Designation: E1621 – 13

Standard Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry[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 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:*[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
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 nonmetallic elements in a wide variety of solid and liquid

[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 Oct. 1, 2013. Published November 2013. Originally approved in 1994. Last previous edition approved in 2005 as E1621 – 05. DOI: 10.1520/E1621-13.

[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.

Copyright © ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States

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 compensate 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-α 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 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 ($Na_2B_4O_7$). 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[3], 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.

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

10.2 *Monitoring Devices,* such as film badges or dosimeters may be used by operators and maintainers. 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 sanding, 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 Note 2 and 7.1. Refinish the surface of the reference materials and test specimens using the same batches of all grit papers on al specimens, even if some samples were previously finished with the same grit, but of a different batch.

NOTE 2—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, by crushing and pulverizing followed by splitting or riffling, 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. (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 of 140 MPa to 550 MPa (20 000 psi 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 increasing it to maximum or pumping 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.

NOTE 3—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. 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. For example, a 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 or vitreous carbon crucible. Heat at a fixed temperature, usually from 950 °C to 1100 °C, until thoroughly melted. Mix the crucible several times to ensure a homogeneous fusion and to remove particles from the crucible walls. Fusion time may vary from 2 min 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 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 4—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 5—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 6—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_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 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 detector gas 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. Drift correction samples and verifiers (see 13.2) should be run at the same time as the calibrants. Prepare an analytical curve 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 concentrations. 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. See Appendix X1.

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 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 instructions in the manufacturer's manual.

13.2.1 Always measure the verifiers if the detector gas or a major component of the spectrometer has been changed. Recalibrate 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, orient the reference materials and test specimens in the specimen chamber so that the relationship between the X-ray beam and the grinding striations is the same for all measurements. This is essential if the spectrometer is not equipped with a specimen spinner, but 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.

NOTE 7—Assuming measurements fit Poisson statistics, where N is the total number of counts, $N^{1/2}$ is a good estimate of the statistical counting uncertainty, provided N is greater than 100. For example, if 0.1 % counting error is acceptable, 10^6 counts, with $N^{1/2} = 10^3$, yielding a relative percent uncertainty of $100 \times 10^3/10^6$ or 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.

14.4 *Spectral Interferences*—X-ray spectrometers may not completely resolve X-ray line pairs for some line combinations (for example, manganese K-α and chromium K-β; vanadium K-α and titanium K-β; and phosphorus K-α and molybdenum L1). Therefore, care must be exercised in the interpretation of X-ray line intensities when both elements are present. In some cases, alternative X-ray lines without interference can be used. Otherwise, mathematical calculations must be used to correct for the interferences. See Appendix X1.

14.5 *Replicate Measurements*—Make a single measurement on each test specimen. Assuming that the conditions in 14.3 are met, the accuracy of an X-ray spectrometric analysis is not improved significantly by making multiple measurements on the same surface of the specimen. Confidence in the accuracy of the analysis of the material will improve by making multiple measurements on freshly prepared surfaces of the same specimen or by analyzing more than one specimen of the same material. Precision can be improved by increasing the counting time. See Note 7.

15. Calculation of Results

15.1 Using the intensities from the test specimen and the appropriate analytical curves, determine the concentration of the various elements.

15.1.1 The intensities may be entered directly into a computer that is programmed with mathematical algorithms to convert the data directly into concentrations. These algorithms

must provide corrections for any spectral interferences and matrix effects. See Section 6 and 14.4.

15.1.2 If mathematical calculations must be made for interelement effects, refer to the equipment manufacturer's manual for the recommended procedure for the instrument being used. Computers are normally interfaced to the X-ray spectrometers to run software employing such correction schemes. See also Guide E1361.

NOTE 8—In cases where there is no appropriate software or the analyst finds shortcomings with the available software, one may choose to employ any of a number of available third-party software packages.

16. Precision and Bias

16.1 *Precision*—An acceptable number of laboratories should test the method in accordance with an acceptable interlaboratory study standard such as Practice E1601. Precision data, including repeatability (precision within laboratories), *r*, and reproducibility (precision between laboratories), *R*, should be provided in table(s).

16.2 *Bias*—If acceptable estimates of the true concentrations are known for the samples used in the interlaboratory study, calculate bias in accordance with Practice E1601 or another accepted standard, and show the results in a table.

16.2.1 Unless the bias data show a systematic deviation from the accepted values, a statement should be made that the test method shows no significant bias.

17. Keywords

17.1 interferences; line overlap; spectroscopy; X-ray

APPENDIX

X1. LINE OVERLAP CORRECTION

X1.1 General

X1.1.1 To make accurate analytical determinations, the contribution of an unresolved line or lines to the measured intensity of an analyte must be subtracted before using the intensity in calculations.

X1.1.2 The methods described may not be applicable if there are severe matrix effects that change the intensity ratio between the interfering line and another line of the same element. For example, with reference to Fig. X1.1, if there is an absorption edge of another element between P_1 and P_2, correction for an absorption effect may be required. See Guide E1361.

X1.1.3 Correcting for line overlap requires relatively precise measurements to avoid inaccuracy from accumulated imprecisions (see 6.1 and Note 7). Choose a counting time that reduces impression to an acceptable level.

X1.1.3.1 To illustrate the potential effect of imprecision in X-ray counting, consider measurements taken in counts per second, using *R* to designate this rate, the relative error is equal to:

$$\Delta R/R = \sqrt{R}/R\sqrt{T} = 1/\sqrt{RT} \quad \text{(X1.1)}$$

where *T* is the time taken for the measurement. Therefore, relative error is reduced by increasing the measurement time, which also increases total counts.

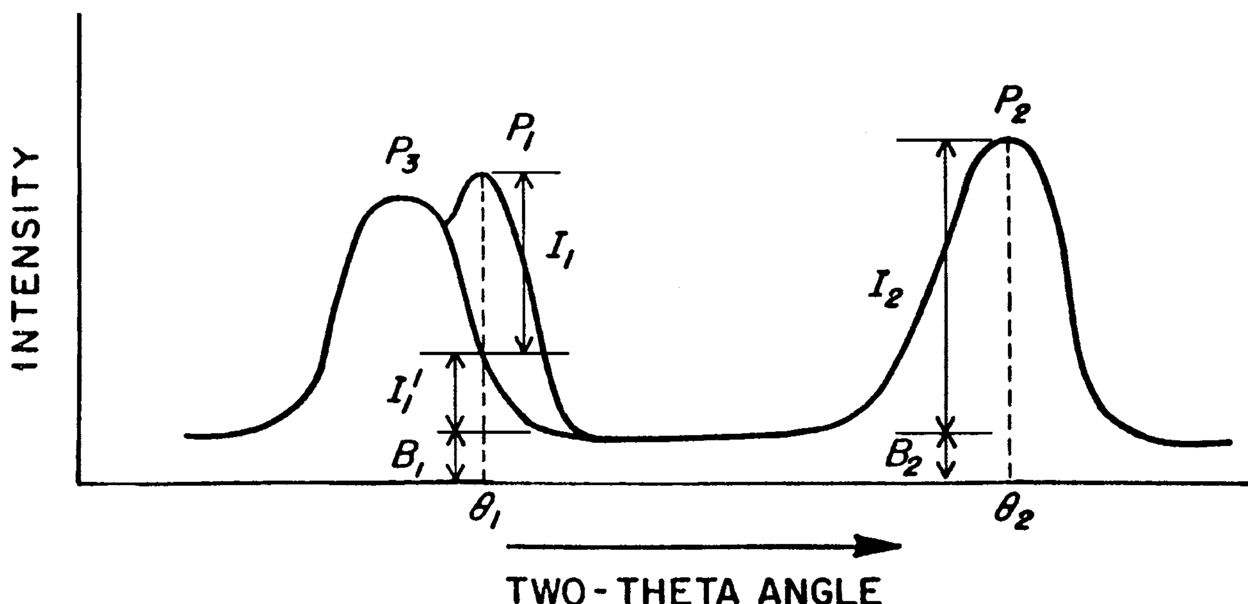

FIG. X1.1 Typical Line Overlap

X1.1.3.2 Because background correction is needed to determine net counts or net count rates, uncertainty in the background intensity contributes to the imprecision in the net count or net count rate. The standard deviation of a net reading, s_N, is the square root of the sum of the squares of the standard deviations of the peak and the background readings, s_P and s_B, respectively, or

$$s_N = \sqrt{s_P^2 + s_B^2} \quad (X1.2)$$

As discussed in Note 7, variance is a function of total counts. Therefore

$$s_N = \sqrt{N_P + N_B} \quad (X1.3)$$

Relative error of the net signal, ε_N, therefore is equal to

$$\varepsilon_N = \sqrt{N_P + N_B} / (N_P - N_B) \quad (X1.4)$$

Because background counts are some fractional part of total measured peak counts, ε_N can be seen to equal

$$\varepsilon_N = \sqrt{N_P + bN_P} / (N_P - bN_P) = \sqrt{1/N_P}\left[\sqrt{1+b} / (1 - b)\right] \quad (X1.5)$$

where b is the fractional factor. Substituting $N = RT$ yields

$$\varepsilon_N = \sqrt{1/RT}\left[\sqrt{1+b} / (1 - b)\right] \quad (X1.6)$$

when readings are taken in terms of counts per second and R is the count rate observed over T seconds. In either case, the factor causing an increase in imprecision is $\sqrt{1+b} / (1 - b)$. It can be seen that if background is 40 % of the peak reading (b = 0.4), the imprecision of the net reading will be increased by approximately two-fold.

X1.1.4 The following methods of correction where overlap factors are determined are based on intensities in terms of total counts. The equations may also be used for intensities in terms of count rates. If total counts are used, it is imperative that the counting time for any one intensity reading is not changed, since such a change would invalidate the correcting factor being used.

X1.2 Determination of the Correction Factor by Direct Measurement

X1.2.1 When the measured intensity of an analyte includes counts from an interfering line, the contribution of the interference may be determined by measuring another line of the interfering element. The alternate line, however, must be free of interference. In Fig. X1.1, P_1 is the analyte line that is being measured at the angular position Θ_1; P_3 is an interfering line that contributes some of its intensity to P_1. P_2 is another line of the interfering element appearing at angular position Θ_2. The observed measurement is:

$$I_{\Theta 1} = I_1 + I'_1 + B_1 \quad (X1.7)$$

where:

$I_{\Theta 1}$ = total intensity, in counts, measured at Θ_1,
I_1 = net intensity, in counts, of the analyte at Θ_1,
I'_1 = net contribution, in counts, of the interfering line, P_3, appearing at Θ_1, and
B_1 = intensity, in counts, of the background at Θ_1.

Determine the factor, F, relating the relative intensity of the overlapping line at Θ_1 to another line, P_2, of the same interfering element at Θ_2 by using a pure specimen of the interfering element or a speciment that contains the interfering element, but no analyte. The specimen may be a metal foil or an oxide powder. Correcting all measurements for background, the determination is as follows:

$$F = I'_1 / I_2 \quad (X1.8)$$

where:

I_2 = net intensity, ($I_{\Theta 2} - B_2$) in counts, of the fully resolved line, P_2, of the interfering element measured at Θ_2,, where B_2 is the intensity in counts, of the background at Θ_2.

Calculate the corrected net intensity of the analyte using:

$$I_{\Theta 1} = I_1 - B_1 - F(I_2) \quad (X1.9)$$

NOTE X1.1—When measuring pure elements it is important to verify that the count rate does not exceed the linearity of the detection system. A plot of count versus tube current will establish the limit of linearity. If curvature is observed, the X-ray power must be reduced. The reduction should be done by reducing the current, not the voltage, of the X-ray tube. If it has been established that the spectrometer operating system software automatically and correctly accounts for nonlinearity resulting from detector dead time, these actions not needed.

X1.3 Determination of the Correction Factor Using Synthetic Specimens

X1.3.1 Prepare specimens containing increasing amounts of the interfering element. The contribution of the interfering element to the intensity of the measured X-ray line can be established mathematically. The net intensity of the X-ray line is plotted against the net intensity measured for a line of the interfering element that is free of interference. The slope will be equal to the overlap correction factor, F, in Eq X1.7.

X1.4 Determination of the Correction Factor Using Regression Analysis

X1.4.1 Frequently it is not possible to prepare specimens specifically for the determination of line overlap correction factors. It is possible, however, to use a series of specimens with varying amounts of both the analyte and the interfering element to determine the overlap correction factor through the use of multiple linear regression using the following relationship:

$$C = a_0 + a_1 I_n + a_2 I_2 \quad (X1.10)$$

where:

C = amount of the analyte,
a_0, a_1, a_2 = constants,
I_n = $I_1 + I'_1$ net counts measure at the analyte wavelength, unresolved peak (see Fig. X1.1), and
I_2 = net counts of the interfering element, measured at another wavelength which is interference free.

NOTE X1.2—Amount (for example, mass fraction or concentration) may be used instead of net count intensity for I_s in Eq X1.10

X1.4.2 Eq X1.10 can be rearranged as follows:

$$C = a_0 + a_1[I_n + (a_2/a_1)I_2] \quad (X1.11)$$

where:

a_2/a_1 = line overlap correction factor, which should be negative.

X1.4.3 When I_n, I_2, and C are known for a series of specimens, the constants a_0, a_1, and a_2 in Eq X1.10 may be calculated by multiple linear regression (Note X1.3). In this case, two regressions on the amount variable are determined: the primary relationship to the intensity measured at the analyte wavelength; and a secondary relationship to an intensity measured for anlother reading of the interfering element. The line correction factor a_2/a_1 is calculated and substituted for F in Eq X1.9, after changing its sign. The operating system software of the X-ray spectrometer may permit a regression to determine the correction factor.

NOTE X1.3—The value of the constant, a_0, is an indication of how well the background correction has been performed. Ideally, a_0 should equal zero. Small positive values indicate residual background. If a large value is obtained, a gross error has been committed in performing the background correction. If a simultaneous spectrometer is used, a_0 would be equal to the background, not to zero.

NOTE X1.4—Experience has shown that this method requires a large spread in the range of analyte and interfering elements in calibrants. For the three constants that must be determined, it is advisable to have a suite of at least ten specimens.

X1.5 Subtraction of Background Using Lorentz Model

X1.5.1 If the Lorentz model is available as a background correction option in the instrument software, it can be used for removal of the line overlap intensity. The Lorentz algorithm has the capability of modeling the shape of the line overlap in cases where there is a partial overlap, such as the Cr-Kβ overlap on Mn-Kα. A minimum of five background points are selected. A number of specimens need to be scanned to assure that there are no small peaks in the region of interest and that there are no anomalies in the shape of the curve. Fig. X1.2 shows an example of the use of this model.

X1.6 Variance

X1.6.1 Whenever an observed measurement is corrected by other measurements, the standard deviation of the corrected measurement is the square root ot the sum of the variances of the individual measurements, weighted by how they are used. In Eq X1.9, the standard deviation of the corrected line is:

$$s = \sqrt{s_t^2 + s_{b1}^2 + F\left(s_i + s_{b2}^2\right)} \tag{X1.12}$$

where:

s_t^2 = variance of the total measurement, $I_{\Theta 1}$,
s_{b1}^2 = variance of the background measurement, B_1,
s_i^2 = variance of the total measurement of the interfering line, I_2, and
s_{b2}^2 = variance of the background measurement, B_2 .

X1.6.1.1 Variation in the factor F will not significantly affect the standard deviation of the corrected line. A poor definition of F, however, will bias the corrected line measurement.

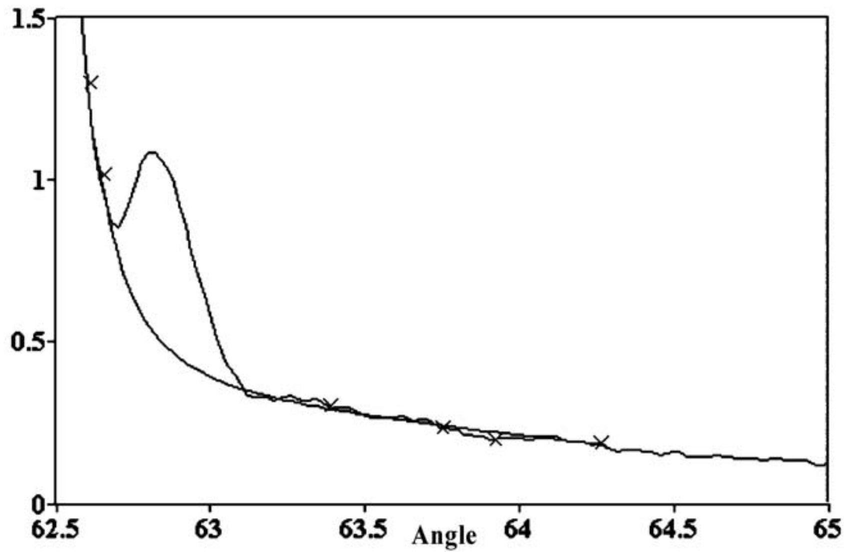

FIG. X1.2 Removal of Line Overlap Using the Lorentz Model

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).