



# Standard Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry<sup>1</sup>

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## 1. Scope

1.1 This guide 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 solids 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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

- 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

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<sup>2</sup> 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.

## Spectrochemical Analysis

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

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E2857 Guide for Validating Analytical Methods

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, refer to Terminologies E135 and the terminology section of 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 measurement procedures, calibrations 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 wavelength 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 analytical curves prepared with suitable calibrants.

4.3 Important aspects of background estimation are covered in an appendix to the guide.

## 5. Significance and Use

5.1 X-ray fluorescence spectrometry can provide an accurate and precise 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 analyst for determining the optimum conditions needed to achieve acceptable accuracy.

5.2 The accuracy of a determination is a function of the calibration scheme, 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 that the net intensities with line overlaps and background subtraction performed before the FP calculations are carried out. Some empirical schemes 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 Additionally, 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 by the use of primary beam filters, with a consequent loss of sensitivity.

6.2 Interelement effects (sometimes called matrix effects, see [Note 1](#)) may be significant for some elements. An empirical way to compensate for these effects is to prepare a series of calibration curves that cover the designated concentration ranges to be analyzed. A large suite of carefully designed reference materials is necessary for this approach. A series of samples in which all elements are relatively constant, except for the analyte, is necessary for each analyte that can be affected by other elements in the matrix. In addition, several series for the same analyte may be necessary, if the analyte is subject to large effects from some other element in the matrix. Typically, more accurate results are obtained when the compositions of the calibrants used to prepare the particular calibration curves are similar to the compositions of materials being analyzed.

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.

**NOTE 1**—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. Caution must be used with empirical mathematical models to be sure that sufficient data are provided to adequately compen-

sate for these effects. Reference materials that were not used in the calibration should be analyzed as unknowns to verify the calibration.

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, an error 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- $\alpha$  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*, 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 sander tends to wear and produce a convex surface on the specimen. If belt sanders are used, care must be exercised to be sure the platen is maintained flat.

7.1.1.2 The grinding material should be selected so that 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 wheel 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 disk. The feed on the cutting tools should be constant, 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 (80 000 psi). 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*, 20-mL to 30-mL capacity, with flat bottom 30 mm to 35 mm in diameter.

7.2.6.2 *95 % Platinum/5 % Gold Alloy*, with 30-mL to 35-mL capacity.

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 roughly uniform thickness across the entire diameter, typically 30 mm to 40 mm.

7.2.8 *Polishing Wheel*, suitable for polishing the fused button 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.

7.3.3 The instrument may be equipped with an external line voltage regulator or a transient voltage suppressor.

7.4 *Spectrometer*, designed for X-ray emission 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. This may also include synthetic multi-layers for low atomic number elements.

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

7.4.3 *Masks*, for restricting the incident beam pattern on the specimen.

7.4.4 *Detectors*—sealed or gas-flow proportional counters and scintillation counters are most commonly used.

7.4.5 *Vacuum System*, for the determination of elements whose radiation is absorbed by air. The system shall consist of a vacuum pump, gage, and electrical controls to provide automatic pumpdown of the optical path, and maintain a controlled pressure, usually 13 Pa (100  $\mu$ m 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  $\mu$ m 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 ( $\text{LiBO}_2$ ), mixtures of tetraborate and metaborate, boric anhydrite ( $\text{B}_2\text{O}_3$ ), and sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ). Pre-fused versions of the borate fluxes are available in high-purity versions, some of which are mixed with halide compound non-wetting agents, fluidizers, and heavy absorbers, for example, lanthanum oxide. There may be additional flux composition suitable for dissolution of samples.

## 9. Reference Materials

9.1 *Certified Reference Materials* are available from the National Institute of Standards and Technology<sup>3</sup>, from other national metrology institutes, and from other private and public organizations that certify reference materials for chemical composition in accordance with a relevant quality system incorporating standards and guides from the International Organization for Standardization (ISO) 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 analyzed in accordance with validated test methods. These reference materials should be sufficiently homogeneous for the intended purpose.

9.3 The reference materials should cover the concentration 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 X-rays, secondary, and scattered X-radiation 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 build appropriate shielding and safety interlocks into X-ray equipment during manufacturing, 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.

<sup>3</sup> Available from Standard Reference Materials Program, National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD 20899 ([www.nist.gov](http://www.nist.gov)).