Production, Testing, and Value Assignment of In-House Reference Materials for Metals, Ores, and Other Related Materials

2.2 ISO Standard:⁴

ISO 17034: 2016 General Requirements for the Competence of Reference Material Producers

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminology E135 and the terminology section of Guide E1361.

4. Summary of Guide

4.1 Important aspects of test equipment for wavelength dispersive X-ray fluorescence spectrometry are discussed including equipment components and accessories, reagents, and materials. Key aspects of the application of X-ray spectrometry to materials analysis are discussed including interferences and correction options, specimen preparation by a variety of procedures, and materials and accessories for presentation of specimens for measurement in spectrometers. Key elements of

² 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.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

measurement procedures, calibration procedures, and result reporting are explained.

4.2 In an X-ray spectrometric test method, the test specimen is prepared with a clean, uniform, flat surface. It may be prepared by grinding, polishing, or lathing a metal surface or by fusing or briquetting a powder. This surface is irradiated with a primary source of X-rays. The secondary X-rays produced in the specimen are dispersed according to their wavelengths by means of crystals or synthetic multilayers. Their count rates at selected wavelengths, hereinafter called intensities, are measured by suitable detector systems. Amounts of the elements are determined from the measured intensities using calibrations prepared with suitable calibrants.

4.3 Important aspects of background estimation are covered in [Appendix X1](#).

5. Significance and Use

5.1 X-ray fluorescence spectrometry can provide an accurate determination of metallic and many non-metallic elements in a wide variety of solid and liquid materials. This guide covers the information that should be included in an X-ray spectrometric analytical method and provides direction to the user for determining the optimum conditions needed to achieve acceptable accuracy.

5.2 The accuracy of a determination is a function of the calibration algorithm, the sample preparation, and the sample homogeneity. Close attention to all aspects of these areas is necessary to achieve acceptable results.

5.3 All concepts discussed in this guide are explored in detail in a number of published texts and in the scientific literature.

6. Interferences

6.1 Line overlaps, either total or partial, may occur for some elements. If sufficient sensitivity exists, it may be possible to reduce or eliminate the overlap by choosing a higher level of collimation in the secondary X-ray path from specimen to dispersive element or detector. See [Appendix X1](#) for optional approaches to the correction of line overlap effects.

6.1.1 Fundamental parameter (FP) equations require net intensities with background subtraction and line overlap corrections performed before the FP calculations are conducted. Some empirical algorithms incorporate line overlap corrections in their equations, and some software allows combinations of empirical and FP calculations chosen by element or other analyte.

6.1.2 In addition, line overlap interferences may occur from characteristic lines generated from the target material of the X-ray tube and scattered from the specimen either inelastically (known as Compton scatter) or elastically (known as Rayleigh scatter). These may be reduced or eliminated using primary beam filters, with a consequent loss of sensitivity.

6.2 Interelement effects (sometimes called matrix effects, see [6.2.2](#)) may be significant for some elements. An empirical way to compensate for these effects is to prepare a series of calibrations that cover the designated mass fraction ranges to be analyzed. Typically, more accurate results are obtained

when the compositions of the calibrants used to prepare the calibrations are similar to the compositions of materials being analyzed. This approach requires many more reference materials (RMs) than more modern methods, and this approach is generally superseded by mathematical methods.

6.2.1 Alternatively, mathematical methods may be used to compensate for interelement or matrix effects. Various mathematical correction procedures are commonly utilized. See [Guide E1361](#). Any of these that will achieve the necessary analytical accuracy is acceptable.

6.2.2 Interelement effects are not interferences in the spectrometric sense but will contribute to errors in the analysis if not properly addressed. Interelement effects result from the absorption of X-rays to differing extents by the atoms in the specimen according to the mass absorption coefficient. Use caution with empirical mathematical models to ensure that sufficient data are provided to adequately compensate for these effects.

6.3 *Errors From Metallurgical Structure*—Because the analyte intensity is affected by the mass absorption of the sample and mathematical models assume a homogeneous sample, a bias may result if the analyte exists in a separate phase, such as an inclusion. For example, in a steel that contains carbon and carbide formers such as titanium and niobium, the titanium may exist in a titanium-niobium carbide that has a lower mass absorption coefficient than iron for the titanium $K\text{-}L_{2,3}$ ($K\alpha$) line. The intensity for titanium is higher in this sample than it would be if the titanium, niobium, carbon, and iron were always in solid solution.

7. Apparatus

7.1 Specimen Preparation Equipment for Solid Metals:

7.1.1 *Surface Grinder or Sander With Abrasive Belts or Disks, or Lathe, or Mill* capable of providing a flat, uniform surface on both the reference materials and test specimens.

7.1.1.1 Abrasive disks are preferred over belts because the platen on a belt grinder tends to wear and produce a convex surface on the specimen. If belt grinders are used, exercise care to ensure the platen is maintained flat.

7.1.1.2 The grinding media should be selected so no significant contamination occurs for the elements of interest during the sample preparation. (Refer to [Guide E1257](#).)

7.1.1.3 Grinding belts or disks shall be changed at regular, specified intervals because abrasives lose their ability to remove material efficiently and without inducing contamination. This is particularly important in alloys that exhibit smearing of a softer component across the surface.

7.1.1.4 Provision of flowing water across the surface of a grinding belt or disk cools the specimen and removes debris. Chemical coolants, such as those used in machine shops, should not be used, except for special purposes.

7.1.1.5 The use of a lathe, or similar type of machine, is recommended for soft metals or metals that have components that can smear when surfaced with an abrasive media. The feed on the cutting tools should be constant, and automatically controlled, to give a consistent finish.

7.2 Specimen Preparation Equipment for Powders:

7.2.1 *Jaw Crusher or Steel Mortar and Pestle*, for initial crushing of larger chunks of material.

7.2.2 *Plate Grinder or Pulverizer*, with one static and one rotating disk for further grinding or crushing.

7.2.3 *Rotary Disk Mill or Swing Mill*, with hardened grinding containers and timer control for final grinding.

7.2.4 *Briquetting Press*, providing pressures of up to 550 MPa. The press shall be equipped with a mold assembly that provides a briquette that is compatible with the X-ray specimen holder.

7.2.5 *Fusion Equipment*, with a timer, capable of heating the sample and flux to at least 975 °C and homogenizing the melt.

7.2.6 *Fusion Crucibles*, compatible with the flux and sample type:

7.2.6.1 *Vitreous Carbon*, flat bottomed with a suitable diameter and capacity to produce a fused disk compatible with the X-ray specimen holder.

7.2.6.2 *95 % Platinum/5 % Gold Alloy*, with a suitable capacity for the casting molds being employed.

7.2.7 *Platinum/Gold Casting Mold (95 %/5 %)*, having a flat, optical-polished bottom and sufficient capacity to hold the quantity of glass needed to make a cast bead of nearly uniform thickness across the entire diameter, typically 30 mm to 40 mm.

7.2.8 *Polishing Wheel*, suitable for polishing the fused bead to obtain a flat uniform surface for irradiation. For machines that cast a bead in a polished dish, this step may not be necessary.

7.3 *Excitation Source:*

7.3.1 *X-Ray Tubes*, with targets of various high-purity elements that are capable of continuous operation at potentials and currents that will excite the elements to be determined.

7.3.2 *X-Ray Tube Power Supply*, providing a stable voltage of sufficient energy to produce secondary radiation from the specimen for the elements specified. The instrument may be equipped with an external line voltage regulator or a transient voltage suppressor.

7.4 *Spectrometer*, designed for X-ray fluorescence analysis, and equipped with specimen holders and a specimen chamber. The chamber may contain a specimen spinner and must be equipped for vacuum or helium-flushed operation for the determination of elements of atomic number 20 (calcium) or lower.

7.4.1 *Analyzing Crystals*, flat or curved crystals with optimized capability for the diffraction of the wavelengths of interest. The term is also applied to synthetic multi-layer structures that are preferred for some applications.

7.4.2 *Collimator*, for limiting the characteristic X-rays to a parallel bundle when flat crystals are used in the instrument. For longitudinally curved crystal optics, a collimator is not necessary, and may be replaced by entrance and exit slits.

7.4.3 *Masks*, for restricting the portion of the specimen viewed by the collimator or entrance slit.

7.4.4 *Detectors*, sealed or gas-flow proportional counters and scintillation counters are most commonly used. Tandem configurations are available to allow simultaneous use of two detectors.

7.4.5 *Vacuum System*, for the determination of elements whose radiation is absorbed to a significant extent by air. The system shall consist of a vacuum pump, gauge, and electrical controls to provide automatic evacuation of the optical path, and maintain a controlled pressure, usually 13 Pa (100 μm Hg) or less.

7.5 *Measuring System*, consisting of electronic circuits capable of amplifying and shaping pulses received from the detectors. The system shall be equipped with an appropriate data output device.

7.5.1 *Pulse Height Selectors*, used to discriminate against pulses from higher order X-ray lines and background.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagents used in X-ray fluorescence test methods must be evaluated for appropriate purity for the stated purpose and the expected performance of the test method.

8.2 *Binder*—One of a wide variety of compounds or materials that provide cohesion of particles in a briquette including polyethylene glycol, cellulose, spectrographic grade graphite (<74 μm briquetting type), borate compounds, and other chemicals.

8.3 *Detector Gas*—Typical detector gas consists of a mixture of 90 % argon and 10 % methane for use with gas-flow proportional counters. Other gases are used to enhance sensitivity over selected wavelength ranges.

8.4 *Fluxes*—Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), lithium metaborate (LiBO_2), mixtures of tetraborate and metaborate, boric anhydride (B_2O_3), and sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$). Prefused versions of the borate fluxes are available in high-purity versions, some of which are mixed with halide compound releasing (non-wetting) agents, fluidizers, and heavy absorbers, for example, lanthanum oxide. There may be additional flux compositions suitable for dissolution of samples.

9. Reference Materials

9.1 *Certified Reference Materials* are available from national metrology institutes and from private and public organizations that certify reference materials for chemical composition in accordance with ISO 17034 and with relevant supplemental standards and guidelines implemented by standards development organizations concerned with a particular business sector.

9.2 *Reference Materials* with matrix compositions similar to that of the test specimen and containing varying amounts of the elements to be determined may be used, provided they have been analyzed in accordance with validated test methods. These reference materials should be sufficiently homogeneous for the intended purpose. See Guide E2972.

9.3 The reference materials should cover the mass fraction ranges of the elements being determined. An appropriate number of reference materials shall be used for each element, depending on the mathematical models being used.

10. Hazards

10.1 Exposure to excessive quantities of high energy radiation such as those produced by X-ray spectrometers is injurious to health. The operator should take appropriate actions to avoid exposing any part of their body to primary, secondary, and scattered X-rays that may be present. The X-ray spectrometer should be operated in accordance with regulations governing the use of ionizing radiation. Manufacturers of X-ray fluorescence spectrometers typically install appropriate shielding and safety interlocks in X-ray spectrometers, which minimize the risk of excessive radiation exposure to operators. Operators should not attempt to bypass or defeat safety devices. Only authorized personnel should service X-ray spectrometers.

10.2 *Monitoring Devices*, such as film badges or dosimeters may be used by operators and service personnel. Periodic radiation surveys of the equipment for leaks and excessive scattered radiation may be required by governing laws or regulations.

11. Preparation of Reference Materials and Test Specimens

11.1 Throughout the procedure, treat reference materials and test specimens exactly the same way. Consistency in preparation of reference materials and specimens is essential to ensure reproducible results. After the preparation procedure is established, it must be followed exactly. Variations in technique, such as grinding time, abrasive grit size or material, particle size, binder material, sample-binder ratio, briquetting pressure, or holding times, can cause unreliable results.

11.2 *Solid Metal Samples*—Prepare the reference materials and test specimens so that each has a clean, flat uniform surface to be exposed to the X-ray beam. For abrasive grinding, select a final grit size and use it exclusively for all reference materials and test specimens. Several coarser grits may be needed before the final grit can be used. Choose the final grit small enough to minimize the effects of grinding striations on measured intensity. See 11.2.1 and 7.1. Refinish the surface of the reference materials and test specimens using the same batches of all grinding media on all specimens, even if some samples were previously finished with the same media, but of a different batch.

11.2.1 The final grit size should be small enough to minimize shadowing effects in which X-rays are absorbed by the raised portions of metal on either side of the grooves created by grinding. To check for problems, place a prepared specimen in the X-ray spectrometer with the grinding marks parallel to the optical path and with spinning disabled. Measure the intensities of all elements. Then, move the specimen so the grinding marks are perpendicular to the optical path and measure again. If the intensities of any elements decrease significantly, there is grinding-induced absorption. During measurements, spinning of all specimens may prevent the effects from causing biases.

11.3 *Nonmetallic Samples*—Dry the material. Then reduce it both in particle size and quantity, for example, by crushing and pulverizing followed by splitting or riffing, ending with approximately 100 g of material that has a particle size distribution with a maximum of 74 μm (200 mesh).

11.3.1 *Briquettes*—Mix the sample with a suitable binder if required. (See 8.2.) Ratios of 10 g + 1 g to 20 g + 1 g of sample + binder are common. Grind and blend the sample and binder for a fixed time (generally 2 min to 4 min in a disk mill). Press the sample-binder mixture into a briquette using a fixed pressure (typical pressures are 140 MPa to 550 MPa) and maintaining the pressure for a minimum of 10 s before releasing the briquette. In some cases, holding the pressure at 140 MPa for about 10 s before increasing it to maximum or applying a vacuum on the side port of a die set allows air to escape from the mixture and reduces the possibility of the briquette bursting from internal pressure. The exact conditions for pressing briquettes are either prescribed in the method or determined experimentally.

NOTE 1—For some samples, an aluminum or plastic pressing cup may be required to support the briquette.

11.3.2 *Fused Beads*—Develop and apply a fusion procedure that is appropriate for the matrix and elements of interest. Automated fusion equipment is readily available from several suppliers. Use a predetermined ratio of sample to flux. For example, 1.0 g of sample plus 4.0 g to 10.0 g of mixed lithium borate fluxes are commonly used. Mix weighed amounts of sample and flux and place the mixture in clean platinum/gold crucible. Heat at a fixed temperature, usually from 975 °C to 1100 °C, until thoroughly melted. Mix the crucible contents to ensure a homogeneous fusion and to remove particles from the crucible walls. Fusion time may vary from 2 min to 10 min, or more, depending on the sample, flux, and sample to flux ratio. (**Warning**—Ensure the sample is completely oxidized prior to fusing with the flux. Un-oxidized metals may alloy with the platinum/gold crucible and destroy it.)

11.3.2.1 When using platinum/gold crucibles, cast the fused mixture into a preheated platinum/gold mold, and allow to solidify and cool in the mold. Remove the bead.

11.3.2.2 For many applications, analysis of the as-cast surface of the bead may be adequate. This demands that the bottom of the casting dish is flat and free from scratches. Each laboratory must determine if polishing is essential for its application. It may be beneficial to polish the bead lightly on 220 grit diamond media or equivalent polishing media to provide a clean, flat surface for analysis.

11.3.2.3 The addition of a small amount of a halide (approximately 100 mg), such as LiI, HBr, LiBr, or LiF, may act as release agent when using platinum/gold crucibles and molds. The ‘releasing agent’ is also called ‘non-wetting agent.’ It is recommended to add the same amount of the releasing agent to all fusions for the same application. If the resulting beads show a distinct spherically shaped upper surface, then excess releasing agent has been added.

11.3.2.4 Alternatively, carbon crucibles and molds may be used.

12. Preparation of Apparatus

12.1 Prepare and operate the spectrometer in accordance with the manufacturer’s instructions, using the specific parameters given for the method.

NOTE 2—It is not within the scope of a method to prescribe details relative to the preparation of the apparatus. For a description and specific

details concerning a particular spectrometer, refer to the manufacturer's manual.

12.1.1 *Start-Up*—Follow the manufacturer's instructions for proper stabilization procedures.

12.2 *Tube Power Supply*—Adjust the excitation voltage of the power supply to excite the desired analyte lines. The following equation may be used as a guide:

$$E = 1.24/\lambda_{abs} \quad (1)$$

where:

E = minimum voltage, keV, required for exciting the line of interest, and

λ_{abs} = wavelength, nm, of the absorption edge of the fluorescent line of interest.

If a K line is measured, the K absorption edge is used. If an L line is measured, the L absorption edge of highest energy is used, generally the L_3 edge. Ideally, the operating voltage should approximate or exceed $3E$.

12.2.1 The X-ray tube voltage and current established as optimum for the method shall be reproduced for subsequent measurements.

12.2.1.1 *X-ray Tube Output Intensity*—The intensity of the continuum is proportional to the current and to the square of the voltage. The intensity of the characteristic line spectrum of the target material is proportional to the current and to the over voltage raised to about the 1.7th power. The over voltage (V_o) is the difference between the tube voltage (V_E) and the excitation potential (V_{EP}) of the target material:

$$V_o = V_E - V_{EP} \quad (2)$$

12.2.1.2 *Analyte Line Intensity*—The analyte line intensity is proportional to the tube current and to the over voltage raised to about the 1.7th power.

12.3 *Spectrometer Conditions*—List the analyte, analytical line, crystal, detector, collimation, background location (if measured), and goniometer position (2θ) (for a scanning spectrometer). In general, background measurements need not be made if the peak to background ratio is greater than 10:1, unless background-corrected intensities are required for fundamental parameter calculations or there are significant differences in background count rates among samples. Theoretical 2θ positions should be given since the actual position can vary with individual spectrometers.

12.4 *Proportional Counter Gas Flow*—When a gas-flow proportional counter is used, adjust the flow of the detector gas in accordance with the manufacturer's instructions. The detectors should be adequately flushed with detector gas before the instrument is used. Pulse height selector conditions should be checked following a change in detector gas supply.

13. Calibration and Drift Correction (Standardization)

13.1 *Calibration*—Using the conditions given in Section 12, measure a series of calibrants that cover the required mass fraction ranges. Drift correction samples and verifiers (see 13.2) should be measured at the same time as the calibrants. Prepare a calibration for each element being determined. Plot the analyte intensities in terms of counts, counts per second, or

relative intensities (relative intensity is the ratio of the intensity of the analyte in the sample to the intensity obtained for the pure element), versus the corresponding mass fractions. Alternatively, plot the ratios of the intensities of the calibrants to the intensities of one of the calibrants, an internal standard line, or the measured background, as a function of mass fraction.

13.1.1 Corrections for background (where required), line overlaps, and interelement effects must be properly incorporated into the calibration algorithm and selection of calibrants or a bias will be introduced into the calculation of the final results. See [Appendix X1](#).

13.2 *Verification and Drift Correction (Standardization)*—Measure the verifiers to confirm the results are within the allowable limits established by a control chart. See Practice [E1329](#). If necessary, use drift correction samples to make appropriate adjustments according to the manufacturer's instructions.

13.2.1 Always measure the verifiers if the detector gas or a major component of the spectrometer has been changed. Drift correct if required.

13.2.2 There are additional aspects to the validation of test methods. Consult Guide [E2857](#) for additional information.

14. Procedure

14.1 *Specimen Loading*—If the spectrometer does not have a sample spinner, it is essential to orient the reference materials and test specimens in the specimen chamber so the relationship between the X-ray beam and the grinding striations is the same for all measurements. This is not necessary when a spinner is used.

14.2 *Excitation*—Expose the specimen to primary X-radiation in accordance with Section 12.

14.3 *Radiation Measurements*—Obtain and record the counting rate measurement for each element. Either fixed count or fixed time modes may be used. Obtain enough counts so that the statistical uncertainty caused by counting is acceptable.

14.3.1 Assuming measurements fit Poisson statistics, where N is the total number of counts, \sqrt{N} is a good estimate of the statistical counting uncertainty, provided $N > 100$. If, for example, 0.1 % counting uncertainty is required, 10^6 counts is required, with $\sqrt{N} = 10^3$, yielding a relative standard uncertainty of $100\% \times 10^3/10^6 = 0.1\%$. For a counting uncertainty of 0.5 %, the total counts required drops to 40 000 counts. The time required for measurement is the total counts required divided by the intensity. For an intensity of 1600 counts per second, a count time of 25 s is required to obtain a 0.5 % uncertainty. To obtain 0.1 % uncertainty, a count time of 625 s is required. These uncertainties can be attained only if other sources of instrumental variance are negligible.

14.3.2 At high count rates, the statistical counting uncertainty can be significantly larger than the one calculated by the square root approximation in 14.3.1. This is a consequence of the corrections for dead time. Consult the instrument manufacturer for more details.

14.4 *Spectral Interferences*—X-ray spectrometers may not completely resolve X-ray line pairs for some line combinations