Designation: E1621 – 05

Standard Guide for X-Ray Emission Spectrometric Analysis[1]

This standard is issued under the fixed designation E1621; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers guidelines for developing and describing analytical procedures using a wavelength-dispersive X-ray spectrometer.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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:*[2]

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

E305 Practice for Establishing and Controlling Atomic Emission Spectrochemical Analytical Curves

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

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

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 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 intensities are measured by suitable detectors at selected wavelengths and converted to counts by the detector. Concentrations of the elements are determined from the measured intensities of analyte X-ray lines using analytical curves prepared with suitable reference materials. Either a fixed multi-channel simultaneous system or a sequential monochromator system may be used to provide determinations of the elements.

5. Significance and Use

5.1 X-ray fluorescence spectrometry can provide an accurate and precise determination of metallic and many nonmetallic elements. 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 an analysis 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 the best results.

6. Interferences

6.1 Line overlaps, either total or partial, may occur for some elements. Fundamental parameter equations require that the net intensities be free from line overlap effects. Some empirical schemes incorporate line overlap corrections in their equations. See Appendix X1 for correction of line overlap effects.

6.2 Interelement effects or matrix effects may exist 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 procedure. 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,

[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.

Current edition approved July 15, 2005. Published August 2005. Originally approved in 1994. Last previous edition approved in 1999 as E1621 – 94 (1999). DOI: 10.1520/E1621-05.

[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.

if the analyte is subject to large effects from some other element in the matrix. The composition of the specimen being analyzed must match closely the composition of the reference materials used to prepare the particular calibration curves.

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. Caution must be used with empirical mathematical models to be sure that sufficient data is provided to adequately compensate for these effects. Reference materials that were not used in the calibration should be analyzed as unknowns to verify the calibration.

6.3 Additionally, interferences may occur from Compton lines or characteristic lines generated by the target material of the X-ray tube. These may be reduced or eliminated by the use of primary beam filters, but this will cause some loss of analyte line intensity.

6.4 *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-α line. The intensity for titanium is higher in this sample than it would be if the titanium were in solid solution.

7. Apparatus

7.1 *Specimen Preparation Equipment for 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 in order that changes in abrasive grit due to repeated use do not affect the repeatability of the roughness of the sample finish. This is particularly important in alloys which exhibit smearing of a softer component over the sample matrix.

7.2 *Specimen Preparation Equipment for Powders:*

7.2.1 *Jaw Crusher or Steel Mortar and Pestle,* for initial crushing of lumps.

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

7.2.3 *Rotary Disk Mill or Shatterbox,* 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 1000°C and homogenizing the melt.

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

7.2.6.1 *Vitreous Carbon,* 20 to 30-mL capacity, with flat bottom 30 to 35 mm in diameter.

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

7.2.7 *Platinum/Gold Casting Mold (95 %/5 %),* 30 to 35-mL capacity, with flat bottom 30 to 40 mm in diameter.

7.2.8 *Polishing Wheel,* suitable for polishing the fused button to obtain a flat uniform surface for irradiation.

7.3 *Excitation Source:*

7.3.1 *X-Ray Tube Power Supply,* providing a stable voltage of sufficient energy to produce secondary radiation from the specimen for the elements specified.

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

7.3.2 *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.

7.4 *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 µm Hg) or less, controlled to ± 3 Pa (± 20 µm Hg).

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 reduce pulses from higher order X-ray lines and background.

8. Reagents and Materials

8.1 *Purity of Reagents*—All reagents used in this test method shall conform to the "Reagent Grade" specifications of the American Chemical Society[3]. Other chemicals may be used provided it is first ascertained that they are of sufficient purity to permit their use without adversely affecting the expected performance of the analysis.

8.2 *Binders*—Sodium tetraborate ($Na_2B_4O_7$), polyethylene glycol, fibrous cellulose, or spectrographic grade graphite (−200 mesh, briquetting type).

8.3 *Detector Gas (P-10),* consisting of a mixture of 90 % argon and 10 % methane, for use with gas-flow proportional counters.

8.4 *Fluxes*—Sodium tetraborate ($Na_2B_4O_7$), fused and dried; lithium tetraborate ($Li_2B_4O_7$), lithium metaborate ($LiBO_2$) or lithium tetraborate and boric anhydrite (B_2O_3) mixture (4 g + 6 g).

9. Reference Materials

9.1 *Certified Reference Materials* are available from the National Institute of Standards and Technology[4] and other certification agencies.

9.2 *Reference Materials* with 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 previously analyzed in accordance with ASTM test methods. These reference materials shall be homogeneous, and free of voids or porosity.

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 Occupational Health and Safety Standards for ionizing radiation[5] shall be observed at all X-ray emission spectrometer installations. Operating and maintenance personnel shall follow the guidelines of safe operating procedures given in current handbooks and publications from the National Institute of Standards and Technology,[6,7] the U.S. Government Printing Office,[8] or similar handbooks on radiation safety, as well as specific state regulations.

10.2 *Monitoring Devices,* either film badges or dosimeters[9] may be worn by all operating and maintenance personnel. Safety practices shall conform to applicable local, state, and federal regulations. To meet local, state, and federal radiation standards, periodic radiation surveys of the equipment for leaks and excessive scattered radiation shall be made by a qualified person using an ionization-chamber detector.[10] The personal film badge survey record, the radiation survey record, and an equipment maintenance record shall be available upon request.

10.3 Special precautions for operators and maintenance personnel shall be posted at the equipment site.

10.4 *Radiation Caution Signs* shall be posted near the X-ray equipment and at all entrances to the radiation area.

10.5 *Fail-Safe "X-Ray On" Warning Lights* shall be used on the equipment.

10.6 Routine checks of safety interlocks shall be documented.

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 *Metal Samples*—Prepare the reference materials and test specimens to provide a clean, flat uniform surface to be exposed to the X-ray beam. For abrasive sanding, select a grit size and use it exclusively for all reference materials and test specimens. See 7.1.1.2 and 7.1.1.3. Refinish the surface of the reference materials and test specimens as needed to eliminate oxidation before measurement.

11.3 *Nonmetallic Samples*—Dry the material. Then reduce it both in particle size and quantity, by crushing and pulverizing integrated with splitting or riffling, ending with approximately 100 g of material that has a particle size of less than 200 mesh (74 μm).

11.3.1 *Briquettes*—Mix the sample with a suitable binder. (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 to 4 min in a disk mill). Press the sample-binder mixture into a briquette using a fixed pressure of 140 to 550 MPa (20 000 to 80 000 psi) and maintaining the pressure for a minimum of 10 s before releasing the briquette. Holding the pressure at 140 MPa (20 000 psi) for about 10 s before

---

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC (www.chemistry.org). For suggestions on the testing of reagents not listed by the American Chemical Society see the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD (www.usp.org).

[4] Available from Standard Reference Materials Program, National Institute of Standards and Technology, U.S. Department of Commerce, Gaithersburg, MD 20899 (www.nist.gov).

[5] ANSI/NBS Handbook 114, General Safety Standard for Installations Using Non-Medical X-Ray and Sealed Gamma-Ray Sources, available from Global Engineering Documents, 15 Inverness Way East, Englewood, CO 80112–5704 (www.global.ihs.com).

[6] NBS Handbook 76, *Medical X-ray Protection Up to Three Million Volts*, available as NCRP Report No. 102 from NCRP Publications, 7910 Woodmont Ave., Suite 400, Bethesda, MD 20814–3095 (www.ncrp.com).

[7] ANSI N43.2-2001, Radiation Safety for X-ray Diffraction and Fluorescence Analysis, available from Health Physics Society, 1313 Dolley Madison Blvd., Suite 402, McLean, VA 22101 (www.hps.org) and NTIS Publication PB282500, available from NTIS, 5285 Port Royal Rd., Springfield, VA 22161 (www.ntis.gov).

[8] Moore, T. M. and McDonald, D. J., *Radiation Safety Recommendations for X-ray Diffraction and Spectrographic Equipment*, NTIS Publication PB182558, available from NTIS, 5285 Port Royal Rd., Springfield, VA 22161 (www.ntis.gov).

[9] Radiation Film Badges, available from Global Dosimetry Solutions, Inc., 3300 Hyland Ave., Costa Mesa, CA 92626 (www.globadosimetry.com) and Landauer, Inc., 2 Science Rd., Glenwood IL, 60425–1586 (www.landaurerinc.com) and, have been found satisfactory.

[10] A survey meter that meets the requirements is available from Nuclear Associates, 120 Andrews Rd., Hicksville, NY 11801 (www.nucl.com/Nuclear_Associates/).

increasing it to maximum allows air to escape from the mixture and reduces the possibility of the briquette bursting from internal pressure.

NOTE 2—For some samples, an aluminum cup may be required to support the briquette.

11.3.2 *Fused Beads*—Use a predetermined mix of sample to flux combination. A 0.3 g of sample to 5.0 g of sodium tetraborate or 1.0 g of sample to 4.0 to 10.0 g of lithium tetraborate are commonly used mixtures. Mix weighed amounts of sample and flux and place the mixture in clean platinum/gold or vitreous carbon crucible. Heat at a fixed temperature, usually from 950 to 1100°C, until thoroughly melted. Swirl the crucible several times to ensure a homogeneous fusion and to remove particles from the crucible walls. Fusion time may vary from 2 to 10 min, 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 in a preheated (800°C) platinum/gold mold, and allow to solidify and cool in the mold. Remove the bead. It may be beneficial to polish the bead lightly on a 220-grit diamond wheel or equivalent polishing wheel to provide a clean flat surface for analysis.

NOTE 3—For some applications, analysis of the as-cast surface of the bead may be adequate. Each laboratory must determine if polishing is essential for its application. Also, fusion made in a carbon crucible may form a spherically shaped bead upon cooling. It has been reported that a flat bead of acceptable size may be obtained by adding wire ring conforming to inside diameter of the crucible to the melt before it solidifies.

NOTE 4—The addition of a small amount (100 mg) of a halide such as HBr, LiBr, or LiF, may act as release agent when using platinum/gold molds.

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 5—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 warm-up 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:

$$E = 12.4/\lambda_{abs} \quad (1)$$

where:

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

λ_{abs} = wavelength, Å , of the absorption edge of the element 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(III) 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 1.7^{th} 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 1.7^{th} power.

12.3 *Spectrometer Conditions*—List the analyte, analytical line, crystal, detector, collimation, background location (if determined), 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. 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 P-10 gas in accordance with the equipment 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 P-10 cylinders.

13. Calibration and Standardization

13.1 *Calibration (Preparation of Analytical Curves)*—Using the conditions given in Section 12, measure a series of calibrants that cover the required concentration ranges. Standardants and verifiers (see 13.2) should be run at the same time as the calibrants. Prepare an analytical curve for each element being determined in each alloy type or material. 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 concentrations (refer to Practice E305). 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 concentration.

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

13.1.2 To verify the calibration, run the calibrants as unknowns. When nonlinear calibration schemes are used, reference materials other than those used to calibrate should be used to verify the calibration.

13.2 *Verification and Standardization*— Measure the verifiers to see if the readings are within the allowable limits