REVIEW

Performing elemental microanalysis with high accuracy and high precision by scanning electron microscopy/silicon drift detector energy-dispersive X-ray spectrometry (SEM/SDD-EDS)

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Abstract Electron-excited X-ray microanalysis performed in the scanning electron microscope with energy-dispersive X-ray spectrometry (EDS) is a core technique for characterization of the microstructure of materials. The recent advances in EDS performance with the silicon drift detector (SDD) enable accuracy and precision equivalent to that of the high spectral resolution wavelength-dispersive spectrometer employed on the electron probe microanalyzer platform. SDD-EDS throughput, resolution, and stability provide practical operating conditions for measurement of high-count spectra that form the basis for peak fitting procedures that recover the characteristic peak intensities even for elemental combination where severe peak overlaps occur, such PbS, MoS_2, $BaTiO_3$, $SrWO_4$, and WSi_2. Accurate analyses are also demonstrated for interferences involving large concentration ratios: a major constituent on a minor constituent (Ba at 0.4299 mass fraction on Ti at 0.0180) and a major constituent on a trace constituent (Ba at 0.2194 on Ce at 0.00407; Si at 0.1145 on Ta at 0.0041). Accurate analyses of low atomic number elements, C, N, O, and F, are demonstrated. Measurement of trace constituents with limits of detection below 0.001 mass fraction (1000 ppm) is possible within a practical measurement time of 500 s.

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Introduction

Origins: electron probe microanalysis with wavelength-dispersive spectrometry

Electron-excited X-ray spectrometry for the measurement Query of elemental composition on the microstructural scale has been an important part of the materials characterization arsenal since the invention of the electron probe microanalyzer (EPMA) in 1951 by Castaing [1, 2]. Castaing not only produced the first working EPMA instrument but he also established the framework for the fundamental measurement science of the technique, including the physical basis for a practical quantitative analysis method. For the first two decades of the EPMA technique, the diffraction-based wavelength-dispersive X-ray spectrometer (WDS) was the only practical way to measure the X-ray intensities. Castaing recognized that the complex dependence of the WDS efficiency on photon energy made it impractical to develop a quantification procedure that compared different elements measured at different photon energies. Besides the variable solid angle of the WDS that is dependent on photon energy, four or more diffractors with different d-spacings and scattering efficiencies are needed to satisfy Bragg's equation over the photon energy range of interest from 100 eV to 10 keV. To overcome this measurement dilemma, Castaing developed the "k-ratio" protocol based on measuring the characteristic X-ray intensity, I, for the *same element* in the unknown and in a standard of known composition:

$$k = I_{unknown} / I_{standard}. \qquad (1)$$

The characteristic X-ray peak intensity is corrected for background and measured under identical conditions of beam energy, known dose, and detector efficiency for both

unknown and standard. By measuring the same peak under identical conditions, the same efficiency value effectively appears in both the numerator and denominator of Eq. (1) as a multiplier of the intensity, and thus the efficiency quantitatively cancels in the k-ratio.

Castaing further described the basis for the physical calculations that are necessary to convert the suite of k-ratios into mass concentrations, which after substantial further contributions by numerous authors (see Ref. [3] for Heinrich's detailed account of these developments) take the following form:

$$C_i/C_{std} = k_i\, ZAFc, \tag{2}$$

where C_{std} is the mass concentration of the element of interest in the standard; and Z, A, F, and c are the "matrix correction factors" that calculate the compositionally dependent interelement effects of electron scattering and energy loss (Z), X-ray self-absorption within the specimen (A), and secondary X-ray emission following self-absorption of the electron-excited characteristic (F) and continuum (c) X-rays. Importantly for the Castaing standards-based k-ratio method, the standards required do not have to closely match the composition of the unknown, which is an enormous advantage when dealing with complicated multi-element unknowns. Suitable standards for the k-ratio measurements include pure elements (e.g., Al, Si, Cr, Fe, Ni, etc.), while stoichiometric compounds can be used for those elements that are not in solid form in a vacuum (e.g., MgO for O), that are highly reactive (e.g., KCl for K and Cl), that deteriorate under electron bombardment (e.g., FeS_2 for S), or that have a low melting temperature (e.g., GaP for Ga and P).

The extremely sharp focal properties of the WDS forced EPMA analysts to develop procedures to establish and maintain the critical condition of identical detection efficiency when measuring the separate intensities for the unknown and standards required for Eq. (1) [3]. To place the specimen reproducibly within the narrow spatial range, spanning a few micrometers, over which the WDS had constant X-ray transmission, a fixed-position optical microscope with a shallow depth of focus was incorporated into the EPMA at the coincident focal position for all spectrometers. The condition of the specimen surface was recognized to be another critical requirement [4]. It came to be understood early in the development of EPMA that the specimen had to metallographically polished to a very high degree of surface finish, but not chemically etched. To create contrast in optical metallography, chemical etching typically produces topography through orientation-dependent etch rates in different grains and phases, but even fine-scale topography can influence measured X-ray intensities, especially for low-energy photons. Moreover, in some cases, chemical etching induces changes in the surface/
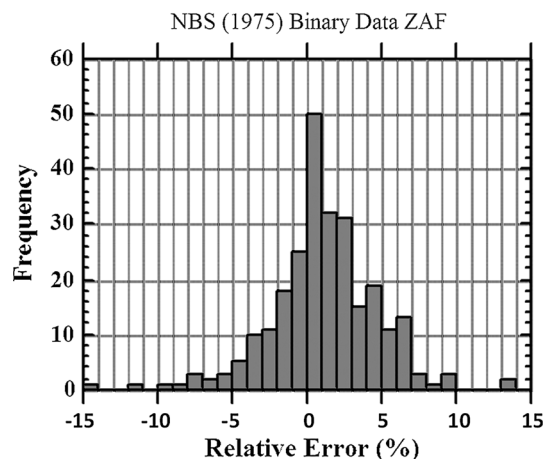

Fig. 1 Distribution of relative errors [(measured − true)/true × 100 %] using the k-ratio protocol with WDS measurements and matrix corrections with the NBS ZAF procedure FRAME (1975) [5]. Note that the *histogram* bins have a width of 1 % relative

near-surface composition, the principal region that is sampled by electron-excited X-rays, rendering the analytical results unrepresentative of the material being measured.

Throughout the development of quantitative electron-excited X-ray microanalysis, researchers rigorously tested the method by measuring as unknowns carefully selected multi-element materials whose microscopic homogeneity could be first confirmed by EPMA and whose overall composition was measured by independent chemical analysis. The distribution of measured relative errors, defined as

$$\text{Relative error} = [(\text{Measured concentration} - \text{Reference})/ \\ \text{Reference}] \times 100\,\%, \tag{3}$$

as determined by a mature version of the k-ratio/matrix correction procedure in 1975 is shown in Fig. 1 for WDS measurements of major[1] constituents [5]. This distribution can be characterized by a standard deviation of 2.5 % relative, so that approximately 95 % of the analyses fall within the span of ± 5 % relative error.

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[1] Note: in this paper, the following arbitrary convention for broadly classifying the concentration range will be followed:

"major," mass concentration $C > 0.1$ (more than 10 wt%)
"minor" $0.01 \leq C \leq 0.1$ (1–10 wt%)
"trace" $C < 0.01$ (<1 wt%).

Further development: energy-dispersive X-ray spectrometry

The development of semiconductor-based X-ray detection in the 1960s led to the first successful energy-dispersive X-ray spectrometer (EDS) using lithium-compensated silicon [Si(Li)-EDS] operated on an electron-column instrument, an EPMA [6]. As compared to the narrow instantaneous energy range of the WDS, the Si(Li)-EDS provided a view of the entire excited X-ray spectrum from a threshold of approximately 100 eV (modern performance) to the Duane-Hunt limit set by the incident beam energy, up to 20 keV or higher. This wide energy range enabled detection of all elements, with the exception of H and He (modern performance), at every location sampled by the beam, which provided an enormous advantage when dealing with complex microstructures where local segregation can create unexpected compositional variation and where unexpected elements can be localized as inclusions. Comprehensive elemental analysis capability, combined with the relative simplicity of non-focusing line-of-sight detection, the large solid angle of collection which exceeds that of WDS by at least a factor of 10, and the long-term operating stability, resulted in the enthusiastic acceptance of EDS, especially by the rapidly developing scanning electron microscope (SEM) community. The combination of SEM imaging with EDS X-ray microanalysis has given the materials community one of its most powerful microstructural characterization tools [2].

The capability of Si(Li)-EDS to perform quantitative X-ray microanalysis was established soon after its introduction by several members of the microanalysis community, most of whom had extensive WDS quantitative microanalysis experience [7–11]. Thus, the initial EDS implementation of quantitative analysis was based upon their experience with the WDS k-ratio protocol. The EDS could be used in an equivalent manner by measuring the intensities for the unknown and appropriate standards under the same carefully controlled conditions of surface condition (highly polished), beam energy, known dose (beam current × detector live time), beam incidence angle, detector elevation angle ("take-off angle"), and detector efficiency (e.g., constant detector-to-target distance to yield constant detector solid angle). The enormous advantages of the EDS over WDS for analysis were quickly recognized: (1) all elements in the unknown were measured simultaneously minimizing the dose to the specimen; (2) the large solid angle of the EDS relative to WDS further improved efficiency of detection which lowered the necessary dose relative to WDS; and (3) the stability of the EDS meant that the spectra of standards could be archived and recalled as needed. Since the measured EDS spectrum consists of the characteristic X-ray peaks superimposed on the X-ray continuum, various strategies were developed to determine characteristic intensities, including digital filtering for background removal followed by multiple linear least squares (MLLS) fitting and background modeling under the peak window constrained by the continuum intensity measured in energy windows where no peaks occurred [8, 10]. The background-corrected characteristic intensities for the unknown and the standards were used to calculate k-ratios followed by the matrix correction procedure. The k-ratio matrix correction procedure with the Si(Li)-EDS was demonstrated to be capable of achieving relative errors within the WDS distribution for major constituents when the characteristic X-ray peaks did not suffer significant overlap from the peaks of other elements. An example is shown in Table 1 for the Si(Li)-EDS analysis of gold-copper alloys (NIST Standard Reference Material 482) where the observed relative errors range from −1.6 to 1.0 %, falling well within the WDS analysis error distribution of Fig. 1.[2] Further development of the EDS quantitative microanalysis method enabled accurate analyses when significant peak overlaps occurred providing the intensities of the mutually interfering species were similar.

Typical SEM/EDS microanalysis practice

Despite the level of analytical accuracy demonstrated for the EDS k-ratio/matrix corrections protocol and the availability of this procedure within most commercial implementations of EDS analytical software, modern SEM/EDS microanalysis practice has developed along a different trajectory that minimizes the need for the user's expertise. As an unintended consequence, EDS microanalysis as performed in the SEM has acquired an unfortunate reputation as a "semi-quantitative" technique. This situation has developed because of three contributing factors: (1) the rise of standardless analysis which now dominates EDS quantitative analysis [14]; (2) the severe effects of specimen geometry on the accuracy of X-ray microanalysis which occur no matter which analytical protocol is followed, standards-based or standardless [15]; and (3) the occasional but significant failures in qualitative analysis, i.e., incorrect elemental identification, which immediately undermines confidence in the method [16–18].

The rise of "standardless" quantitative analysis

By necessity, WDS measures each element in the sample relative to the same element in an appropriate standard to

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[2] Materials analyzed in this paper include NIST Standard Reference Materials, NIST microanalysis research materials (glasses), natural minerals, and stoichiometric compounds confirmed to be homogeneous on a micrometer lateral scale.

Table 1 Si(Li)-EDS analysis of NIST Standard Reference Material 482 Copper–Gold Alloys[a] (all concentration values in mass fraction)

Cu (certified)	Analyzed	Rel. error (%)	Au (certified)	Analyzed	Rel. error (%)	Total
0.198	0.198 ± 0.002	0.0	0.801	0.790 ± 0.002	−1.4	0.988
0.396	0.399 ± 0.001	0.8	0.603	0.594 ± 0.002	−1.6	0.993
0.599	0.605 ± 0.001	1.0	0.401	0.402 ± 0.002	0.1	1.007
0.798	0.797 ± 0.001	−0.1	0.200	0.199 ± 0.003	−1.2	0.996

Analysis performed with Cu Kα and AuLα; beam energy = 20 keV; quantitative calculations with NIST Desktop Spectrum Analyzer [12]; uncertainty expressed as 1σ from the measured counts (from Ref [13])

[a] See footnote 2

eliminate the need to accurately know the spectrometer efficiency. Because the EDS spectrum provides, in every measurement, the complete photon energy range revealing all characteristic X-ray peaks and the X-ray continuum background, it became attractive to develop an alternative approach for quantitative EDS microanalysis that employed the whole spectrum. The so-called "standardless analysis" method requires only the EDS spectrum of the unknown and eliminates the need to measure standards locally or to specify the electron dose [2, 14]. "Standardless analysis" seeks to provide the necessary standard intensity for the denominator of Eq. (1) for each element in the unknown either by theoretical calculation of X-ray generation and propagation in a pure element target ("first principles" standardless) or by the use of a library of actual standards measured on a well-characterized EDS detector at several beam energies under defined conditions that can be related to the efficiency as a function of photon energy of the local EDS ("remote standards" standardless). The resulting suite of k-ratios is then subjected to the same matrix correction calculations of Eq. (2). Because a true first principles implementation of standardless analysis requires an extensive database of X-ray parameters such as the ionization cross section, X-ray fluorescence yield, X-ray mass absorption coefficient, and others, many of which are poorly known, especially for the L-shell and M-shell X-ray families, the "remote standards" method, which actually anchors the quantitative calculations to a suite of archived experimental measurements, is the basis for the typical modern software implementation.

The performance of a recent commercial version of "standardless analysis" is shown in the error histogram of Fig. 2. While this error distribution appears similar to that of the classic k-ratio protocol with WDS or EDS as shown in Fig. 1, it is in fact much broader, with the errors binned in increments of 5 % relative error, compared to the 1 % relative error increments of Fig. 1. For this particular implementation of standardless analysis, the width of the error range that is necessary to capture 95 % of the analytical results is approximately ±30 % relative. While this level of performance may be adequate for some
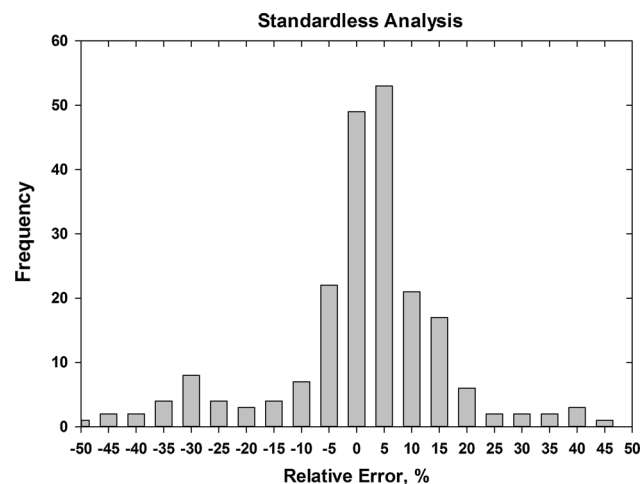

Fig. 2 Distribution of relative errors observed for a commercial implementation of standardless analysis (2013). Note that the histogram bins have a width of 5 % relative

applications, the prospective user of the analytical results of such a procedure needs to be aware of the inherent limitations imposed by such a wide error distribution. Table 2 provides specific examples of the application of this standardless analysis procedure to the analysis of metal sulfides. While the analytical accuracy achieved for FeS (troilite, a meteoritic mineral) is excellent with relative errors less than ±2 % for S and Fe, the relative errors for the analysis of FeS_2 (pyrite), CuS (covellite), ZnS (sphalerite), and PbS (galena) exceed 20 % relative, a level of performance so poor that it would not be possible to properly assign the formula for these compounds from the analyzed mass concentrations.

Another often overlooked consequence of using the standardless analysis procedure is the requirement that the calculated concentrations must be internally normalized to a sum of unity. This requirement occurs because the relation of the electron dose and the absolute EDS efficiency of the measured spectrum to the remote standards database is lost so that internal normalization is needed to place the calculated concentration values on a meaningful scale. That the

Table 2 Standardless analysis of sulfides (2013 Commercial Software)

Compound	Metal	Analysis	Relative error (%)	Sulfur	Analysis	Relative error (%)
FeS	0.635	0.629	−1.0	0.365	0.371	1.8
FeS	0.466	0.642	38	0.534	0.358	−33
CuS	0.665	0.764	15	0.335	0.236	−30
ZnS	0.671	0.762	14	0.329	0.239	−28
SrS	0.732	0.758	3.6	0.268	0.242	−10
CdS	0.778	0.808	3.8	0.222	0.192	−13
Sb_2S_3	0.717	0.739	3.1	0.283	0.261	−7.8
PbS	0.866	0.914	5.5	0.134	0.086	−36

analyzed mass concentration total of all constituents in a standardless analysis equals exactly 1.000 (100 wt%) may seem comforting, but the internal normalization that must occur does in fact represent a loss of critical information. In the standards-based k-ratio/matrix corrections protocol performed with WDS or EDS, the sum of the individual constituents rarely coincides exactly with unity, but tends to vary from 0.98 to 1.02, as shown in the example presented in Table 1, a consequence of the inevitable errors that arise in measuring the characteristic intensities and in calculating the matrix correction factors. Analytical totals outside of this range can occur because of uncontrolled deviations in the experimental conditions between measuring the unknown and standards (e.g., differences in coating thickness or in the thickness of native surface oxides), but a low analytical total may also reveal the presence in the analyzed volume of a previously unrecognized constituent. For example, a region of the specimen that is oxidized rather than metallic will contain oxygen at a concentration from 0.2 to 0.3 mass fraction. The analytical total if oxygen is not considered (either by directly measuring its X-ray intensity and making the appropriate matrix correction calculation or by indirectly calculating oxygen by the method of assumed stoichiometry of the cations) will be 0.7–0.8, significantly below unity, which should trigger the curiosity of a careful analyst to further examine the measured spectrum and discover the oxygen peak. While this may seem a trivial example that even a novice analyst should not miss, in fact as we enter an era in which much of our data are collected under automation, the lack of manual inspection combined with the loss of a meaningful analytical total by the standardless method will result in questionable data appearing in the final results that may be difficult to review after collection and processing. As discussed below, a more frequently encountered source of deviation in the analytical total is the impact of uncontrolled "specimen geometry," i.e., the effects of size, shape, and local surface inclination on beam electron—specimen interaction and the generation and propagation of X-rays, on the measured X-ray intensities. A "zeroth" level assumption in standards-based and standardless analysis procedures is

that the specimen composition is the only factor affecting the X-ray intensities. When the specimen geometry deviates from the ideal flat surface placed at known angles to the incident electron beam and the X-ray spectrometer, very large effects on the X-ray intensities can occur, especially when low-energy and high-energy photons are measured in the same analysis.

Despite these limitations, the simplicity of operation required for standardless analysis, which only requires the analyst to measure the EDS spectrum of the unknown and to specify the beam energy and the X-ray emergence angle, has resulted in its widespread acceptance by the SEM/EDS community. Based on our informal surveys of the field, probably more than 98 % of reported quantitative EDS microanalysis results are obtained with some implementation of standardless analysis. However, the modest analytical performance revealed in Fig. 2 and Table 2 is surely a major contributor to the reputation of SEM/EDS as only achieving "semiquantitative" results, while the internal normalization of all results to unity conveys a false sense of accuracy and confidence.

Specimen geometry effects: we can be our own worst enemies when it comes to performing accurate quantification

When analytical results are automatically normalized, an even more egregious source of large, uncontrolled, and likely unrecognized errors in SEM/EDS microanalysis arises from specimen geometry effects [2]. The line-of-sight acceptance of the EDS spectrometer enables the analyst to record an X-ray spectrum from almost any location where the beam strikes the specimen, which can be a useful feature in qualitatively surveying the complex microstructure of a specimen with complex topography. However, specimen geometry effects such as shape and local surface inclination to the beam can have a profound impact on electron scattering and even more importantly, on the path length along which X-rays must travel to the detector and along which they suffer absorption. These "geometric effects" modify

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