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Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy¹

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1. Scope

1.1 This guide is intended to assist those using energy-dispersive spectroscopy (EDS) for quantitative analysis of materials with a scanning electron microscope (SEM) or electron probe microanalyzer (EPMA). It is not intended to substitute for a formal course of instruction, but rather to provide a guide to the capabilities and limitations of the technique and to its use. For a more detailed treatment of the subject, see Goldstein, et al. (1) This guide does not cover EDS with a transmission electron microscope (TEM).

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

1.4 *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

E3 Guide for Preparation of Metallographic Specimens

E7 Terminology Relating to Metallography

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)³

¹ This guide is under the jurisdiction of ASTM Committee E04 on Metallography and is the direct responsibility of Subcommittee E04.11 on X-Ray and Electron Metallography.

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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.

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, see Terminologies E7 and E673.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accelerating voltage*—the high voltage between the cathode and the anode in the electron gun of an electron beam instrument, such as an SEM or EPMA.

3.2.2 *beam current*—the current of the electron beam measured with a Faraday cup positioned near the specimen.

3.2.3 *Bremsstrahlung*—background X rays produced by inelastic scattering (loss of energy) of the primary electron beam in the specimen. It covers a range of energies up to the energy of the electron beam.

3.2.4 *critical excitation voltage*—the minimum voltage required to ionize an atom by ejecting an electron from a specific electron shell.

3.2.5 *dead time*—the time during which the system will not process incoming X rays (real time less live time).

3.2.6 *k-ratio*—the ratio of background-subtracted X-ray intensity in the unknown specimen to that of the standard.

3.2.7 *live time*—the time that the system is available to detect incoming X rays.

3.2.8 *overvoltage*—the ratio of accelerating voltage to the critical excitation voltage for a particular X-ray line.

3.2.9 *SDD (silicon drift detector)*—An x-ray detector characterized by a pattern in the biasing electrodes which induces generated electrons to move laterally (drift) to a small-area anode for collection, resulting in greatly reduced capacitance which to a first approximation does not depend on the active area, in contrast to conventional detectors using flat-plate electrodes. (2)

3.2.10 *shaping time*—a measure of the time it takes the amplifier to integrate the incoming charge; it depends on the time constant of the circuitry.

3.2.11 *spectrum*—the energy range of electromagnetic radiation produced by the method and, when graphically displayed, is the relationship of X-ray counts detected to X-ray energy.

4. Summary of Practice

4.1 As high-energy electrons produced with an SEM or EPMA interact with the atoms within the top few micrometres of a specimen surface, X rays are generated with an energy characteristic of the atom that produced them. The intensity of such X rays is proportional to the mass fraction of that element in the specimen. In energy-dispersive spectroscopy, X rays from the specimen are detected by a solid-state spectrometer that converts them to electrical pulses proportional to the characteristic X-ray energies. If the X-ray intensity of each element is compared to that of a standard of known or calculated composition and suitably corrected for the effects of other elements present, then the mass fraction of each element can be calculated.

5. Significance and Use

5.1 This guide covers procedures for quantifying the elemental composition of phases in a microstructure. It includes both methods that use standards as well as standardless methods, and it discusses the precision and accuracy that one can expect from the technique. The guide applies to EDS with a solid-state X-ray detector used on an SEM or EPMA.

5.2 EDS is a suitable technique for routine quantitative analysis of elements that are 1) heavier than or equal to sodium in atomic weight, 2) present in tenths of a percent or greater by weight, and 3) occupying a few cubic micrometres, or more, of the specimen. Elements of lower atomic number than sodium can be analyzed with either ultra-thin-window or windowless spectrometers, generally with less precision than is possible for heavier elements. Trace elements, defined as <1.0 %, ² can be analyzed but with lower precision compared with analyses of elements present in greater concentration.

6. Test Specimens

6.1 Suitable specimens are those that are normally stable under an electron beam and vacuum and are homogeneous throughout the volume of X-ray production. If the specimen is inhomogeneous at the micrometre level, then a truly quantitative analysis is not possible, and a bulk technique such as X-ray fluorescence should be used.

6.2 The concentration of each element to be analyzed should equal or exceed about 0.1 wt %. Lower limits of detection are possible with longer counting times, but the precision of trace element analysis is poorer than when the element is present at the percent level. The silicon drift detector allows lower minimum detectable limits in practical counting times, down to several hundred parts per million in favorable cases, because it retains good energy resolution at much shorter shaping times (thus higher count rates) than Si(Li) detectors.

7. Specimen Preparation

7.1 Specimens for quantitative EDS analysis should be prepared in accordance with standard metallographic or petrographic techniques. Guidelines are given in Methods E3. The specimen must be flat in the region to be analyzed. This requirement does not preclude scratches; however, any scratches in the immediate vicinity of the analyzed region must

be insignificant with respect to the X-ray volume. The operator must also be aware of the possibility of spurious X rays from parts of the chamber, polishing compound elements, or from adjacent phases or a combination thereof. Note that these requirements for surface preparation preclude the quantitative analysis of casual samples, such as unpolished surfaces like fracture surfaces and particles. Although data can be generated on these casual surfaces, the results would be of significantly lower precision with unpredictable variations.

7.2 Unetched or lightly etched specimens are preferred. If they are etched, the operator must make sure that the composition in the region to be analyzed has not been altered and that the region to be analyzed is flat.

7.3 Nonconducting specimens should be coated with a conductive material to prevent charging. Lowering the accelerating voltage may reduce or eliminate the effect of charging in some samples, but applying a conductive coating is still the most common method. Evaporated carbon is usually the most suitable coating material. Heavy metals such as gold that are often used for SEM imaging are less suitable because they heavily absorb X rays; if the coating is thick enough, X-ray lines from those metals will be seen in the spectrum. If one is analyzing carbon in the specimen, then aluminum makes a good coating. The coatings are usually applied in thicknesses of several tens of nanometres. Carbon that appears to be tan in color on the specimen surface, or on a piece of filter paper in the evaporator, is probably thick enough. For the most accurate analysis, standards and unknowns should be coated at the same time to assure equal coating thicknesses. Specimens mounted in a nonconducting medium must make electrical contact with the microscope stage. This is often accomplished by painting a stripe of carbon or silver paint from the specimen to the specimen holder.

8. Spectrum Collection

8.1 *Calibration*—The analyzer shall be calibrated on two X-ray peaks or other methods implemented by the equipment manufacturer in software to set the amplifier gain and offset. Often aluminum and copper are used, and sometimes both the K and L lines of copper are used. The two elements need not be in the same specimen. A spectrum from pure aluminum could be collected followed by pure copper in the same spectrum. Single-peak (gain only) calibration is possible for pulse processing electronics with internal means of establishing the offset (location of zero eV). Software is usually available to calibrate the EDS system, and one should consult the system manual for the details of operation. To ensure reproducible results, calibration should be checked periodically.

8.2 *Operating Parameters:*

8.2.1 The accelerating voltage of the SEM must be chosen to provide an adequate overvoltage to excite the X-ray lines of interest. An overvoltage that is too low will not sufficiently excite X rays; one that is too high yields low spatial resolution and causes absorption as X rays escape from deep within the specimen. An overvoltage of at least 1.5 times the critical excitation potential of the highest energy X-ray line analyzed is

recommended. When analyzing hard and soft X rays in the same specimen, analyses at two voltages may be necessary. For materials such as minerals and ceramics, which contain light elements (that is, of low atomic number), 15 kV is usually a good compromise. For many metals containing medium atomic number elements, 20 to 30 kV is a good choice. Heavy elements (those of higher atomic number) may be analyzed using L or M lines, and so higher voltages are not necessary. The actual accelerating voltage of the electron beam does not always correspond with the voltage selected on the instrument. It can be determined by expanding the vertical scale of the EDS spectrum and observing the energy above which continuum X rays do not occur.

8.2.2 Almost all elements can be analyzed using characteristic X-ray lines in the range of 0–10 keV. This range contains K lines of the first transition series (scandium–zinc (Sc-Zn)), L lines of the second transition series plus the lanthanides, and M lines of the third transition series plus the actinides. Accordingly, most operators choose a 0–10 keV display at higher display resolution rather than a 0–20 keV display at lower resolution. Tables of X-ray energies can be found in various texts, such as Goldstein, et al. (1) or Johnson and White. (3).

8.2.3 X-ray spatial resolution degrades with overvoltage, because as the electrons penetrate deeper into the specimen, X rays are generated from a larger volume. An approximation of the diameter of this tear-drop-shaped excitation volume, referred to as the X-ray range, can be obtained using the following equation. (4)

$$R = 0.064(E_o^{1.68} - E_c^{1.68})/\rho \quad (1)$$

where:

- R = the range in μm ,
- E_o = the accelerating voltage in kV,
- E_c = the critical excitation potential in keV, and
- ρ = the density in g/cm^3 .

More accurate interaction volumes can be computed by Monte Carlo computer methods to generate random electron trajectories, but Eq 1 provides a reasonable estimate for most purposes.

8.2.4 The beam can be placed in the spot mode to form a probe to analyze the minimum volume, or it can be scanned over a homogeneous region to lower the electron dose at any one point. Defocusing the beam or scanning it over an area of varying composition does not provide an average composition, because the correction factors applied to the intensity ratio are themselves a function of composition.

8.2.5 The current in the electron beam determines the flux of X rays that are generated. It does not affect spatial resolution for X-ray analysis in the same way it detracts from electron image resolution. Typically it is adjusted to keep the dead time in the EDS system below 40 %. Dead times of 20 to 30 % produce good spectra, whereas dead times above 40 % can lead to spectra containing artifacts, such as those discussed in 8.3.1. Maximum throughput, that is, the most X rays/real time, is achieved at about 40 % dead time. Higher count rates can be achieved by lowering the shaping time on the system amplifier from about 10 μs , but spectral resolution will be lost. For

quantitative analysis, a shaping time of about 10 μs or greater is used for conventional detectors. SDDs are operated with shaping times between 3 and 10 times shorter than Si(Li) detectors for the same spectral resolution, (in the 120-129 eV range) resulting in higher maximum throughput while remaining under 40% dead time, provided the specimen can withstand the required beam current without damage. The beam current must remain stable throughout the analysis, because the counts collected are directly proportional to the beam current. Thus, a 1 % upward drift in beam current will produce a 1 % increase in all the reported mass fractions, resulting in a reported total >100 %. For quantitative analysis using standards, the beam current (not specimen current) must be the same for both the specimen and the standards or one must be normalized to the other.

8.2.6 The geometric configuration of the sample and detector, shown schematically in Fig. 1, also affects the analysis. The number of X-ray photons that reach the detector is a function of the solid angle and take-off angle, including the effect of specimen and detector tilt. The count rate incident on an X-ray detector is directly proportional to the size of the solid angle defined as follows for a detector normal to the line of sight to the specimen:

$$\Omega = A/r^2 \quad (2)$$

where:

- Ω = solid angle in steradians,
- A = active area of the detector crystal; for example, 30 mm^2 , and
- r = sample-to-detector distance, mm.

8.2.6.1 The larger the active area of the detector, the more counts will be collected, but at the expense of spectral resolution. Most detectors have a movable slide and can be brought closer to the sample if a higher count rate at a given beam current is needed. The take-off angle is defined as the angle between the surface of the sample and a line to the X-ray detector. If the sample is not tilted, the take-off angle is defined as follows:

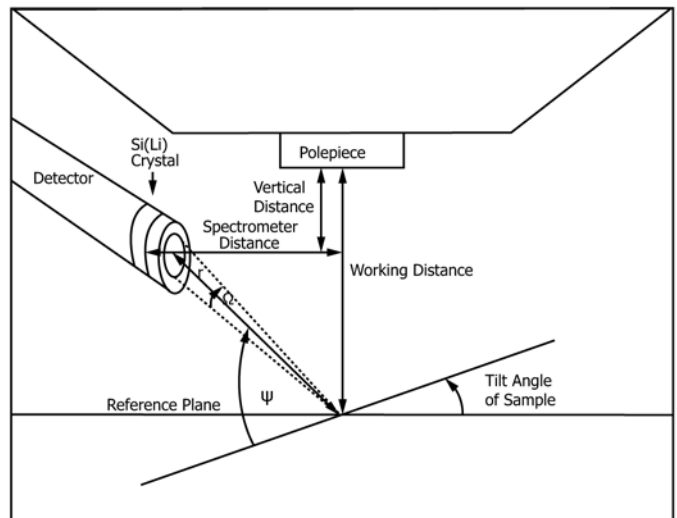


FIG. 1 Schematic Diagram of Electron Microscope System

$$\psi = \arctan(W - V)/S \quad (3)$$

where:

- ψ = take-off angle,
- W = working distance,
- V = vertical distance, and
- S = spectrometer distance.

8.2.6.2 Working distance is measured in the microscope; its accuracy depends on the method used to measure it and the specimen position. Vertical distance is the distance from the bottom of the pole piece of the final lens to the centerline of the detector; it usually can be measured within the microscope with a ruler or obtained from the manufacturer. Spectrometer distance is the horizontal distance from the spectrometer to the beam; it is measured using the scale provided by the manufacturer on the spectrometer slide. All distances must be in the same units. The take-off angle should be as high as possible to minimize absorption of X rays within the specimen and maximize the accuracy of quantitative analysis. If the specimen is tilted such that the beam is not perpendicular to the specimen surface, an effective take-off angle is used. There are several expressions in use by commercial manufacturers to calculate this, and all produce similar results if the tilt angle is not extreme. When analysis is performed on a tilted specimen, the azimuthal angle between the line from the analysis point to the EDS detector and the line perpendicular to the stage tilt axis must be known. If standards are used, they must be collected under the identical geometrical conditions as the unknowns. To set W , move the stage in the z-axis until it is in focus with the objective lens, preset to the desired W .

8.3 Spectral Artifacts:

8.3.1 There are a number of artifacts possible with EDS, and these are discussed by Fiori, et al.(5) Most of them are related to detector electronics and are rarely seen in a properly functioning system. However, two artifacts that are commonly seen are pulse pileup peaks and silicon escape peaks. Pileup peaks occur when several X-ray photons reach the detector at the same time, and the pulse processing electronics erroneously record the sum of their energies rather than each one individually. Lowering the beam current to lower the count rate usually eliminates the problem. The ratio of pileup peak to parent peak(s) is proportional to the input count rate of the parent peak(s). For the same total input count rate, a complex spectrum will have smaller relative pileup peaks than a simple spectrum having a few dominant peaks. The pileup peak for two parent peaks of different energies is larger than for a single peak with the same count rate as the two-peak pair. Relative pileup peak height is inversely related to energy for the same count rate. Systems with SDDs generally have smaller pileup peaks under the same conditions, because the reduced capacitance of the SDD makes it easier for the pulse processing electronics to recognize close coincidences as separate events. EDS systems often have software to model pileup peaks and correct for them.

8.3.2 A silicon escape peak occurs when an ionized atom of silicon in the detector generates an X ray. If that X ray escapes from the detector, its energy that would ordinarily have been measured is lost. The result is a peak at 1.74 keV (Si K_{α}) below

the proper peak. This artifact is greatest at about 2 keV, near the P K_{α} or Zr L_{α} peaks. The artifact cannot occur at energies below the absorption edge of the Si K line, and it becomes negligible at higher energies such as the Cu K_{α} line. SDDs have larger escape peaks relative to the parent peak because they are thinner (typically 0.4 to 0.5 mm compared to several mm for Si(Li) detectors) and thus have a higher surface-to-volume ratio.

9. Quantification Analysis

9.1 Before performing a quantitative analysis on an unknown specimen, the elements present must be identified, that is, a qualitative analysis must be performed. Qualitative analysis may be performed on polished specimens or on flat regions of unpolished surfaces, see 7.1.

9.1.1 All manufacturers of EDS systems provide some sort of automatic identification routine. The ability of these systems to identify all of the elements present varies from one EDS system to another and with the nature of the specimen, particularly for trace elements. These programs are quite helpful but should be viewed with caution. For a discussion of their pitfalls, see Newbury (6). The analyst can use his knowledge of chemical principles and of the specimen. Be careful not to disregard elements reported by the computer too quickly. The peaks of these elements may be overlapped with those of other elements. For critical analyses, it is essential for the analyst to confirm the computer output with a manual systematic procedure such as outlined in 9.2. Remember, the analyst is responsible for the results.

9.2 *Step-by-Step Identification*—The following procedure is similar to the one described by Lyman et al. (7) and is sometimes referred to as the “Lehigh Method.”

9.2.1 Begin with the most intense line towards the high-energy region of the spectrum where lines within a family are well separated. If it falls above 3.5 keV, it will be either a K or L line.

9.2.2 Using the KLM markers, compare the location of each peak to that of the marker. If it is off by one channel or less, the same should be true for all nearby lines. If the markers can be scaled, check the relative intensities. If you identified a K_{α} line, then the K_{β} line should be about 10 % of the K_{α} intensity. K_{α} and K_{β} lines are typically resolved at sulfur and above. If a K line is identified, look for L lines, if they occur for that element. This will aid in identifying the lines at low energy later.

9.2.3 If the line chosen does not correspond to a K line, try an L series. If the line is identified as the L_{α} , several other lines both above and below the L_{α} should be present and correspond to the element. The EDS system should be able to display them at their correct relative intensities. M_{α} lines do not exist above 3.2 keV, so one would not look for them at this step.

9.2.4 While working with the most intense line, look for escape and sum peaks. If they are not found for this line, they are unlikely to cause interferences. If they are present, keep looking for them after other identifications.

9.2.5 Next look for peak overlaps. If (1) a peak is displaced relative to its marker, (2) relative intensities are wrong, or (3) there is a distortion in the peak shape, then there is an overlapping element. All three conditions will be present in an