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Mistakes Encountered During Automatic Peak Identification of Minor and Trace Constituents in Electron-Excited Energy Dispersive X-Ray Microanalysis

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DALE E. NEWBURY

National Institute of Standards and Technology, Gaithersburg, Maryland

Summary: Automated peak identification in electron beam-excited X-ray microanalysis with energy dispersive X-ray spectrometry has been shown to be subject to occasional mistakes even on well-separated, high-intensity peaks arising from major constituents (arbitrarily defined as a concentration, C, which exceeds a mass fraction of 0.1). The peak identification problem becomes even more problematic for constituents present at minor ($0.01 \leq C \leq 0.1$) and trace ($C < 0.01$) levels. "Problem elements" subject to misidentification as major constituents are even more vulnerable to misidentification when present at low concentrations in the minor and trace ranges. Additional misidentifications attributed to trace elements include minor X-ray family members associated with major constituents but not assigned properly, escape and coincidence peaks associated with major constituents, and false peaks owing to chance groupings of counts in spectra with poor counting statistics. A strategy for robust identification of minor and trace elements can be based on application of automatic peak identification with careful inspection of the results followed by multiple linear least-squares peak fitting with complete peak references to systematically remove each identified major element from the spectrum before attempting to assign remaining peaks to minor and trace constituents. SCANNING 31: 1–11, 2009. © 2009 Wiley Periodicals, Inc.

Key words: energy dispersive X-ray spectrometry, automatic peak identification, peak fitting, qualitative analysis, scanning electron microscopy, trace elements, X-ray microanalysis

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Address for reprints: Dale E. Newbury, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899. E-mail: dale.newbury@nist.gov

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Introduction

Electron-excited energy dispersive X-ray spectrometry (EDS) performed in the scanning electron microscope (SEM) or other electron beam platforms has become established as a core compositional characterization method for a broad range of physical and biological sciences as well as many branches of engineering and technology (Goldstein *et al*. 2003). Commercial SEM/EDS instrumentation has matured with the development of extensive software resources for computer-controlled microscope operation and computer-assisted X-ray analysis. Advanced software controls EDS X-ray spectrum acquisition and spectrum analysis, including automatic qualitative analysis (X-ray peak identification) and automatic quantitative analysis that can be standards-based or that does not require local standardization ("standardless analysis"). Perusal of recent EDS advertising shows an increasing tendency in software systems to simplify the operation of this complex instrumentation by minimizing the need for the operator's input to the analysis. Indeed, advertising claims are frequently found for "one button" analysis, whereby the entire process of operation is encapsulated in an automatic software routine that requires the operator only to select the desired beam location or image region where the analysis is to be performed and initiate the spectrum collection, with the software doing the rest of the task, directly leading to a final report of analysis entry for that specimen location that identifies the elemental constituents present and assigns concentration values. Although this article is written from the perspective and experience of the SEM-EDS analytical community, it has been noted by a colleague of the author that these considerations apply equally well to the technique of energy dispersive X-ray fluorescence (EDXRF) analysis (Sieber 2009). AQ2

Correctly identifying the elements present in the beam-excited volume during the qualitative analysis procedure is obviously the required foundation, if the subsequent quantitative analysis is to make any sense. The skeptical analyst will carefully test automated analysis systems, starting with the automatic peak identification. Two earlier articles examined the occurrence of mistakes that sometimes occur during automatic peak identification with commercial software for major constituents (arbitrarily, a ‘‘major’’ constituent will be defined as an element present at a mass fraction >0.1; see further definitions below) under ‘‘conventional’’ electron-excited EDS microanalysis conditions (Newbury 2005a) and under low-beam-energy microanalysis conditions (Newbury 2007). ‘‘Conventional’’ analysis conditions are generally regarded as involving selection of the incident beam energy in the range 15–30 keV, a choice that provides excitation of at least one readily measurable characteristic X-ray peak family (i.e. peaks from one atomic shell) for all elements of the periodic table with atomic number greater than or equal to 4 (beryllium). Those previous studies considered only the simplest peak identification problem, namely the identification of elemental constituents present at sufficiently high concentration to produce high-intensity characteristic peaks with a high peak-to-background (characteristic to continuum) ratio. Moreover, only those spectrometric situations were considered where there were no significant interelement peak overlaps and no peaks below 0.9 keV photon energy, which are subject to large self-absorption in the specimen. Despite the apparent simplicity of this challenge, the study of automatic peak identification under conventional analysis conditions found that misidentifications of major constituent peaks occurred in approximately 3–5% of the cases tested (Newbury 2005a) when specimens contained elements selected throughout the periodic table, but excluding Be to Ne, which could only be analyzed with low-photon-energy, K-shell peaks below 0.9 keV. Moreover, the peak misidentifications were generally found to be systematic and independent of the number of counts accumulated. As an example, Br Lα (note that in this article Siegbahn peak notation will be used because it is still the dominant choice in analytical software) was consistently misidentified by some software systems as Al Kα in the EDS spectra of a wide range of bromine-containing compounds such as reagent-grade potassium bromide (KBr) (Newbury 2005a).

When the beam excitation conditions were restricted to ‘‘low-beam-energy microanalysis,’’ where ‘‘low’’ is defined as the incident beam energy of 5 keV or less, the problem of peak misidentification was found to be further exacerbated (Newbury 2007). When the well-defined peaks with photon energies above 5 keV were excluded from the spectrum by the choice of the beam energy, further mistaken peak identifications were encountered when only more poorly separated low-photon-energy peaks were available for consideration.

The occurrence of a mistake in identifying the element responsible for a peak during the qualitative analysis procedure has a catastrophic impact upon the overall measurement process. Such egregious mistakes are properly considered as ‘‘blunders,’’ which are defined as ‘‘illegitimate measurement errors’’ (Bevington and Robinson 1992). That is, the occurrence of a blunder during the qualitative analysis procedure renders the entire measurement invalid. Thus, a proper determination of an error budget to associate with the concentration assigned to the incorrect element is not possible or even meaningful. Clearly, an accurate compositional measurement has no value if it is assigned to the wrong element! Such blunders are analytical ‘‘showstoppers.’’ Performing a quantitative analysis that determines a concentration for an element that is not actually present in the specimen is obviously nonsense. Moreover, these peak identification blunders were generally found to be systematic and not random occurrences. The same peak identification failures were observed with a particular software system in repeated tests of materials when the element of interest was present in different compounds. For example, when a software system misidentified the Br Lα peak in KBr as Al Kα or Yb Mα, this peak was consistently misidentified when different bromine-containing compounds were tested.

For this final article of this study, the problem of peak identification for minor and trace constituents is considered. For the purposes of this discussion, the following arbitrary definitions will be used for mass fraction (C) ranges:

‘‘major’’ constituent: $C>0.1$ mass fraction (10 wt%),
‘‘minor’’ constituent: $0.01\leq C\leq 0.1$ mass fraction (1–10 wt%),
‘‘trace’’ constituent: $C<0.01$ mass fraction (1 wt%).

The impact of misidentification of a minor or a trace element at these concentration levels on the overall value of an analysis may seem to be less consequential compared with misidentifying a major constituent. Nevertheless, for certain problems, minor and trace constituents have critical importance in controlling the overall behavior of a system, such as the strength of a material or the corrosion resistance. Also, minor and trace elements may be used as analytical ‘‘fingerprints’’ where the presence of a particular set of elements is considered as an indicator of a process or a location so that an accurate identification procedure is vital if such fingerprints are to give a robust result.

Experimental Details

Test materials were selected that were either pure elements or stoichiometric compounds or that contained known constituents present at minor and trace levels. Material sources included NIST standard reference materials, reference materials and internal research materials such as the NIST microanalysis glasses (Table I). In addition, reagent-grade chemical compounds obtained from commercial sources were utilized.

All X-ray spectrometric measurements were performed with an incident beam energy selected in the range 10–25 keV so as to provide efficient excitation of the photon energy range up to 12 keV depending on the particular problem. EDS spectra were recorded with conventional Si(Li) detectors as well as the silicon drift detector (SDD). The commercial EDS software systems were calibrated for photon energy following suggested procedures, e.g. using as reference peaks the pairs Cu L–Cu Kα or Al K–Cu Kα, or for some systems the Cu Kα peak only with the zero-strobe peak. The amplifier time constant (variously referred to as "peaking time," "shaping time," etc.) was selected to provide "best resolution" performance, generally 135 eV (full width at half peak maximum intensity (FWHM)) measured at Mn Kα or better. The input count rate was selected so that system deadtime was generally less than 30% to minimize the effects of pulse pileup and peak distortion. For most examples, test materials were selected to yield X-ray spectra with well-separated peaks that did not suffer significant interference from the major constituents of the specimen.

When peak fitting or quantitative analytical calculations were required, the NIST software engines Desktop Spectrum Analyzer (DTSA: Fiori *et al*. 1991) AQ3 and DTSA-II (Ritchie 2008) were employed. AQ4

TABLE I Composition of microanalysis Glasses K456 and K493 (mass fraction)

	K456 (matrix)	K493 (matrix+traces)
B		0.00044
O	0.204	0.206
Al		0.00106
Si	0.134	0.130
Ti		0.00192
Fe		0.00224
Zr		0.00363
Ce		0.00554
Ta		0.00721
Pb	0.661	0.641

Results: Examples of Mistakes Observed in Automatic Peak Identification of Minor and Trace Constituents

"Problem Elements" at Low Concentrations

Based upon previous experience (Newbury 2005a, 2007), AQ5 Table II contains an extensive, but not necessarily complete, list of observed and suspected "problem regions" with specific peak interpretation challenges for photon energies < 5 keV. A "problem region" is a spectral region where two or more elements produce primary characteristic peaks sufficiently close in energy, which both might be possible solutions to an unknown peak detected by an automatic peak-finding algorithm in this region. In compiling this list, only the principal peak in each possible family is considered. If the database of all possible X-ray peaks is included in constructing such a table so that a minor member of an X-ray family may be considered as a possible solution in competition with a major member of a second X-ray family, then the list of possibilities will greatly expand. Such a situation has been discarded in constructing Table II on the assumption that if an element is represented in a spectral region of interest only by a minor family member, then it is reasonable to assume that the principal peak for that element will be discovered first in the energy region where it occurs. As the identification process operates for that element, all related minor family members should be properly marked and thus removed from further consideration in the region of interest. However, it must be noted that mistakes of this type were encountered in the previous studies where such meticulous bookkeeping of X-ray peak families was not rigorously performed (Newbury 2005a, 2007).

Many problem elements reported in Table II have been directly observed to produce blunders during automatic peak identification of *major* constituents. It is therefore not surprising that the identification problem is exacerbated when such an element is lowered in concentration to the minor and trace constituent levels so that the peak intensity and the peak-to-background are reduced. Figure 1 shows an example of the misidentification of Br L as Al K in an experimental polymer mixture (30% polystyrene and 70% polymethylmethacrylate) treated with decabromyldiphenyl ether as a fire retardant. Bromine is present in the bulk at a mass fraction of 0.023 and is thus a minor constituent. A second example is shown in Figure 2, where the Zr L peak is misidentified as Pt M in a glass where the Zr is present at a mass fraction of 0.074, also a minor constituent level.

TABLE II “Problem regions” for automatic peak identification, photon energies from 200 eV to 5 keV

Below 1 keV	
0.390–0.395 keV	N K (0.392); Sc Lα (0.395)
0.510–0.525 keV	O K (0.523); V Lα (0.511)
0.670–0.710 keV	F K (0.677); Mn Lα (0.636); Fe Lα (0.705)
0.845–0.855 keV	Ne Kα (0.848); Ni Lα (0.851)
0.900–0.950 keV	Cu Lα (0.928); Pr Mα (0.929)
1–2 keV	
1.00–1.05 keV	Na Kα (1.041); Zn Lα (1.012)Pm Mα (1.032)
1.20–1.30 keV	Mg Kα (1.253); As Lα (1.282)Tb Mα (1.246)
1.45–1.55 keV	Al Kα (1.487); Br Lα (1.480)Yb Mα (1.521)
1.69–1.80 keV	Si Kα (1.740); Rb Lα (1.694); Sr Lα (1.806); Ta Mα (1.709)W Mα (1.774)
2–3 keV	
2.00–2.05 keV	P Kα (2.013); Zr Lα (2.042)Pt Mα (2.048)
2.10–2.20 keV	Nb Lα (2.166)Au Mα (2.120); Hg Mα (2.191)
2.28–2.35 keV	S Kα (2.307); Mo Lα (2.293)Pb Mα 2.342)
2.40–2.45 keV	Tc Lα (2.424)Bi Mα (2.419)
2.60–2.70 keV	Cl Kα (2.621); Rh Lα (2.696)
2.95–3.00 keV	Ar Kα (2.956); Ag Lα (2.983)Th Mα (2.996)
3–4 keV	
3.10–3.20 keV	Cd Lα (3.132); U $M\alpha_1$ (3.170)
3.25–3.35 keV	K Kα (3.312); In Lα (3.285)U Mβ (3.336)
3.60–3.76 keV	Ca Kα (3.691); Sb Lα (3.605); Te Lα (3.769)
4–5 keV	
4.05–4.15 keV	Sc Kα (4.090); Xe Lα (4.111)
4.45–4.55 keV	Ti Kα (4.510); Ba Lα (4.467)
4.84–4.95 keV	Ti Kβ (4.931); V Kα (4.952); Ce Lα (4.840); Pr Lα (5.034)

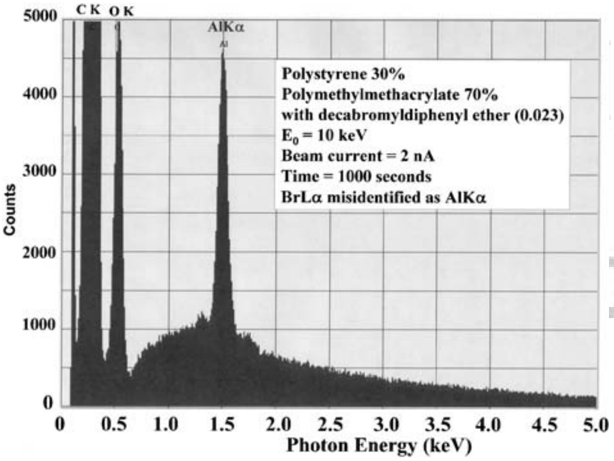

Fig 1. EDS spectrum of an experimental polymer mixture (30% polystyrene and 70% polymethylmethacrylate) treated with decabromyldiphenyl ether as a fire retardant. (Specimen courtesy of Takashi Kashiwagi, Building and Fire Research Laboratory, NIST.). The Br L family peak, where Br is present at a mass fraction of 0.023, is misidentified as Al Kα.

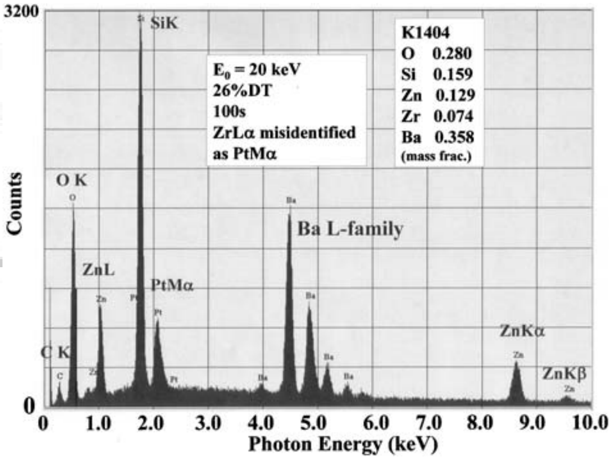

Fig 2. EDS spectrum of NIST Microanalysis Glass K1404, showing the misidentification of the Zr L peak family, where Zr is present at 0.074 mass fraction, as Pt Mα.

Misidentification of Minor Family Members

The complex X-ray families produced from the L- and M-shells include one or more peaks that occur at relatively low intensity compared with the principal peaks of the family, but with sufficient separation from the principal peaks to be well resolved with EDS, e.g. Ll, Lγ, Mζ, Mγ and M_2N_4. If the automatic peak identification program does not use a complete database of X-ray peaks that includes these minor family members, then it is possible that these minor peaks will be assigned to a different and incorrect element. An example is shown in Figure 3 for a gold–copper alloy (NIST Standard Reference Material 482 Gold–Copper Wires for Microanalysis; Au40–Cu60), where the automatic peak identification procedure has properly identified the Cu Kα, Cu Kβ, Cu L, Au Lα and Au Mαβ peaks, but the minor family member

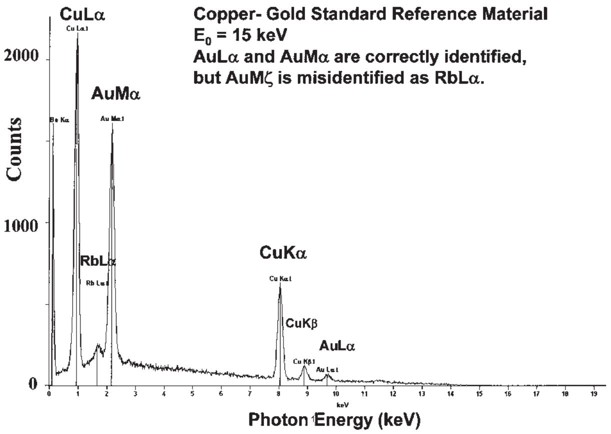

Fig 3. EDS spectrum of NIST Standard Reference Material 482 Gold–Copper Wires for Microanalysis Au40–Cu60 showing the misidentification of the Au Mζ peak as Rb Lα.

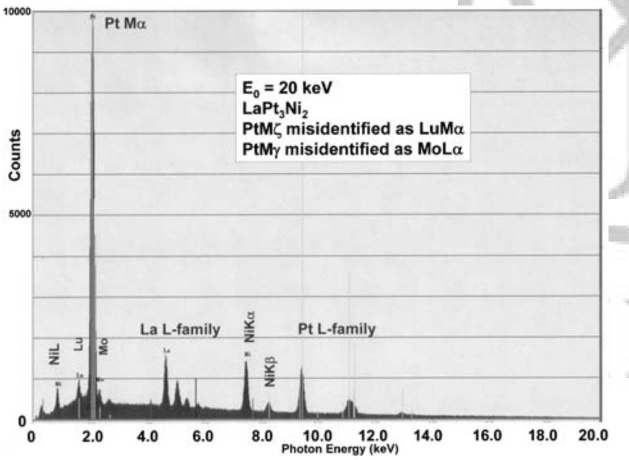

Fig 4. EDS spectrum of $LaPt_3Ni_2$ showing the misidentification of Pt Mζ as Lu Mα and Pt Mγ as Mo Lα.

Au Mζ is misidentified as Rb Lα. Similar misidentifications of the minor family members of the Pt M family are seen for the spectrum of the intermetallic compound $LaPt_3Ni_2$ in Figure 4, where Pt Mζ is misidentified as Lu Lα and Pt Mγ is misidentified as Mo Lα.

Misidentification of Major Peak Artifacts: Escape Peak and Coincidence Peak(s)

High-intensity peaks in the EDS spectrum are accompanied by two classes of artifact peaks: silicon escape peaks (of energy equal to the principal peak energy—1.74 keV, resulting from the loss of an Si Kαβ peak during the photon energy-to-charge conversion process) and coincidence peaks (e.g. A+A, when two A photons enter the active volume of the detector in a time shorter than the time resolution of the pulse pileup inspection circuit; if there are two large peaks A and B, then A+B will also be observed). Unless the automatic peak identification procedure includes the appropriate escape peak and coincidence peak energies in its database for each element and considers the possible set of coincidence peaks, these peaks of low relative intensity are likely to be misidentified as minor or trace element peaks.

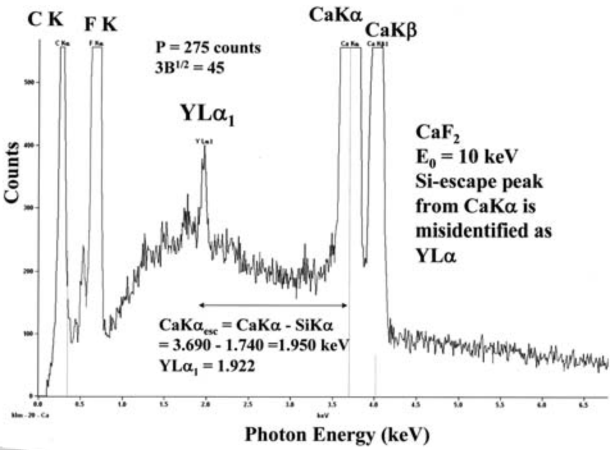

Fig 5. Si(Li) EDS spectrum of CaF_2 showing misidentification of the Ca Kα escape peak as Y Lα.

An example of the misidentification of the Si escape peak is shown in Figure 5, where the escape peak from Ca Kα (3.690−1.740 = 1.950 keV) in CaF_2 is incorrectly interpreted to be Y Lα (1.922 keV). The escape peak is a fixed fraction of the parent peak, with the fraction decreasing as the energy of the parent peak increases. For this particular case in which the Ca Kα escape peak is misidentified as Y Lα, the equivalent yttrium *k*-value (peak count rate from the unknown/pure element peak count rate) is 0.0049. When this Y *k*-value is evaluated with a ZAF-matrix correction (atomic number–absorption–fluorescence effects) quantification procedure, an apparent Y mass fraction of 0.0090 in the host CaF_2 would be determined.

Figure 6 shows the misidentification of a coincidence peak from Al Kα (1.487+1.487 = 2.974 keV) as Ag Lα (2.984 keV). The occurrence and the relative abundance of coincidence peaks depend on the rate of arrival of photons into the detector. This rate can be controlled by operating at low system deadtime through the choice of the beam current and/or the EDS solid angle. For deadtime <10%, coincidence peaks are generally of negligible intensity. However, for parent peak energies below approximately 2 keV, the charge pulse associated with the parent peak photon is close to the noise limit of the pulse inspection function reducing its efficiency so that a small coincidence peak is still likely to be present, as shown in Figure 6.

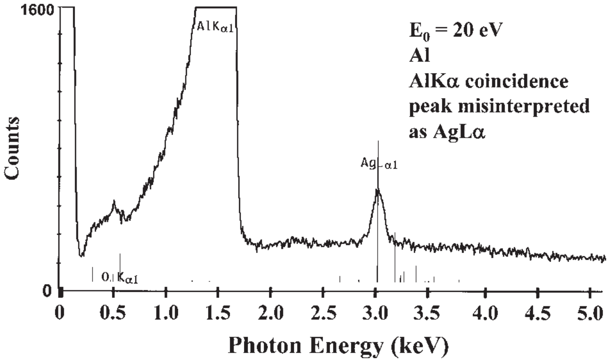

Fig 6. Si(Li) EDS spectrum of high-purity aluminum showing the Al Kα sum peak misidentified as Ag Lα.

Moreover, choosing a low deadtime conflicts with the legitimate need to maximize the number of counts that can be obtained in the measured spectrum within the time constraints imposed on the analysis and thus improve detectability. When minor and trace constituents are of interest, a more typical strategy would be to work at a higher deadtime, e.g. 30–40%, to record a much greater number of photons per unit of clock time and to accept the inevitable occurrence of coincidence peaks by having a protocol in place to detect and recognize these peaks as artifacts. (See further discussion below.) For the particular case illustrated in Figure 6 involving a deadtime of approximately 20%, the misidentification of the Al Kα coincidence as Ag Lα would result in a *k*-value of 0.0054 and, after matrix corrections, an apparent Ag mass fraction of 0.0077 in the host Al.

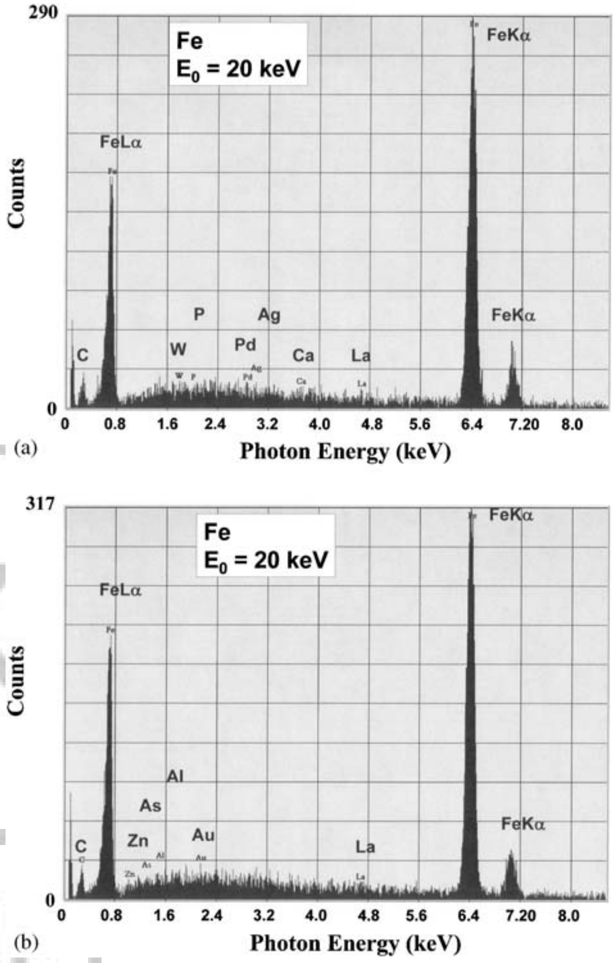

Fig 7. (a) Si(Li) EDS spectrum of high-purity iron with numerous trace constituent peaks identified. Note the maximum channel intensity of only 290 counts. (b) Spectrum taken from the same area after the maximum channel intensity is increased to 317 counts. Note that most of the "trace" element solution has changed.

False Peaks

The automatic peak identification process involves first applying a "peak-finding algorithm" to the spectrum. This process is sensitive to noise in the X-ray continuum that forms the spectral background because random groupings of background counts can mimic a characteristic peak. It is common practice to set a user-defined statistical threshold to define what constitutes a significant peak above this random variation in the background. If this threshold is not invoked or is set too low (that is, too sensitive to the noise), then the effect shown in Figure 7 may be encountered. In this spectrum of high-purity iron with a thin (~7 nm) carbon coating in Figure 7(a), there are four valid peaks: Fe Kα, Fe Kβ, Fe Lα and C K with a maximum channel count of 290. However, six additional peaks for W M, P K, Pd L, Ag L, Ca Kα and La L at apparent trace levels are also labeled. These false peaks arise from random variations in the counting statistics of the background. When this spectrum accumulation is continued a few seconds longer so that the maximum channel count rises to 317 in Figure 7(b), the apparent trace element solution is substantially altered: only La L remains from the original set of six trace elements, but now Zn L, As L, Al K and Au M are reported. If this spectrum accumulation is continued for a substantially longer time to a maximum channel count of 1,000, then all of these apparent trace element peaks, W M, P K, Pd L, Ag L, Ca Kα, La L, Zn L, As L, Al K and Au M, will be rejected by the peak identification algorithm. However, with this particular automatic peak identification system, false peaks will be found in virtually all low count spectra. The analyst should be especially wary of an unstable trace peak solution that changes with the accumulation time (see continued discussion below).

Discussion

In the original study of mistakes in the automatic peak identification of major constituents, it was estimated that 3–5% of peak identifications were wrong when sample compositions were broadly drawn from the elements of the periodic table accessible to SEM/EDS analysis, that is, $Z \geq 4$ (beryllium). These mistaken peak identifications are not random. When a particular automatic peak identification tool is found to fail on a given element present as a major constituent, it will typically fail consistently on that element no matter how many counts are accumulated in the spectrum. At the minor constituent level, the rate of such systematic mistakes increases. However, as illustrated in Figure 7, at the trace level all of the peak identifications may sometimes be incorrect, but if the analyst takes care to record a sufficiently high spectral count, many and perhaps all of the false trace-level peaks will eventually disappear from the automatic peak identification solution.

Considering the range of problems revealed in the examples above, it is perhaps not surprising that some commercial EDS automatic peak identification systems are designed to avoid attempting to identify peaks belonging to legitimate trace constituents, as well as the lower end of the minor constituent concentration range. That is, the user-selected statistical threshold parameter cannot be made sensitive enough to actually force the identification of low-relative-intensity peaks that might belong to trace-level constituents. Although this conservative approach will at least avoid the extensive mistakes seen in Figure 7, such a software tool does not aid the analyst who is actually in need of correct detection and identification of trace constituent peaks.

As the minor/trace element identification problem is effectively left as an exercise for the analyst, it is useful to have an appropriate analytical strategy that makes use of the spectrum-processing software tools typically available in the commercial computer-assisted analysis software.

A suitable procedure to achieve robust minor/trace constituent peak identification consists of two stages: (1) collecting spectra that are statistically adequate for trace-level work and (2) systematically interpreting the peaks from major constituents and removing all spectral features associated with these major constituents before attempting the possible trace constituents.

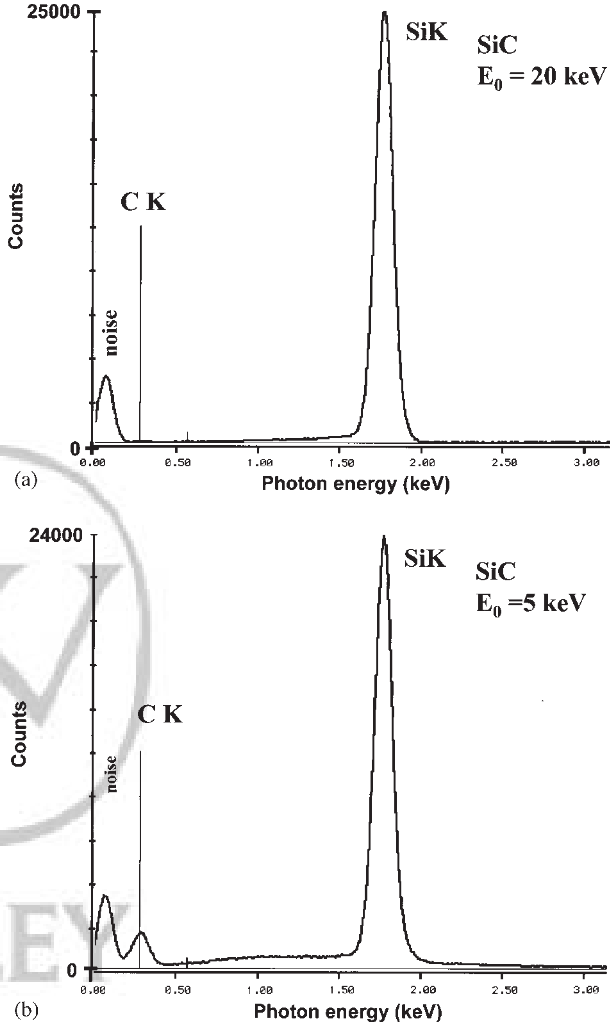

Fig 8. (a) (Top) Si(Li) EDS spectrum of SiC, $E_0 = 20$ keV. Note that with the Si K peak channel determining the vertical expansion, the C K peak is not visible. (b) (Bottom) Si(Li) EDS spectrum of SiC at $E_0 = 5$ keV. The C K peak is now recognizable with the same vertical scale that contains the full Si Ka peak.

Acquisition Conditions for Adequate Spectra

Beam energy: A beam energy $E_0 = 20$ keV should be selected to begin the analysis as this incident energy will provide adequate overvoltage to excite peaks from major constituents to a photon energy of at least 12 keV. Such a beam energy provides at least one family of X-rays for all elements with $Z \geq 4$ (beryllium), and increases the likelihood that more than one family of X-rays will be excited for elements with $Z \geq 22$ (titanium). However, it must be recognized that a second spectrum of the same region of the specimen should be measured with a low beam energy, $E_0 = 5$ keV, to ensure that low-photon-energy elements in the range from 0.1 to 1 keV are not lost owing to specimen self-absorption. This possibility is illustrated in Figure 8(a) for silicon carbide where at $E_0 = 20$ keV the C K peak can be easily overlooked owing to the strong absorption resulting from the Si L_{III} absorption edge, which lies just below the C K peak energy, despite the presence of carbon in SiC at 0.50 atomic fraction = 0.30 mass fraction. At $E_0 = 5$ keV in Figure 8(b), the C K peak is much more evident owing to the substantial reduction in the primary electron range, which results in lower self-absorption by the specimen.

EDS resolution: To achieve the best possible limits of detection, choose an amplifier time constant that gives the best resolution. (*Note*: The analyst should be aware of the resolution vs. time constant performance of the EDS.) Resolution improves as the time constant is increased, but the throughput decreases. The analyst should not automatically choose the longest amplifier time constant available. The resolution may not significantly deteriorate with a choice of time constant that is a factor of two shorter, but an improvement in the output count rate of a factor of two will be obtained.

Deadtime: Choose dose conditions (beam current and EDS solid angle) to maintain a deadtime of not greater than approximately 30%, but recognize that the most highly excited peaks are likely to produce coincidence peaks. If the analyst is careful to account for these coincidence artifact peaks, then the increase in counts obtained by operating at a higher deadtime is worth the possible coincidence penalty.

Count time: Virtually every aspect of X-ray microanalysis improves as the number of counts in the spectrum increases, and robust identification of minor and trace peaks demands high numbers of counts. The number of counts P needed to detect the major peak of a particular element above the bremsstrahlung background can be estimated as

$$P > 3B^{1/2} \tag{1}$$

where B is the number of background counts in the peak window (typically selected as 1.5 FWHM). Consider a particular example of detecting trace iron in a silicon–lead–oxygen glass. NIST Microanalysis Glass K456 provides this matrix, whereas K493 provides the same matrix with several additional elements (Al, Ti, Ce, Fe) present at trace levels, as listed in Table I. Together, these materials enable examination of the spectrum with and without trace elements present. Table III contains the total spectrum integral (0.1–20 keV, including all peaks) for a silicon–lead–oxygen glass, the number of background counts in the window for Fe Kα (6.284–6.516 keV), and the calculated concentration limit of detection for Fe from Equation (1), based upon the measured Fe Kα intensity from a pure element standard. To detect Fe at a mass fraction of 0.002, Equation (1) predicts that a total spectrum count of approximately 290,000 counts is needed. Figure 9(a) shows the spectrum of K493 containing this total integral, but the trace Fe peak is difficult to detect by visual inspection. Increasing the dose to yield total spectrum integrals of 700,000 and 1,450,000 counts, illustrated in Figures 9(b) and (c), suggests that for detection of trace peaks by visual inspection, the statistical criterion given by Equation (1) must be exceeded by at least a factor of two, and preferably five.

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Locating and Interpreting the Minor and Trace Peaks

With adequate counting statistics achieved, the analyst should make use of the automatic peak identification solution of the major peaks to provide a starting point. Each peak identification should be considered only as a suggestion, and the analyst should follow a systematic approach to confirm the peak assignment:

(a) Choose a labeled high-intensity peak with photon energy > 5 keV.
(b) For a Kα identification, confirm the presence of the corresponding Kβ peak. Then, locate the corresponding low-photon-energy L-shell peak(s).
(c) Similarly, for a high-photon-energy Lα identification, confirm the presence of the full suite of L family lines: Lβ, Lγ, Ll, etc. Then, locate the low-photon-energy M-shell peak(s). After the tentative peak identification is confirmed or an alternative is chosen, check for the escape peak and sum peak(s) (which may involve

TABLE III NIST microanalysis Glass K456 (Si–Pb–O); $E_0 = 20$ keV

Dose (nA s)	Total integral (0.1–20 keV)	Integral Fe Kα window (6.284–6.516 keV)	Limit of detection (mass fraction)
10	145,127	1,160	0.00280
20	290,373	2,329	0.00193
50	728,155	5,820	0.00122
100	1,454,542	11,613	0.000862
200	2,907,573	23,633	0.000615
500	7,269,268	58,705	0.000388
1,000	14,534,623	118,222	0.000275
2,000	29,065,175	235,441	0.000194

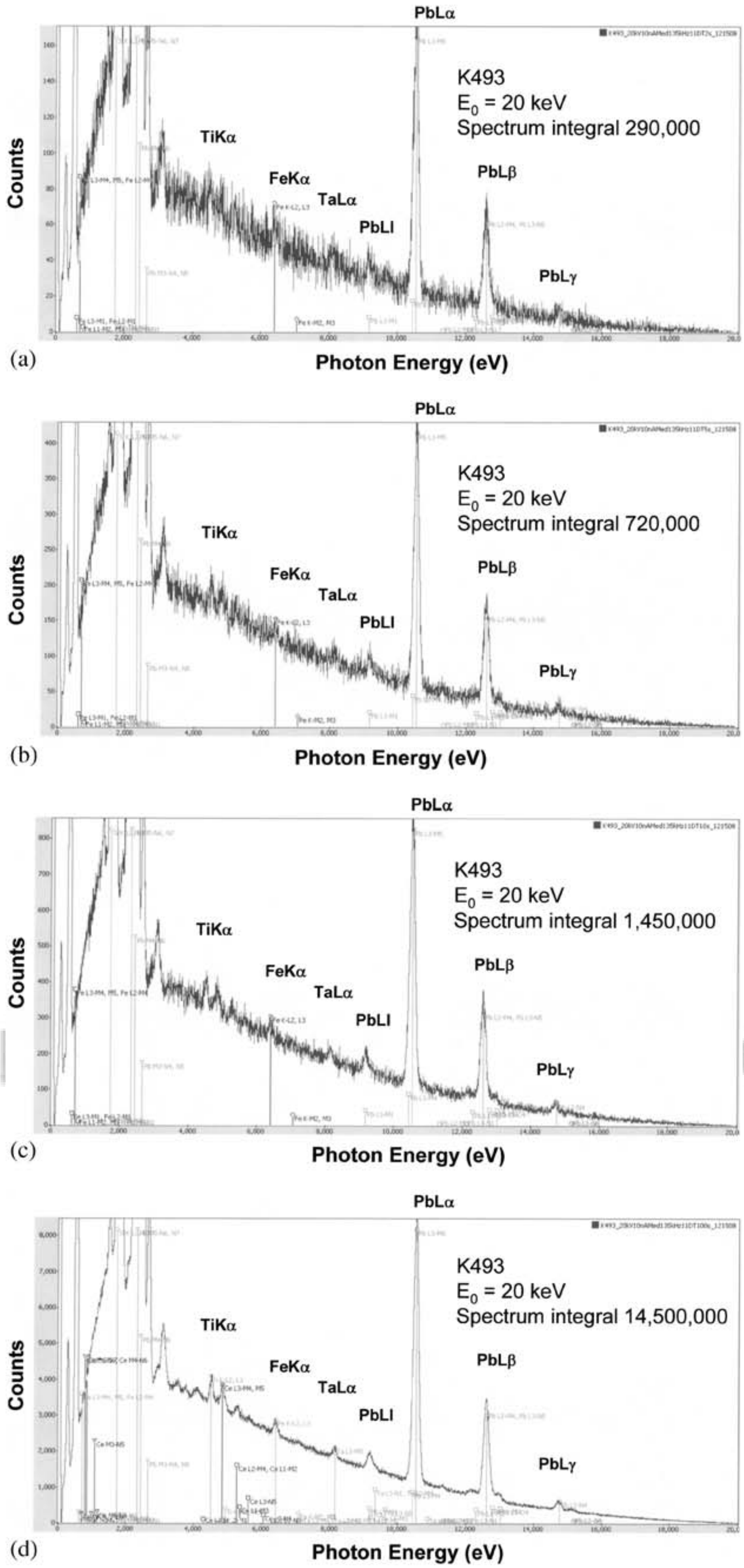

Fig 9. (a) SDD EDS spectrum of NIST Microanalysis Glass K493 with a total spectrum integral (0.1–20 keV) of 290,000 counts. (b) Dose increased to 720,000 counts. (c) Dose increased to 1,450,000 counts. (d) Dose increased to 14,500,000 counts.

combinations of different high-intensity peaks) associated with the highest-intensity member of the family.

(d) Strip all peaks from each family associated with this element from the spectrum with the multiple linear least-squares (MLLS) peak fitting tool commonly available in computer-aided analysis software. Be sure that the MLLS procedure uses a full peak reference that contains all family members, preferably from a spectrum measured on the EDS system being used for the analysis rather than a remote library spectrum (check by stripping peaks from a pure element standard to be sure all minor family members are properly accounted for).

(e) Proceed down in photon energy to the low-energy region of the spectrum, recognizing that the decreased separation of the family members and the relatively poor resolution of EDS mean that eventually only one peak will be available for identification. The analyst must make use of every feature available, such as the asymmetry of the L and M family peaks owing to the relative heights and separations of the Lα–Lβ and Mα–Mβ peak pairs. Again the quality of the fit when the MLLS peak stripping is applied is the measure by which the automatic peak ID solution is to be judged, such as the Al K–Br L–Yb M recognition problem.

(f) This MLLS stripping process has been applied in Figure 10(a) to the spectrum of K493 (thick trace) showing the residuals (fine trace) after MLLS fitting and subtraction of the Si Kα,β Pb M and Pb L families. Note the series of peaks that arise from coincidence of the O K, Si K and Pb M, which are found in both the matrix and the matrix+trace elements spectra. After all the peaks associated with the major constituents have been identified and stripped from the spectrum, the peaks remaining are likely to belong to legitimate minor and trace elements. Again starting at the high-photon-energy end of the spectrum, use the KLM markers to select a candidate element for a peak. As can be seen in Figure 10, even with extremely large numbers of counts (14,500,000 in this case), only a single K-shell peak is likely to be detected when identifying trace elements for photon energies <8 keV. Above 3 keV, two L-shell peaks (Lα and Lβ1 in a ratio of 1 to 0.25 to a ratio of 1 to 0.45 depending on the element) may be found because of their increasing separation and relatively similar weights. Figure 10(b) shows the residuals after MLLS stripping of both K456 (matrix) and K493 (matrix plus trace elements). Note the appearance of the coincidence peaks in both spectra. The trace elements Ti, Ce, Fe and Ta can be identified without peak stripping. However, identifying the Al peak requires peak stripping to be sure that all minor family members of Pb have been removed, whereas the Zr L can only be revealed by stripping off the major interference from Pb M.

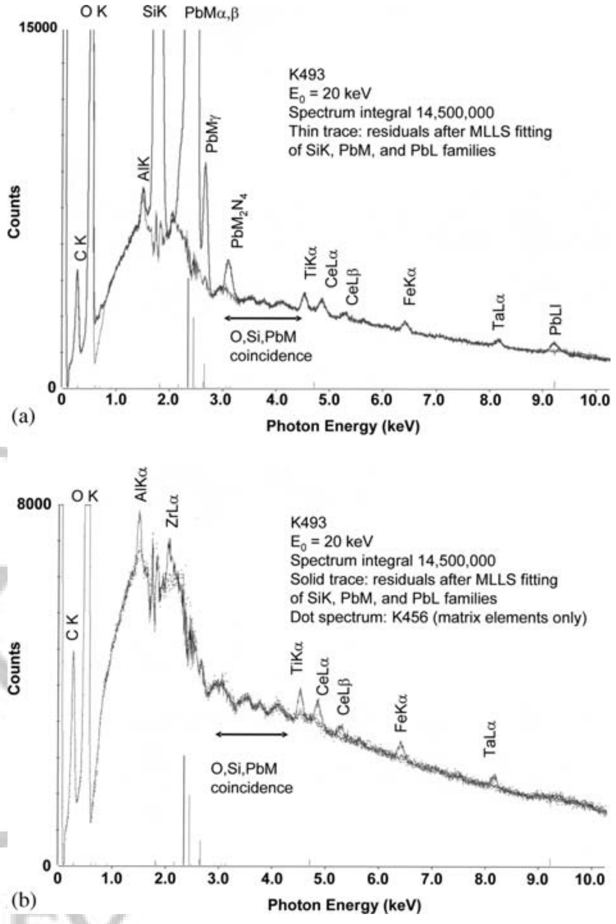

Fig 10. (a) SDD EDS spectrum of NIST Microanalysis Glass K493 (thick trace) with a total spectrum integral (0.1–20 keV) of 14,500,000 counts and after MLLS peak stripping of the Si K, Pb M and Pb L families (thin trace). (b) Overlay of K456 (dot spectrum) and K493 (solid line) after MLLS fitting.

From the sequence of spectra in Figure 9, the issue of recording adequate spectrum counts before attempting to perform trace element analysis is seen to be of critical importance. Obtaining a total spectrum integral of 200,000 counts with a conventional Si(Li) EDS, spectrometer technology that still dominates the microanalysis field, operating at or at least near optimum resolution with modest deadtime represents a considerable task. With a throughput of approximately 1 kHz to constrain the deadtime, a live time of 200 s would be required, and if the five-fold criterion is applied, the time required expands to 1,500 s to obtain 1,500,000 counts. Judging by the appearance of EDS spectra reported in the literature, many analysts seem to collect spectra for far less time. The emergence of the SDD EDS, which for a given resolution has an output count rate improved by a factor of 10–100 compared with the Si(Li), represents a great improvement for trace element analysis because the required spectrum integral can be obtained in time periods more consistent with the patience of analysts (Newbury 2005b).

Finally, when applying EDS to the identification of trace elements in the mass fraction range 0.001–0.01, there is inevitably a lack of redundancy of information compared with the situation that is routinely obtained during the identification of major constituents (i.e. finding multiple members within a family and often two families; having peak shape as a guide for the single peak regime below 3 keV photon energy), which means that the confidence with which a trace element can be reported is inevitably going to be lower. When it is critical to report the presence of a trace element with the best possible confidence, these inevitable limitations imposed upon EDS because of the poor resolution may force the analyst to make use of wavelength dispersive X-ray spectrometry (WDS), which is generally capable of spectral resolution that is better by a factor of ten or more (2–15 eV) than the EDS resolution. Such a resolution improvement leads to better peak-to-background, more accurate knowledge of the peak channel energy, and detection of more family members, all of which contribute to a much improved degree of confidence in trace element identification.

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