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

This standard is issued under the fixed designation E1508; 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 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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E673 Terminology Relating to Surface Analysis (Withdrawn 2012)[3]

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

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[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.

Current edition approved Dec. 1, 2012. Published February 2013. Originally approved in 1993. Last previous edition approved in 2012 as E1508 – 12. DOI: 10.1520/E1508-12A.

[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.

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**)

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

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:

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

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:

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

where:

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

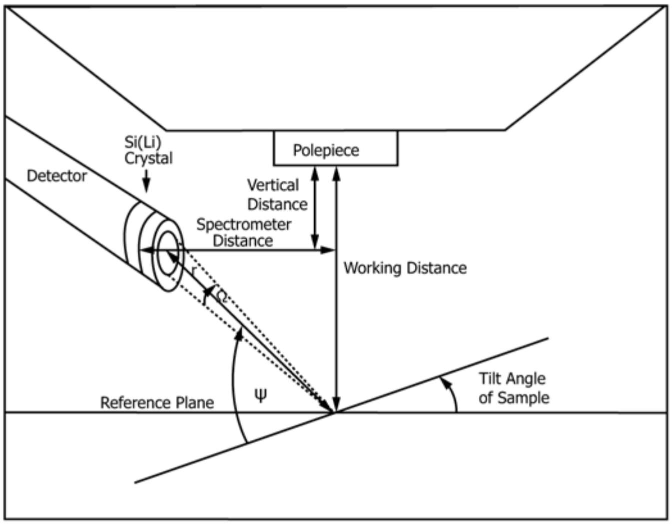

FIG. 1 Schematic Diagram of Electron Microscope System

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 Kα line, then the Kß line should be about 10 % of the Kα intensity. Kα and Kß 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 Lα, several other lines both above and below the Lα should be present and correspond to the element. The EDS system should be able to display them at their correct relative intensities. Mα 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 overlap situation. If one condition is seen, look for the others, to identify the second element.

9.2.6 Continue to identify lines while working towards lower energies and consider the possibility of M lines below 3.2 keV. The lines of an M series are generally not all resolved but contribute to an asymmetrical peak. In fact, M lines can often be recognized by this distortion but beware of overlaps that may look similar.

9.2.7 When all high-energy lines and low-energy L and M lines are identified, light element identification can be attempted. These will be K lines and may be overlapped with L lines from heavier elements. If it is not possible to distinguish them, peak deconvolution software or peak stripping may be necessary.

9.2.8 After all major and minor peaks are located, trace element identification can be attempted. In this case, the problem is finding a peak above background with confidence. Only the major peak of a series will be visible but trace element peaks may be lost in the background. If a peak cannot be identified with some certainty, the first step is to collect more counts. If it still cannot be confirmed, it is either not present or present below the limits of detectability, and another technique such as WDS is warranted.

10. Quantification

10.1 *Background Subtraction and Peak Deconvolution:*

10.1.1 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.

10.1.2 The other step that has to 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.

10.1.3 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.

10.1.4 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.

10.1.5 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.

10.2 *Matrix Corrections:*

10.2.1 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.

10.2.2 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 account for absorption better than the older ZAF programs. Consequently, one would expect the most improvement using a phi-rho-z method in light element analysis. However, in the absence of light elements, it is unlikely that the accuracy of most EDS analyses is limited by the matrix correction.

10.3 *Reporting Results:*

10.3.1 The analytical conditions are normally reported with the elemental concentrations determined by EDS. These conditions include the accelerating voltage, take-off angle and tilt, and the analytical line (KLM) used. The report should also specify whether standards or standardless methods were used, what matrix corrections were applied, and whether any elemental concentrations were calculated by difference or by stoichiometry. Additional items that may be reported include what standards were used, if any, the beam current, and the Z, A, and F factors. It would also be informative to mention the type of window on the EDS detector, if other than a conventional beryllium window. Concentrations are normally reported to a tenth of a percent; although many computer programs report more significant figures, they are rarely warranted.

11. Light Element Analysis

11.1 Light elements can be analyzed with an ultra-thin window detector that provides better efficiency for the soft X rays that light elements generate. Windowless detectors approach the theoretical highest efficiency of the detecting crystal, but in the open position contaminants in the sample chamber are free to condense on the cold crystal. Additionally, in the windowless mode any light, such as from cathodoluminescence, can be picked up by the crystal and will contribute to the overall noise of the system. Quantitative light element analysis is less precise than that of heavier elements, because the count rate of soft X rays is lower. The minimum detectability limit of light elements is also degraded because of the lower peak-to-background ratios found with soft X rays. If the stoichiometry of compounds containing light elements is known, then calculation by stoichiometry is the most accurate method. For example in silicates, analyzing silicon and multiplying by the gravimetric factor for SiO_2 (2.14) is more accurate than analyzing oxygen directly. The best SDD energy resolution is now superior to the best resolution of conventional detectors because of the SDD's much lower capacitance. The improvement as a percentage of peak width is greatest at low energy, so SDDs have better detection limits (P/B ratios) and better direct light-element quantitative precision than Si(Li) detectors under the same conditions.

12. Standards

12.1 Suitable standards for EDS microanalysis must be *1*) homogeneous at the micrometre level, *2*) of known composition as analyzed by an independent method, and *3*) stable under the electron beam. For the highest accuracy, standards should be as similar as possible to the unknowns to minimize matrix effects. However, most matrix correction programs are sufficiently accurate to permit the use of pure element standards. Nevertheless, metals do not make good standards for nonmetals, and vice versa.

12.2 Standards may be obtained from microscopy suppliers, the National Institute for Standards and Technology, or from other microscopists. However, one of the best sources of standards similar to the materials analyzed is one's own facility, if they are checked for homogeneity.

12.3 Standards can also be used to check the performance of standardless programs. In many cases, the results are similar, and the standardless method may be used for convenience.

TABLE 1 Standardized Operating Parameters for Second Round-Robin Test Program

Accelerating voltage	20 kV
Acquisition time	200 s
Detector dead time	≈25 %
Take-off angle	≈40°

13. Precision and Bias

13.1 *Interlaboratory Test Program*—An interlaboratory study using two different metallurgical specimens was conducted to determine the precision of energy-dispersive spectroscopy (EDS). Both specimens were analyzed by various metal producers, EDS system manufacturers, and one university. A total of nine laboratories participated in the study. Each of the specimens was analyzed with a lithium-drifted silicon detector using a set of standardized operating parameters after an initial round-robin wherein parameters were selected by each participant. Both sets of data are reported, and the standardized operating parameters are listed in Table 1.

13.1.1 The specimens selected for the round-robin were Type 308 stainless steel and INCONEL[4] alloy MA 6000. To ensure homogeneity, the Type 308 stainless steel specimens were homogenized at 1975°F (1079°C) for one hour followed by a water quench. This produced a 100 % austenitic structure. This material was chosen as a routine analysis for iron, chromium, and nickel. Some manganese was also present, but because its Kα line overlaps the Cr K_β it was not required to be reported, although some participants did. The alloy MA 6000 specimen was selected because of its inherent homogeneity and because it presented several analytical problems. The alloy contained both high and low atomic number elements necessitating the use of K, L, and M lines. There was also a severe overlap between the M lines of tantalum and tungsten. The presence of eight elements also added to the difficulty in analyzing this material. The compositions of both alloys, as determined by wet chemical analysis, are given in Table 2.

13.1.2 Individual specimens of both materials were sent to each of the nine participants, all of whom reported the specimens to be homogeneous. Each participant was requested to analyze five random areas in each specimen using a standard beryllium window EDS detector and their own operating parameters. The nominal composition of each specimen was also included for reference. A second round-robin test program,

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[4] INCONEL is a registered trademark of Inco Alloys International.

TABLE 2 Wet Chemical Analysis of Samples of Commercial Type 308 Stainless Steel and INCONEL Alloy MA 6000 Used in ASTM Round Robin

Sample	Chemical Composition—Wt %									
	Tantalum	Tungsten	Chromium	Titanium	Aluminum	Molybdenum	Nickel	Iron	Manganese	Y_2O_3
Commercial Type 308 Stainless Steel	—	—	19.62	—	—	—	9.50	69.0	1.30	—
INCONEL Alloy MA 6000	1.91	3.91	14.76	2.26	4.0	1.91	68.12	1.00	—	0.97

which required the use of a standard accelerating voltage, detector dead time, take-off angle, and acquisition time, was also initiated. It was requested that analyses by both standards and standardless methods be reported.

13.2 *Precision:*

13.2.1 The results from the round-robin test program were analyzed in accordance with Practice E691 to develop repeatability and reproducibility standard deviations (see Table 3 and Table 4). The inherent precision of the EDS method is controlled by counting statistics. Clearly, for a given overall counting time, the relative precision associated with major elements is greater than for minor or trace elements, insofar as there are necessarily fewer counts in minor peaks. Practice E691 is used to analyze the round-robin data for consistency and calculates intralaboratory repeatability and interlaboratory reproducibility statistics. The 95 % repeatability and reproducibility, r and R, are defined by E691 as 2.8 times the standard deviations, Sr and SR, respectively. When these standard deviations are divided by the mean concentration for each element, the result is a measure of relative precision within and between laboratories.

13.2.2 In the case of the Type 308 stainless steel, the 95 % repeatability limit is 7 % of the mean value or better for each element. For example $\frac{r}{x} = 0.64/9.43 = 0.068$ for nickel, and about 2 % is possible for iron when present at 70 wt %. The 95 % reproducibility limit ranges from about 14 % to 3 %. Requiring set parameters had little effect on the repeatability but improved the reproducibility for chromium and iron, but not for nickel. Standardless methods were about equivalent to those using standards for this specimen. The results obtained from this specimen represent a typical metallurgical microanalysis with no unusual problems. As such, the precision obtained should be representative of the technique. The interlaboratory reproducibility under standard conditions averaged 8.4 %, and the standardless method averaged 6.2 % relative to the mean.

TABLE 3 Precision Statistics of an Interlaboratory Study for Quantitative Analysis by Energy Dispersive Spectroscopy

Quantitative EDS Analysis of Type 308 Stainless Steel with No Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.04	0.21	0.35	0.58	0.98
Chromium	20.48	0.27	0.87	0.77	2.43
Iron	70.47	0.68	2.44	1.90	6.84

Quantitative EDS Analysis of Type 308 Stainless Steel with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.43	0.23	0.49	0.64	1.36
Chromium	20.31	0.23	0.47	0.65	1.32
Iron	69.41	0.38	1.05	1.06	2.95

Standardless Quantitative EDS Analysis of Type 308 Stainless Steel with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Nickel	9.23	0.22	0.29	0.60	0.82
Chromium	20.25	0.15	0.48	0.41	1.34
Iron	69.60	0.21	0.78	0.60	2.18

$\bar{x}$ = cell average
Sr = repeatability standard deviation
SR = reproducibility standard deviation
r = repeatability limit
R = reproducibility limit

TABLE 4 Precision Statistics of an Interlaboratory Study for Quantitative Analysis by Energy Dispersive Spectroscopy

Quantitative EDS Analysis of MA 6000 with No Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	0.96	0.09	0.12	0.24	0.32
Tantalum	1.89	0.26	0.37	0.72	1.04
Titanium	2.36	0.26	0.26	0.72	0.72
Molybdenum	2.43	0.16	0.86	0.45	2.41
Tungsten	3.67	0.30	0.67	0.84	1.87
Aluminum	4.49	0.22	1.31	0.63	3.67
Chromium	15.33	0.33	0.49	0.92	1.38
Nickel	67.78	1.66	2.43	4.64	6.81

Quantitative EDS Analysis of Type MA 6000 with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	1.04	0.05	0.10	0.14	0.29
Tantalum	1.81	0.17	0.47	0.49	1.33
Molybdenum	2.02	0.07	0.12	0.20	0.34
Titanium	2.31	0.16	0.20	0.46	0.56
Tungsten	3.82	0.15	0.38	0.41	1.07
Aluminum	4.78	0.23	0.59	0.63	1.66
Chromium	15.07	0.33	0.46	0.91	1.30
Nickel	68.97	0.51	1.25	1.43	3.51

Standardless Quantitative EDS Analysis of MA 6000 with Set Parameters

Elements	$\bar{x}$	Sr	SR	r	R
Iron	0.99	0.08	0.12	0.22	0.32
Molybdenum	1.96	0.11	0.53	0.31	1.49
Tantalum	1.98	0.15	1.19	0.42	3.34
Titanium	2.30	0.15	0.18	0.43	0.51
Tungsten	3.48	0.17	1.39	0.48	3.90
Aluminum	4.56	0.22	2.33	0.63	6.53
Chromium	15.31	0.23	0.56	0.64	1.55
Nickel	64.29	0.43	3.06	1.21	8.56

$\bar{x}$ = cell average
Sr = repeatability standard deviation
SR = reproducibility standard deviation
r = repeatability limit
R = reproducibility limit

13.2.3 In the case of alloy MA 6000, the 95 % repeatability values improve with increasing concentration with the exception of tantalum and tungsten. Those two elements are present at the level of a few percent and their lines are overlapped. The occurrence of these two conditions together resulted in considerably lower precision than for the other elements. The 95 % reproducibility limit varied greatly when the parameters were not specified, but improved with set parameters. It may be that differences in background subtraction, peak deconvolution method, matrix correction, and possibly geometric configuration caused this. It was not possible to specify all of these conditions because some are inherent to the system used.

13.2.4 The standardless method produced intralaboratory repeatability results similar to the standards methods but considerably less interlaboratory reproducibility, owing to the different standardless routines in use by different manufacturers. Although results of the standardless analyses were rather good on the Type 308 stainless steel, they may be considerably inferior on other types of specimens. On the MA6000 alloy, the reproducibility among laboratories was much less than that of the standards technique (R in Table 4). And even though the average errors compared with the reference composition (Table 5) are not great, they are probably the result of positive and negative errors among laboratories canceling each other. These errors arise from the different ways various systems generate the pure element intensities, rather than from differences in ZAF or phi-rho-z matrix corrections. Accordingly, before routinely using a standardless method for quantitative analysis, it is important to validate the method for a particular class of materials by comparing it against analysis with standards or against a completely different quantitative technique, such as X-ray fluorescence or wet chemical analysis if the specimen is homogeneous. If the results are comparable, the standardless method may be used for specimens of composition similar to those on which it was validated.

13.2.5 Precision can usually be improved by acquiring more counts in the spectrum if that is possible. Longer counting times and increased beam current produce more counts. There are practical limits, however, such as beam drift or carbon contamination increasing on the specimen and causing the total counts to be nonlinear with time. Decreasing the amplifier time constant also increases count rate, but at the expense of resolution. The 200s count specified for the round-robin was intended to represent typical operating conditions, not the best achievable precision.

13.3 *Bias:*

13.3.1 If the wet chemical analysis of each specimen (Table 2) is taken as an accepted reference value, the difference between it and the concentration measured by EDS can be determined. These values are given in Table 5. The EDS values are the average of five measurements in each of nine laboratories. To the extent that this number of replicate analyses averages out the effects of precision, the remaining error may be attributed to bias. For the Type 308 stainless steel, the average error was 0.7 % of the amount present—a value close enough to zero to be insignificant. For the alloy MA 6000, the average was 3.12 %. There are many potential sources of bias, but the effect of each is hard to predict. Some sources of bias that are under operator control are as follows.

13.3.1.1 *Geometric Configuration*—This must be known and reproducible among standards and unknown specimens.

13.3.1.2 *Standards*—The composition of these must be known accurately, and they have to be homogeneous at the micrometre level.

13.3.1.3 *Electron Beam Current*—This must be stable throughout standard collection and unknown analysis or corrected for instability through continuous monitoring with an integrating picoammeter or beam current monitoring before and after analysis if the drift is linear.

13.3.1.4 *Conductive Coating*—This must be thick enough to prevent changing of the specimen, yet thin enough so as not to absorb X rays significantly. It should also be of similar composition and thickness between the standards and the unknowns.

13.3.2 Some sources of bias often not under operator control are as follows.

13.3.2.1 *Method of Background Subtraction and Peak Deconvolution*—These must use appropriate constants such as detector efficiency for the specific detector being used, background fitting regions, filter width, and others.

13.3.2.2 *Matrix Correction*—This program is dependent on the accuracy of many constants such as mass absorption coefficients, mean ionization potentials, fluorescent yields, and others.

13.3.2.3 *Standardless Programs*—These are dependent on the accuracy of the intensity curves built into them as well as the sources of bias listed above.

13.4 Overall, when elements are present in major amounts, an intralaboratory repeatability of 6 % or better and an interlaboratory reproducibility of 14 % or better are possible. With

TABLE 5 Comparison Between EDS and Reference Wet Chemical Analysis

	Wet Chemistry	No Set Parameters (% error)	Set Parameters (% error)	Standardless (% error)
Type 308 Stainless Steel				
Nickel	9.50	9.04 (−4.84)	9.43 (−0.78)	9.23 (−2.84)
Chromium	19.62	20.48 (4.39)	20.31 (3.51)	20.25 (3.23)
Iron	69.00	70.48 (2.14)	69.41 (0.59)	69.60 (0.88)
Average error		0.56 %	1.11 %	0.42 %
Alloy MA 6000				
Iron	1.00	0.96 (−4.24)	1.04 (3.67)	0.99 (−1.43)
Tantalum	1.91	1.88 (−1.30)	1.81 (−5.08)	1.96 (2.62)
Titanium	2.26	2.36 (4.30)	2.02 (−10.55)	1.98 (−12.18)
Molybdenum	1.91	2.43 (27.31)	2.31 (20.82)	2.30 (20.19)
Tungsten	3.91	3.67 (−6.02)	3.82 (−2.27)	3.48 (−11.11)
Aluminum	4.00	4.49 (12.16)	4.78 (19.38)	4.56 (13.91)
Chromium	14.76	15.33 (3.87)	15.07 (2.09)	15.31 (3.71)
Nickel	68.12	67.78 (−0.49)	68.97 (1.24)	64.28 (−5.63)
Average error		4.45 %	3.66 %	1.26 %
Average Error for Type 308		0.70 %		
Average Error for MA 6000		3.12 %		
Overall Average Error		1.91 %		

trace elements, and especially with peak overlaps among trace elements, precision is significantly degraded and more X-ray counts must be collected. Most sources of bias are either insignificant or under operator control, and the overall accuracy of the technique is better than ±4 % relative to the reference composition.

14. Keywords

14.1 EDS; elemental analysis; energy-dispersive spectroscopy; light element; matrix correction; microanalysis; phi-rho-z; quantitative analysis; spectrum; standardless analysis; standards; X ray; X-ray microanalysis; ZAF

REFERENCES

(1) 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*, 3rd ed., Plenum Press, New York, 2003.

(2) Gatti, E. and Rehak, P *Semiconductor drift chamber – an application of a novel charge transport scheme*. NIM-A 225:608-621, (1984).

(3) 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

(4) 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

(5) 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.

(6) Newbury, D. E., Microscopy and Microanalysis, Vol 11, 2005, pp. 545-561.

(7) Lyman C. E., Newbury, D. E., Goldstein, J. I., Williams, D. B., Romig, A. D., et al, Scanning Electron Microscopy, X-ray Microanalysis, and Analytical Electron Microscopy-A Laboratory Workbook 36, 1990.