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Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy[1]

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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.[2] This guide does not cover EDS with a transmission electron microscope (TEM).

1.2 *This standard does not purport to address all of the safety problems, 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:*

E 3 Methods of Preparation of Metallographic Specimens[3]
E 7 Terminology Relating to Metallography[3]
E 673 Terminology Relating to Surface Analysis[4]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, see Terminologies E 7 and E 673.

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 *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.

3.2.10 *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 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

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[1] This guide is under the jurisdiction of ASTM Committee E-4 on Metallography and is the direct responsibility of Subcommittee E04.11 on X-Ray and Electron Metallography.

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[2] Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Jr., Lyman, C. D., Fiori, C., and Lifshin, E., *Scanning Electron Microscopy and X-ray Microanalysis*, 2nd ed., Plenum Press, New York, 1992.

[3] *Annual Book of ASTM Standards*, Vol 03.01.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

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.

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 E 3. 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. 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. 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[2] or Johnson and White.[6]

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.[7]

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

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[6] Johnson, G. G., Jr., and White, E. W., *X-Ray Emission Wavelengths and KeV Tables for Nondiffractive Analysis*, ASTM Data Series DS 46, ASTM, Philadelphia, 1970.

[7] Andersen, C. A., and Hasler, M. F., *X-Ray Optics and Microanalysis, 4th Intl. Cong. on X-Ray Optics and Microanalysis*, Hermann, Paris, 1966, p. 310.

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. 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:

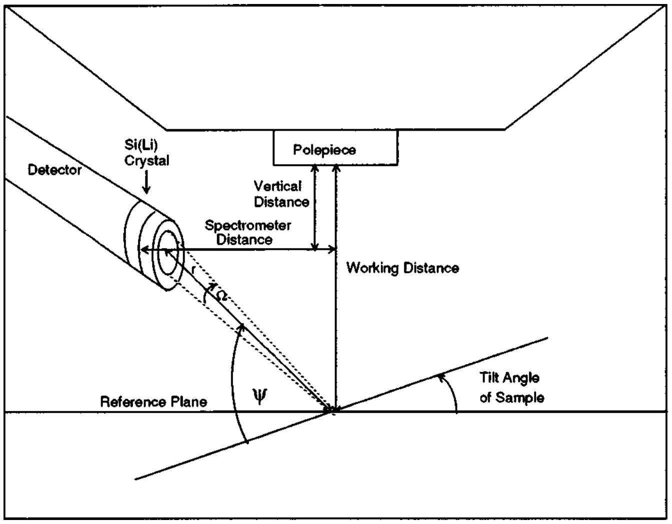

FIG. 1 Schematic Diagram of Electron Microscope System

$$\Omega = A/r^2 \tag{2}$$

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.

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:

$$\psi = \arctan (W - V)/S \tag{3}$$

where:

ψ = take-off angle,

W = working distance,

V = vertical distance, and

S = spectrometer distance.

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. 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.

8.3 *Spectral Artifacts*:

8.3.1 There are a number of artifacts possible with EDS, and these are discussed by Fiori, et al.[8] 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

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[8] Fiori, C. E., Newbury, D. E., and Myklebust, R. L., "Artifacts Observed in Energy Dispersive X-ray Spectrometry in Electron Beam Instruments—A Cautionary Guide," *NIST Special Publication 604, Proceedings of the Workshop on Energy Dispersive Spectrometry*, National Institute of Standards and Technology, Gaithersburg, Maryland, 1981.

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. Alternatively, the amplifier shaping time can be decreased; this action will allow pulses to be processed faster, but at the expense of degraded spectral resolution.

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.

9. Quantification

9.1 *Background Subtraction and Peak Deconvolution*:

9.1.1 Before the proportionality between X-ray intensity and elemental concentration can be calculated, several steps are required to obtain the intensity ratio (k-ratio) between unknown and standard. Or, if the standardless technique is used, then a pure net intensity is required. A spectrum of X rays generated by electrons interacting with the specimen contains a background consisting of continuum X rays, often called Bremsstrahlung. Observing the high-energy cutoff of the continuum, as noted in 8.2.1, gives the most accurate determination of the beam voltage, and this is the value that should be used for quantitative analysis. If the voltage measured in this manner is much lower than the voltage setting, it may be an indication that the specimen is charging. The background in the spectrum is not linear and simple interpolation is inadequate. Two approaches to this problem commonly used in commercial systems are background modeling and digital filtering. The background models are based on known physics plus a suitable correction for the real world. This method lets the user pass judgment on the quality of the model by comparing the model with the actual spectrum. The digital filter method treats the background as a low frequency component of the spectrum and mathematically sets it to zero. This method is not based on any model and, therefore, is more general. It is also useful for the light element region of the spectrum where the models were never intended to be used; however, it does not take into account absorption edges. Some software also allows the operator to fit his own background.

9.1.2 The other step that must be accomplished before an intensity ratio can be measured is peak deconvolution. EDS detectors do not resolve all peaks. For example, the S K_α, Mo L_α, and Pb M_α lines are all within about 50 eV of each other and therefore are severely overlapped. Even though one cannot see the individual components of a peak envelope in a spectrum, there are computer methods of deconvolution. Two methods in common use are *1*) the method of overlap factors and *2*) the method of multiple least squares. Both methods work well, and they are usually combined with one of the background subtraction methods in the manufacturer's software. One should consult the manufacturer's instructions for their use.

9.1.3 Although in most cases these computer methods handle spectra well, the operator should be aware of conditions that are difficult. For example, trace element analysis is sensitive to background subtraction because the computer is looking for a small peak above the continuum. Accordingly the spectrum must be collected long enough to provide enough statistics to discern small peaks. In like manner, deconvolution routines work well in most cases, but not when the overlapped lines arise from elements present in widely different concentrations. For example, if one element constitutes 90 % of the specimen and the other element 10 %, precision will be greatly degraded. In this situation use of a different analytical line may be possible, or if not, a technique with higher spectral resolution such as wavelength dispersive spectrometry is indicated.

9.1.4 Once the background is subtracted and the peaks are stripped of interferences, one can calculate their ratio to those of similarly background-subtracted, deconvoluted standard spectra. The unknowns and standards must have been collected *1*) under the same geometrical configuration, *2*) at the same accelerating voltage, *3*) at the same count rate per current unit, and *4*) with the same processing algorithm.

9.1.5 Even standardless analysis requires background subtraction and peak deconvolution, but the intensity is calculated from pure intensity curves and the ratio of peak integrals in the unknown spectrum. Standardless analyses always total 100 %, or some other value specified by the analyst. In normalizing the total concentrations to 100 %, important information is lost. A true mass total, as in analysis against standards, provides information about the quality of the analysis. It calls attention to problems such as elements not specified for analysis or analysis of more than one phase under the beam. Analyses totaling exactly 100 % should always be viewed with skepticism, whether they be standardless or normalized standards analyses. Whichever method is used, all elements present must be specified even if some need not be analyzed. This is because a correction is necessary to account for the effect of other elements (the matrix) present in the specimen.

9.2 *Matrix Corrections*:

9.2.1 The k-ratio of an element is a starting estimate of that element's concentration. There are, however, effects of atomic number, absorption, and fluorescence between the unknowns and the standards. The atomic number or "Z" factor corrects for differences in the number of X rays generated. The absorption or "A" factor corrects for differences in the number of X rays that escape the sample to be detected. The fluorescence or "F" factor corrects for non-electron generated X rays, that is, those fluoresced by other X rays. If the unknown and standard were identical, each of these factors would equal one. There are many such "ZAF" computer programs available, each one using a set of fundamental parameters thought to give the best results. The differences in the results each produces are usually much less than the precision of the analysis.

9.2.2 There are also many computer programs using the" phi-rho-z" method. These approach the problem of matrix correction using more fundamental physics and sometimes combine the effects of Z and A into one, but they too require a set of fundamental parameters optimized to each program. Many phi-rho-z programs claim greater accuracy because they