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Standard Guide for
Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry[1]

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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.*

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E1329 Practice for Verification and Use of Control Charts in Spectrochemical Analysis (Withdrawn 2019)[3]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

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[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-$L_{2,3}$ (Kα) 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 ($Li_2B_4O_7$), lithium metaborate ($LiBO_2$), mixtures of tetraborate and metaborate, boric anhydrite (B_2O_3), and sodium tetraborate ($Na_2B_4O_7$). 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.