

Misidentification of Major Constituents by Automatic Qualitative Energy Dispersive X-ray Microanalysis: A Problem that Threatens the Credibility of the Analytical Community

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Abstract: Automatic qualitative analysis for peak identification is a standard feature of virtually all modern computer-aided analysis software for energy dispersive X-ray spectrometry with electron excitation. Testing of recently installed systems from four different manufacturers has revealed the occasional occurrence of misidentification of peaks of major constituents whose concentrations exceeded 0.1 mass fraction (10 wt%). Test materials where peak identification failures were observed included ZnS, KBr, FeS₂, tantalum-niobium alloy, NIST Standard Reference Material 482 (copper-gold alloy), Bi₂Te₃, uranium-rhodium alloys, platinum-chromium alloy, GaAs, and GaP. These misidentifications of major constituents were exacerbated when the incident beam energy was 10 keV or lower, which restricted or excluded the excitation of the high photon energy K- and L-shell X-rays where multiple peaks, for example, K α (K-L_{2,3})-K β (K-M_{2,3}); L α (L₃-M_{4,5})-L β (L₂-M₄)-L γ (L₂-N₄), are well resolved and amenable to identification with high confidence. These misidentifications are so severe as to properly qualify as blunders that present a serious challenge to the credibility of this critical analytical technique. Systematic testing of a peak identification system with a suite of diverse materials can reveal the specific elements and X-ray peaks where failures are likely to occur.

Key words: analytical electron microscopy, automated analysis, energy dispersive X-ray spectrometry, peak identification, qualitative analysis, scanning electron microscopy, transmission electron microscopy, X-ray microanalysis

INTRODUCTION

Energy dispersive X-ray spectrometry (EDS) performed in the scanning electron microscope (SEM) and the transmission electron microscope (TEM)/analytical electron microscope (AEM) has assumed a dominant role in the arsenal of microstructural characterization tools used across a wide range of the physical and biological sciences, engineering and technology, and forensic applications (Williams & Carter, 1996; Goldstein et al., 2003). Historically, manufacturers of EDS systems have been among the most aggressive developers of computer-based analysis systems to aid the EDS user in achieving meaningful results with a high degree of efficiency. Software systems provide active control over spectral acquisition to provide proper corrections for paralyzable deadtime, to minimize the effects of pulse coincidence, to monitor the amplifier gain that defines the energy axis calibration, and to maintain a quality measurement environ-

ment. Software tools are generally provided to perform peak identification (qualitative analysis) and to convert measured characteristic X-ray intensities into equivalent concentrations (quantitative analysis) either by standardization and matrix correction or by the “standardless” method (Goldstein et al., 2003). It is now becoming common practice for the software system to directly prepare a report, so that as the analyst selects locations for analysis on the specimen, the software automatically makes peak assignments to specific elements and interprets the measured peak intensities as concentrations that are presented with associated measurement statistics. The final, automatically prepared report of results is often divorced from the basic measurement, the EDS spectrum, which can only be recovered from the original archived data on the EDS host computer. This increasing tendency toward a comprehensive, fully automated EDS analytical procedure is perhaps inevitable given the extraordinary advances in computing power now available. However, one serious consequence of having such comprehensive software is the effect of divorcing the analyst from the details of the EDS measurement and interpretation process. For novice analysts, this trend results in a lack of challenge

to their knowledge and an increasing dependence on the software. Because the novice analyst is no longer required to manually “solve” a spectrum to identify the peaks, the critical knowledge base needed for manual qualitative analysis is not being acquired, which greatly reduces the likelihood that a novice or even a more “experienced” analyst who has trained in such an environment will recognize an incorrect peak identification made by automatic qualitative analysis. Moreover, there are users for whom SEM-EDS or AEM-EDS is just one of several or even many analytical tools that they must use in the course of their work. Such individuals often come to depend on the accuracy of a comprehensive computer-aided analysis system that produces finished reports that can be handed directly to a client.

What if such an automatic analytical system is occasionally utterly wrong in its identification of a major constituent (arbitrarily, concentration > 0.1 mass fraction or 10 wt%), even if the analytical system is being properly operated? Such a mistake when identifying a major constituent would be so egregious it would completely destroy the value of the analysis. It is a procedural failure so severe as to constitute a blunder (Bevington & Robinson, 1992; Taylor, 1997). Its subsequent impact on the utilization of the analytical results could be catastrophic, whether it is in the context of a research result that supports a new interpretation of nature or evidence presented in a court case. Do such blunders in the identification of major constituents actually occur in modern EDS analytical systems? To examine this possibility, several commercial EDS systems of recent manufacture were tested with a series of known binary materials where all elements were present as major constituents and the electron excitation was sufficient that the peaks used for identification were well above the continuum background.

MATERIALS AND METHODS

A series of specimens was subjected to the automatic qualitative analysis function of recent EDS analysis systems, each less than 2 years of age since installation, offered by four manufacturers. For obvious reasons, the manufacturers will not be identified.

For all specimens examined, the elements of interest were present as major constituents for which the concentration exceeded 0.1 mass fraction (all concentrations listed below are in mass fraction). Materials included reagent grade ZnS, KBr, FeS₂, Bi₂Te₃, GaAs, and GaP, NIST Standard Reference Material 482 (copper–gold alloys), and uranium–rhodium, platinum–chromium, and tantalum–niobium alloys. All of the materials were tested on all of the systems examined. Prior to testing each EDS system, the system calibration was performed using a pure copper target and using the manufacturer’s calibration software. Examination of the characteristic peaks for various K-shell elements

showed them to be in the correct channel positions. All test spectra were obtained under “best resolution” conditions (i.e., longest available time constant) and with a count rate such that the deadtime was kept below 25% to minimize possible peak distortions and coincidence artifacts. Sufficient counts were accumulated to provide at least 1000 counts (integrated) above background in the principal peak(s) that was misidentified. For many spectra tested, the misidentified peaks contained at least 10,000 counts (integrated). The misidentifications of major constituents were reproducible and did not disappear with additional accumulation of counts (with one very interesting exception described below). These blunders were not induced by improper operation of the software system.

RESULTS: MISTAKES ENCOUNTERED IN AUTOMATIC QUALITATIVE ANALYSIS

(Note that Figs. 1–12 are adapted directly from the screen display of commercial software systems. The original labels assigned by the automatic qualitative analysis software have been retained, but for easier visibility, larger labels have been added.)

The Siegbahn notation for characteristic X-rays is commonly used in the field of electron beam X-ray spectrometry for these peak labels and will be used in this article. The equivalent IUPAC notation is indicated in parentheses at the first use.)

Manufacturer 1

Figure 1a shows the results of automatic peak identification with the software of manufacturer 1 for a tantalum–niobium alloy (0.3 mass fraction Ta–0.7 mass fraction Nb) excited with an incident beam energy of $E_0 = 10$ keV. Although the NbL α (L₃–M_{4,5}) peak was properly identified, the TaM α (M₅–N_{6,7}) peak (1.710 keV) was misidentified as SiK α (K–L_{2,3}) (1.740 keV). When the beam energy was increased to $E_0 = 20$ keV (Fig. 1b), the Ta L-family was excited and properly identified, but despite this additional information, the incorrect identification of TaM α peak (1.710 keV) as SiK α (1.740 keV) was maintained, and no indication was provided in the labeled spectrum that TaM α had to exist at approximately the same photon energy location.

Figure 2a shows the results of automatic peak identification for zinc sulfide (0.671 Zn–0.329 S) with an incident beam energy of $E_0 = 10$ keV. Although the S K α peak was properly identified, the ZnL α peak was misidentified as NaK α . When the beam energy was increased to $E_0 = 20$ keV (Fig. 2b), the Zn K-family was excited and properly identified, but despite this additional information, the incorrect identification of the ZnL α peak (1.012 keV) as NaK α (1.041 keV) was maintained.

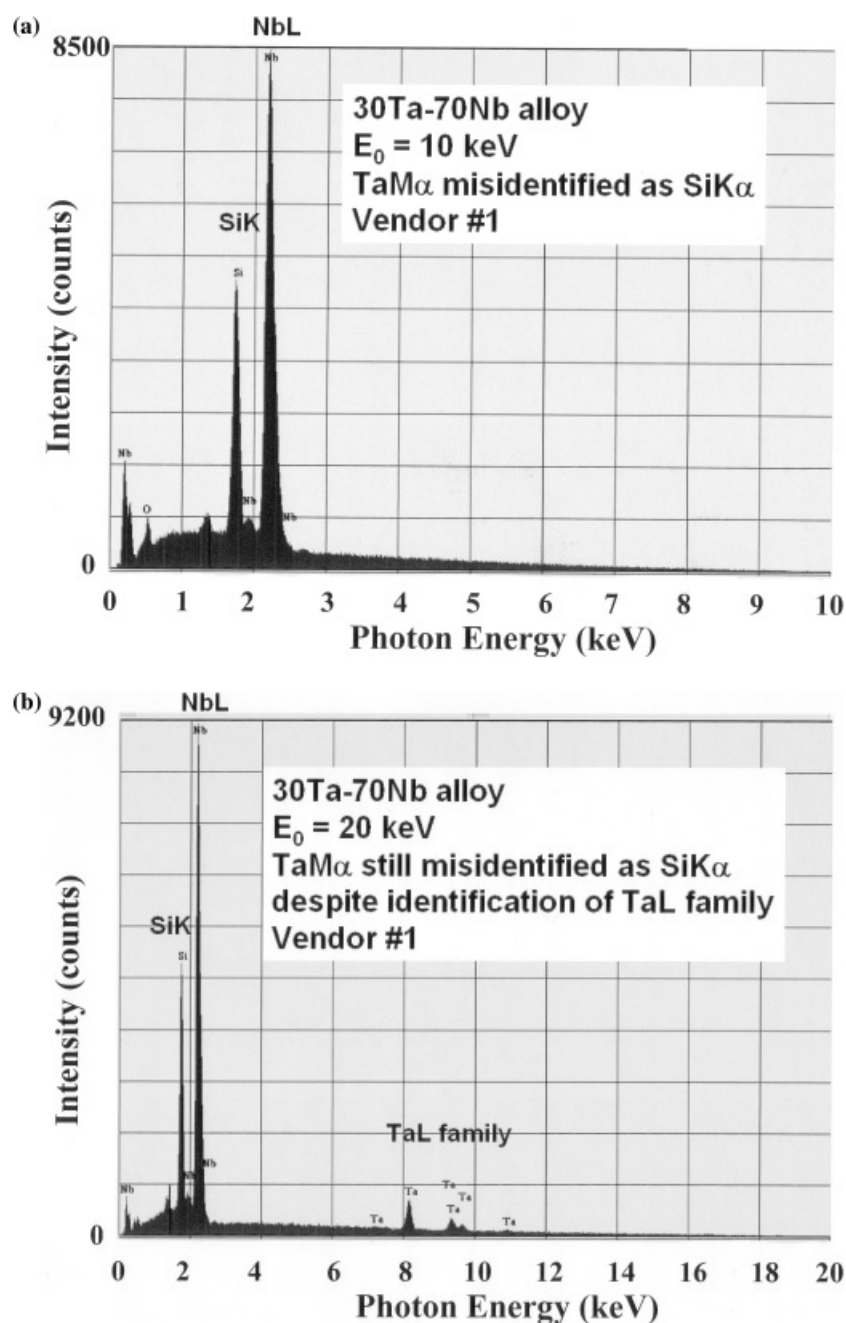


Figure 1. a: Automatic qualitative analysis peak identification of 30 Ta–70 Nb alloy ($E_0 = 10$ keV) performed with the commercial software system of vendor 1. NbL is correctly identified, but TaM is misidentified as SiK. **b:** Beam energy increased to 20 keV; TaL family is identified, but TaM is still misidentified as SiK. (Note that Figures 1–12 are adapted directly from the screen display of commercial software systems. The original labels assigned by the automatic qualitative analysis software have been retained, but for easier visibility, larger labels have been added.)

Continuing this pattern of favoring a K-shell identification when a possible peak interference exists, Figure 3a shows the results of automatic peak identification for potassium bromide (0.328 K–0.672 Br) with an incident beam energy of $E_0 = 10$ keV. Although the K $K\alpha$ and K $K\beta$ ($K-M_{2,3}$) peaks are properly identified, the BrL α peak was misidentified as AlK α , and the BrLl (L_3-M_1) peak was misidentified as AsL α . When the beam energy was increased to $E_0 = 20$ keV (Fig. 3b), the BrK α and BrK β peaks were excited and properly identified, but despite this additional

information, the incorrect identifications of the BrL α peak as AlK α and of the BrLl peak as AsL α were maintained.

Manufacturer 2

Figure 4a shows the results of automatic peak identification with the software of manufacturer 2 for potassium bromide (0.328 K–0.672 Br) with an incident beam energy of $E_0 = 20$ keV. Although the BrK and BrL peaks were properly identified, the K $K\alpha$ peak was misidentified as U M α , and

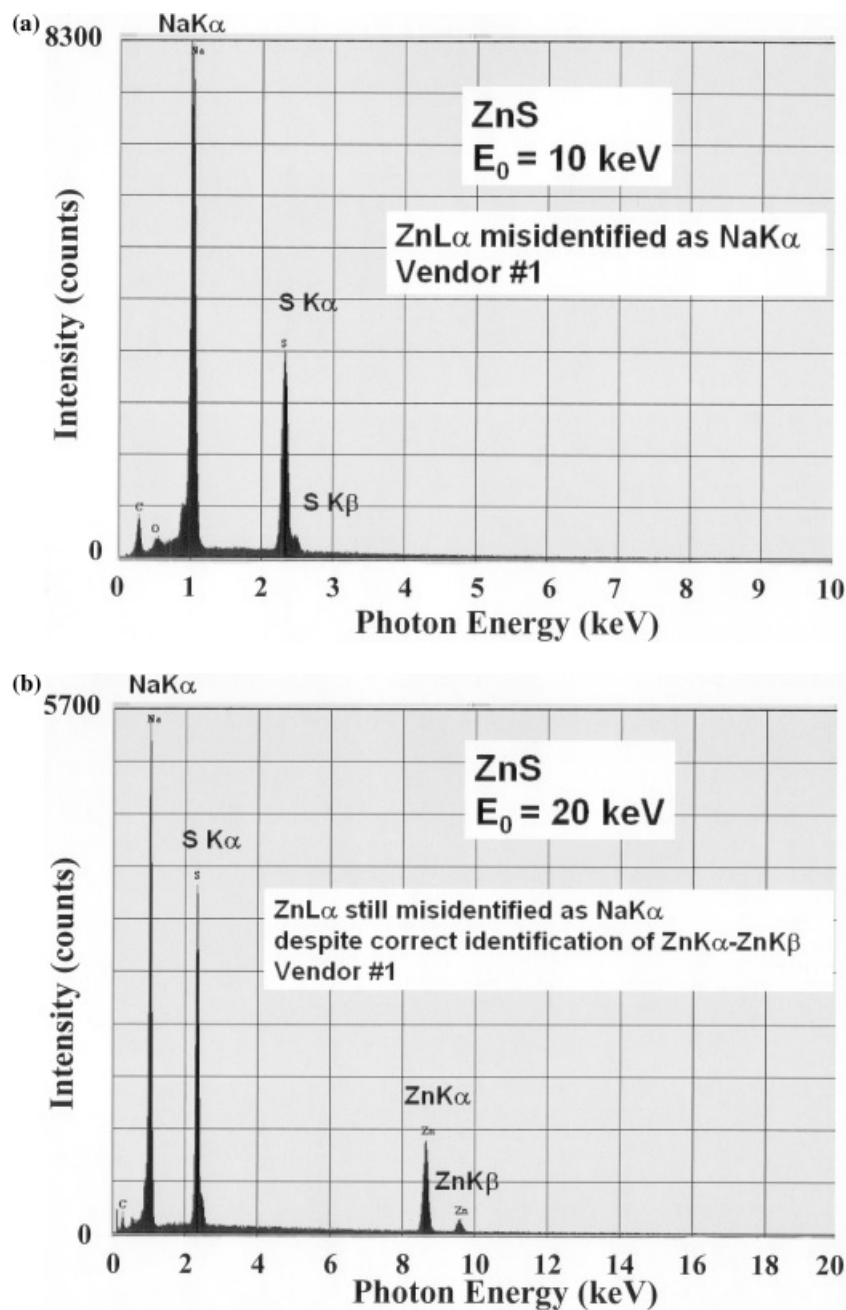


Figure 2. a: Automatic qualitative analysis peak identification of ZnS ($E_0 = 10$ keV) performed with the commercial software system of vendor 1. ZnL α is misidentified as NaK α . b: Beam energy increased to 20 keV; ZnK α and ZnK β are now identified, but ZnL α is still misidentified as NaK α .

the K $\text{K}\beta$ peak was misidentified as SbL α . When the beam energy was reduced to $E_0 = 10$ keV (Fig. 4b), the previously correct identification of BrL α was abandoned and replaced by a misidentification of the peak as YbM α .

Figure 5 shows the results of automatic peak identification for pyrite (FeS_2 , 0.466 Fe–0.534 S) excited with an incident beam energy of $E_0 = 20$ keV. The FeK α peak was correctly identified, but the S K α peak was misidentified as PbM α , despite the absence from the spectrum of the Pb L-family, which would be sufficiently excited with a 20-keV beam energy for detection if lead were actually present.

These examples suggest that manufacturer 2 favors M-shell peaks before L-shell and L-shell before K-shell

peaks, the reverse of the bias effectively shown by manufacturer 1.

Manufacturer 3

Figure 6 shows the results of automatic qualitative analysis with the software of manufacturer 3 for an NIST Standard Reference Material, SRM 482 (gold–copper alloys for microanalysis), using the 0.401 Au–0.599 Cu member, as excited with a beam energy of $E_0 = 10$ keV. In this peak identification, the CuK α –CuK β and the CuL peaks were properly identified, confirming the energy calibration, but the AuM α was incorrectly assigned as NbL α and the minor AuM ζ

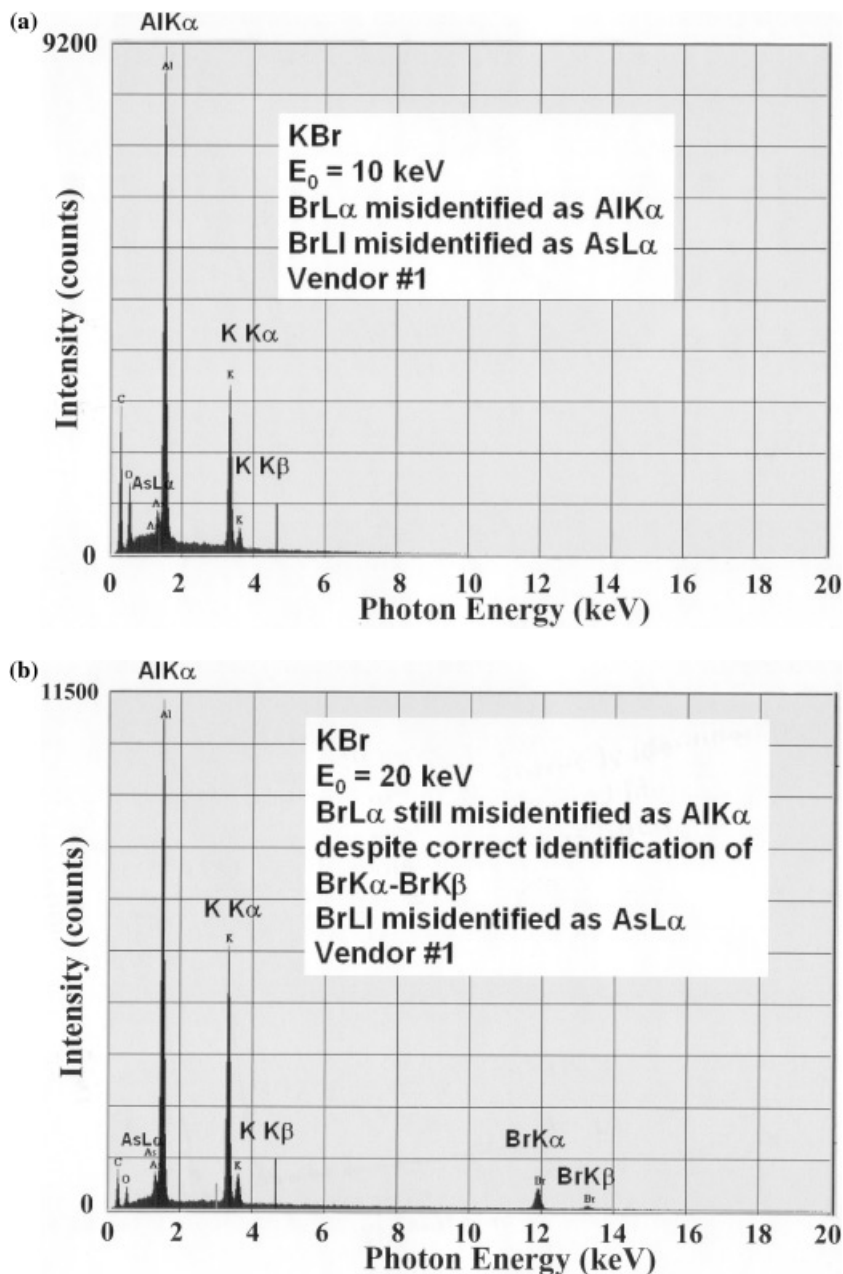


Figure 3. a: Automatic qualitative analysis peak identification of KBr ($E_0 = 10$ keV) performed with the commercial software system of vendor 1. BrL α is misidentified as AlK α and BrLI is misidentified as AsL α . **b:** Beam energy increased to 20 keV; BrK α and BrK β are now identified, but BrL α is misidentified as AlK α and BrLI is misidentified as AsL α .

(M_{4,5}-N_{2,3}) peak was misidentified as RbL α . The beam energy was then increased to $E_0 = 15$ keV, which was sufficient to excite the Au L_{III}-edge ($E_{LIII} = 11.919$ keV) but only with an overvoltage $U = E_0/E_c = 1.26$. With this low overvoltage, the counts in the AuL α peak were initially too low relative to the background so that the AuL α peak was below the noise threshold for the automatic qualitative analysis procedure. The peak identification solution was initially the same, as shown in Figure 7a, with the CuK α -CuK β and the CuL peaks properly identified, but with AuM α incorrectly assigned as NbL α . At this stage in the spectrum accumulation, the minor AuM ζ peak was below the peak detection criterion. However, as soon as the counts

in the AuL α peak relative to background exceeded the statistical criterion for detection by the automatic qualitative analysis procedure, the proper identification of the AuL α peak was made and this identification immediately resulted in a change in the assignment of the peak at 2.12 keV from the incorrect NbL α to the correct AuM α . The moment in the spectrum accumulation at which the AuL α peak identification occurred is captured in Figure 7b. Note that the level of the counts in the AuM peak bundle exceeded 1500 in the peak channel at this point where proper identification was finally achieved. Note also that despite the correct identification of AuM α finally being made, the now-detected AuM ζ peak was again misidentified as RbL α .

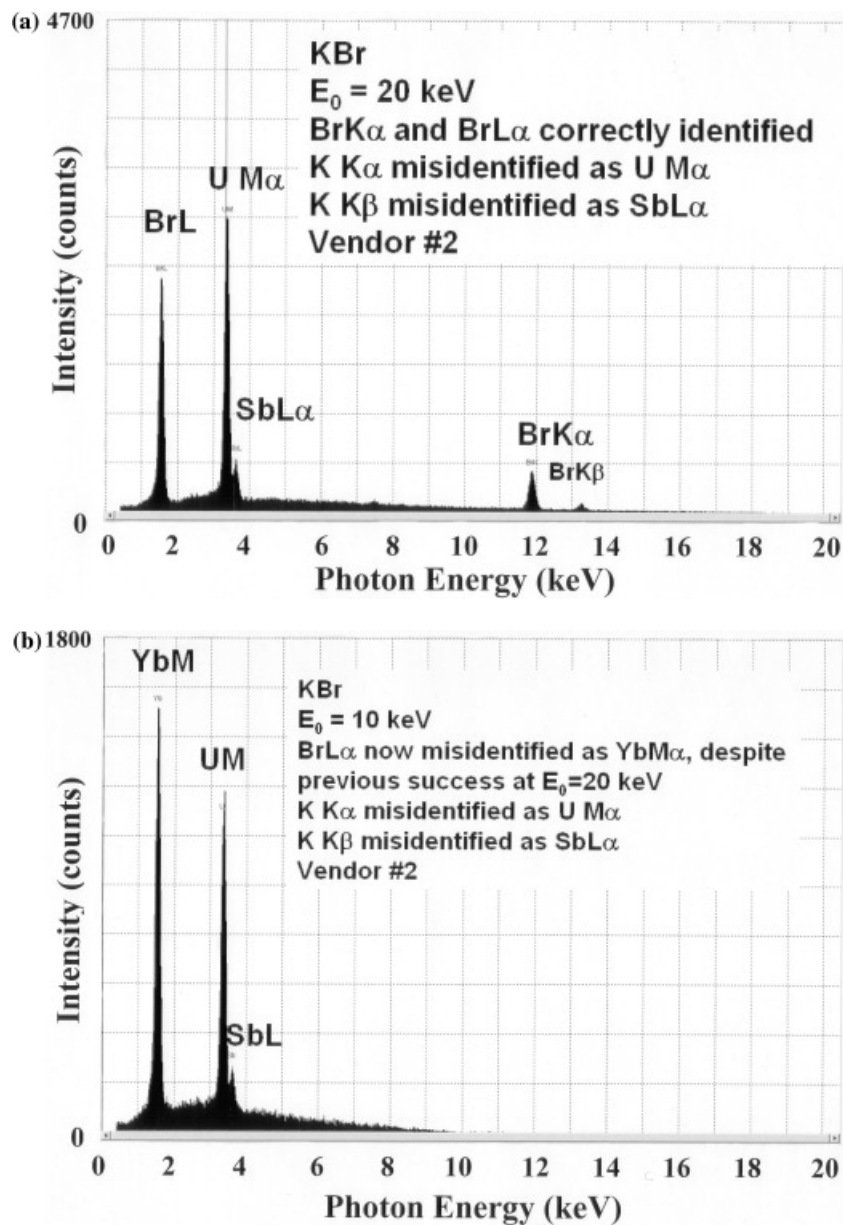


Figure 4. a: Automatic qualitative analysis peak identification of KBr ($E_0 = 20$ keV) performed with the commercial software system of vendor 2. BrK α , BrK β , and BrL α are all correctly identified, but K K α is misidentified as U M α and K K β is misidentified as SbL α . **b:** Beam energy decreased to 10 keV. Without BrK α and BrK β , BrL α is misidentified as YbM, K K α is misidentified as U M α and K K β is misidentified as SbL α .

Figure 8 shows the results of automatic qualitative analysis with the software of manufacturer 3 for bismuth telluride (Bi_2Te_3 ; 0.522 Bi–0.478 Te). The Te L-family peaks were properly identified, but the BiM α peak was misidentified as TcL α , and the BiM ζ peak was misidentified as YL α . (For the novice EDS user, it must be noted that technetium [Tc, $Z = 43$] is an artificial element with high radioactivity per unit mass that is highly unlikely to be encountered except in very special circumstances; promethium [Pm, $Z = 61$] is also an artificial radioactive element that is similarly unlikely.)

Figure 9 shows the results of automatic qualitative analysis with the software of manufacturer 3 for a uranium–rhodium alloy (0.80 U–0.20 Rh). The Rh L-family peaks

were properly identified, but the U M-family peaks were misidentified as CdL α for U M α , U M β as RhL γ_3 (L_1 – N_3), and U M γ (M_3 – N_5) as SbL α .

Manufacturer 4

Figure 10 shows the results of automatic qualitative analysis with the software of manufacturer 4 for zinc sulfide (0.671 Zn–0.329 S) with an incident beam energy of $E_0 = 10$ keV. Although the S K α peak was properly identified, the ZnL α peak was misidentified as NaK α and the ZnL β peak was misidentified as NeK α . When the beam energy was raised to $E_0 = 20$ keV to excite the Zn K-family (no figure), the

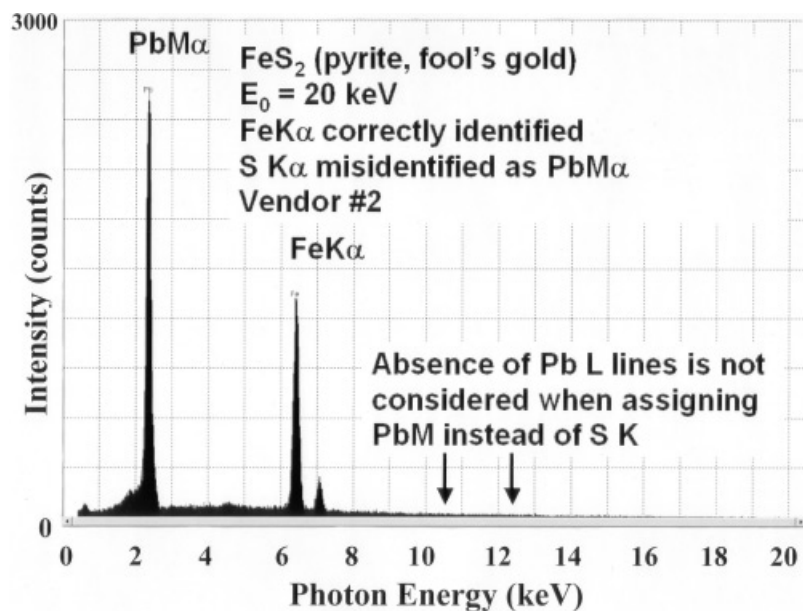


Figure 5. Automatic qualitative analysis peak identification of FeS₂, the mineral pyrite (fool's gold) ($E_0 = 20$ keV) performed with the commercial software system of vendor 2. The FeK α peak is correctly identified, but S K is misidentified as PbM. Note that the beam energy is sufficient to excite the Pb L-family, but the absence of required peaks at the positions indicated by the arrows did not affect the solution in the S K and PbM region of the spectrum.

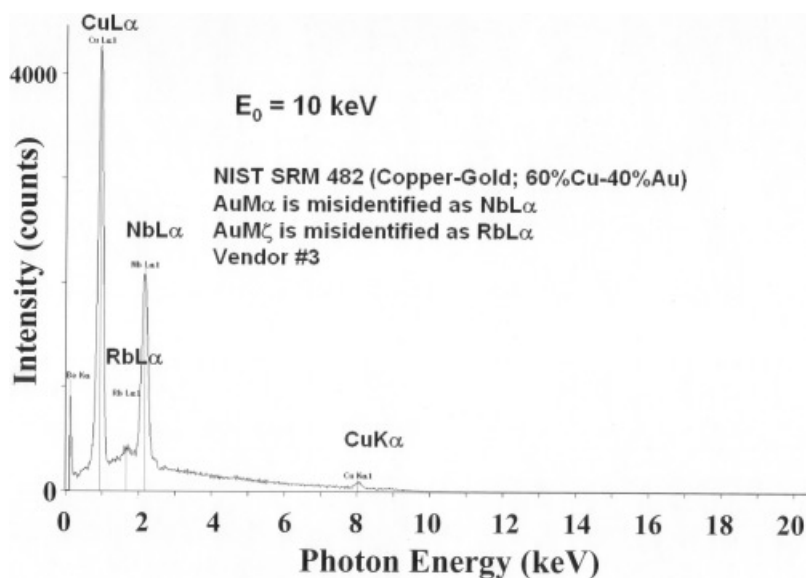


Figure 6. Automatic qualitative analysis peak identification of NIST SRM 482 (copper-gold alloys; 60%Cu-40%Au) ($E_0 = 10$ keV) performed with the commercial software system of vendor 3. AuM α is misidentified as NbL α and AuM ζ is misidentified as RbL α .

identification of ZnK α and ZnK β changed the identification of the low energy peak from NaK α to ZnL α .

Figure 11 shows the results of automatic qualitative analysis with the software of manufacturer 4 for a chromium-platinum alloy (0.75 Cr-0.25 Pt) excited with $E_0 = 10$ keV. Although the CrK α and CrL α peaks were properly identified, the Pt M-family peaks were ignored, despite the fact that this Pt M-family peak bundle had a substantially higher intensity than the Cr peaks.

Figure 12a shows the results of automatic qualitative analysis with the software of manufacturer 4 for gallium

arsenide (GaAs, 0.482 Ga-0.518 As) with $E_0 = 10$ keV. In this case, the GaL α and AsL α peaks were properly identified despite their close proximity. However, when gallium phosphide (GaP, 0.692 Ga-0.308 P) was attempted immediately after the successful GaAs analysis, the automatic qualitative analysis procedure failed entirely (Fig. 12b), despite working with peaks having a much larger energy separation and having a K-shell peak for P. Although no incorrect peak identifications were made in this case, the analyst was still left with the problem of solving the spectrum manually.

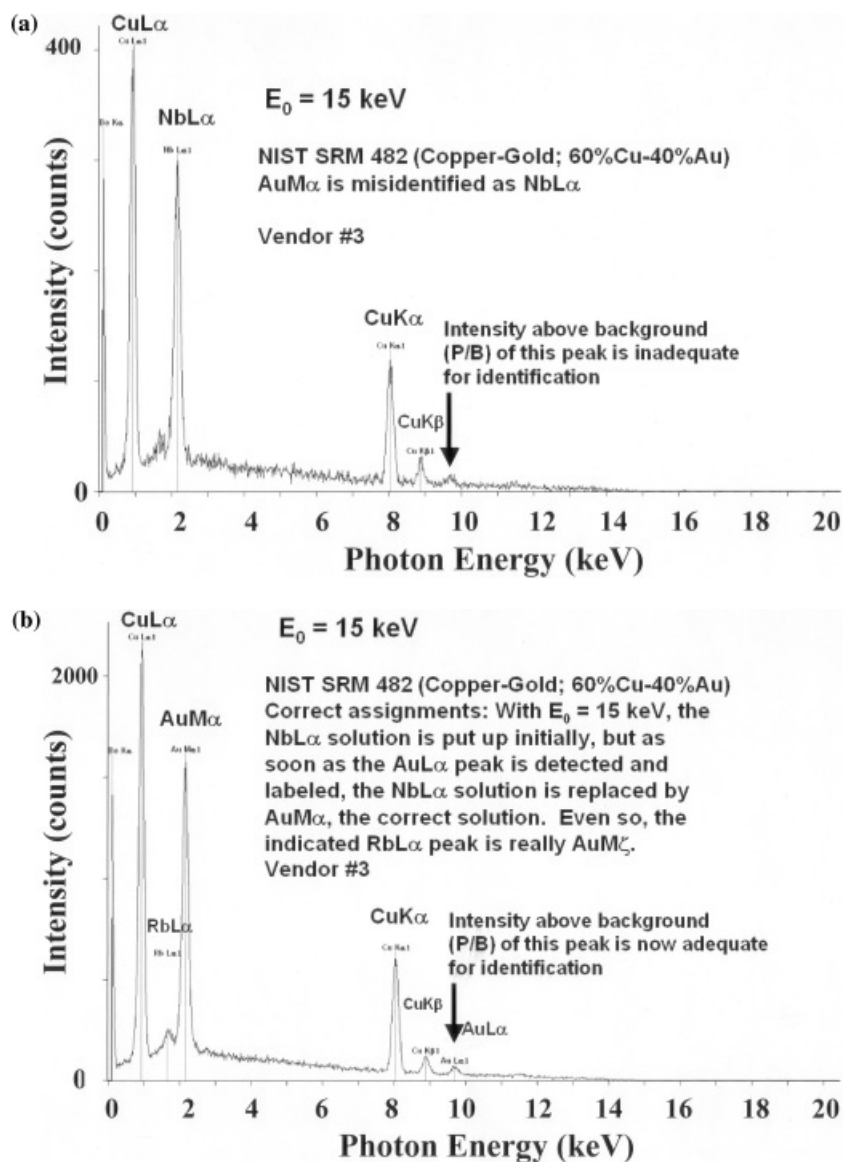


Figure 7. a: Automatic qualitative analysis peak identification of NIST SRM 482 (copper–gold alloys; 60%Cu–40%Au) ($E_0 = 15 \text{ keV}$) performed with the commercial software system of vendor 3. AuM α is misidentified as NbL α . The spectrum accumulation has progressed to the point where there are 300 counts in the peak channel of AuM α . The peak for AuL α does not yet have enough counts to exceed the threshold for peak identification. **b:** Continuation of spectrum accumulation to approximately 1500 counts in AuM α . At this point, the AuL α peak reached the threshold for peak identification. As soon as AuL α was recognized and labeled, the identification of NbL α was changed to AuM α . However, even after this correct identification, AuM ζ was still misidentified as RbL α .

DISCUSSION

How Serious Is This Problem?

This study was not sufficiently detailed to permit adequate estimates of the frequency of occurrence of these blunders for the systems tested, and clearly a selection of only four manufacturers does not represent the entire EDS industry. Moreover, commercial software systems are constantly evolving, and therefore it is nearly impossible for such a study to be comprehensive and current. Nevertheless, these peak identification blunders were discovered while testing materials that were not particularly exotic, for example, ZnS, FeS₂, Cu–Au alloy, and so forth, and in general it did not require many test materials before blunders were encountered. This was particularly true when low incident beam energies ($E_0 \leq 10 \text{ keV}$) were employed so that the higher

energy K-family and L-family peaks above a photon energy of approximately 5 keV were not efficiently excited or were below the excitation threshold. Without the well-separated multiple peaks in the high photon energy range, the automatic qualitative analysis software was much more likely to fail when identifying the low energy L-family and M-family peaks, for example, for ZnS identifying NaK α instead of ZnL α when ZnK α and ZnK β were not available. As a crude estimate, the automatic qualitative analysis procedures applied to a broad range of problems appear to be correct for major constituent peaks about 95% of the time. A reviewer of this article questioned the “charged language” that it contains, noting words like “blunder,” “egregious,” “devastating,” and “so wrong,” because, as the reviewer notes, “the results are 95% right.” But, can we afford 5% of such blunders when identifying major constituents, or even 1%? Mistakes of this type, when a major constituent of a sub-

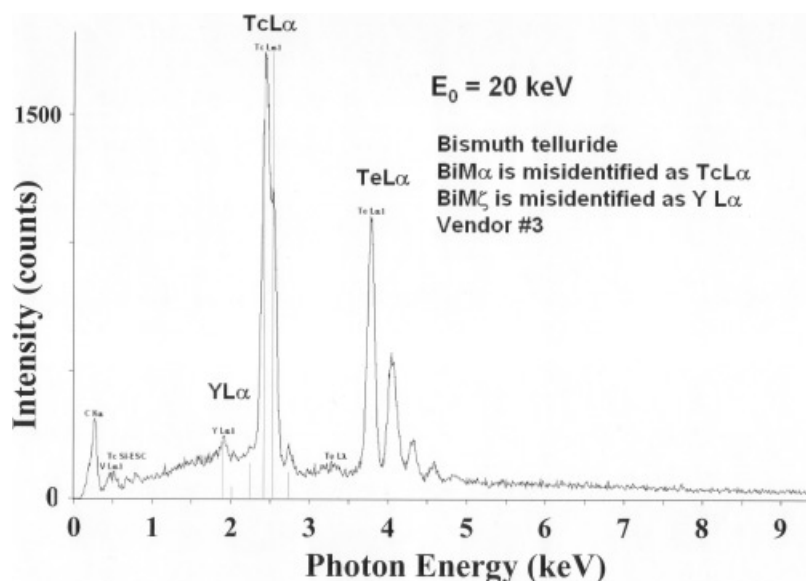


Figure 8. Automatic qualitative analysis peak identification of bismuth telluride ($E_0 = 20$ keV) performed with the commercial software system of vendor 3. BiM α is misidentified as TcL α and BiM ζ is misidentified as YL α .

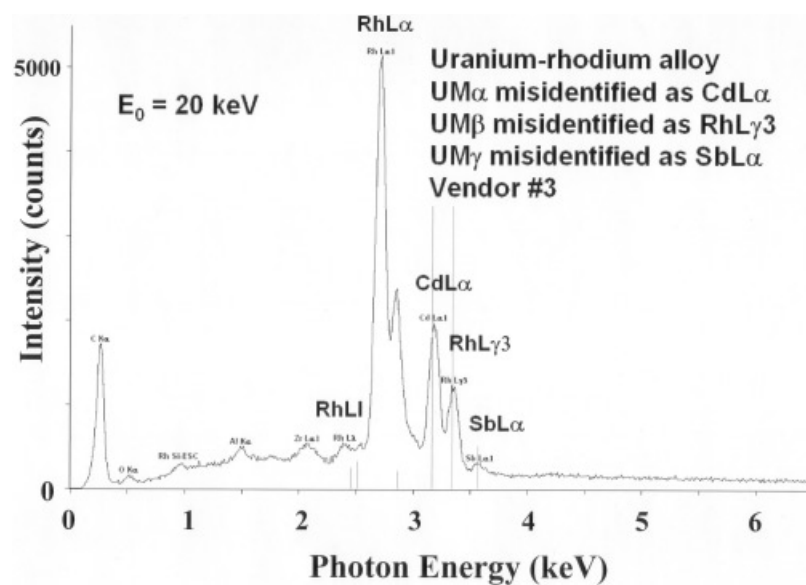


Figure 9. Automatic qualitative analysis peak identification of 80%U-20%Rh alloy ($E_0 = 20$ keV) performed with the commercial software system of vendor 3. UM α is misidentified as CdL α , UM β is misidentified as RhL γ_3 , and UM γ is misidentified as SbL α .

stance under examination is identified as a completely different element that is not actually present above some trace level, are not excusable or defensible. Such a mistake is not a quantifiable error of the type that inevitably occurs in quantitative measurements and that can be described by an appropriate statistical measure. Such blunders constitute a real threat to our credibility as an analytical community. For example, such mistakes will not only severely compromise the value of forensic evidence presented in a specific court case, but repetition will eventually call into question the credibility of SEM/EDS for all such forensic applications. When minor constituents ($0.01 \leq \text{concentration} \leq 0.1$ mass fraction) or trace constituents (concentration < 0.01 mass

fraction) are considered, the rate of incorrect identifications by automatic qualitative analysis is likely to be even greater, as suggested by some of the minor peak misidentifications included in the examples given above.

How long have people been aware of this problem? When this article was originally submitted, the phrase "emerging threat" was used in the title. A reviewer offered the following observation: "Many of the 'blunders' have been present in systems for more than 20 years. Many of the 'blunders' are so well known that sales people from competing microanalysis companies use the information during the sales process." Based on this information, "emerging threat" has been removed from the title. Despite the consid-

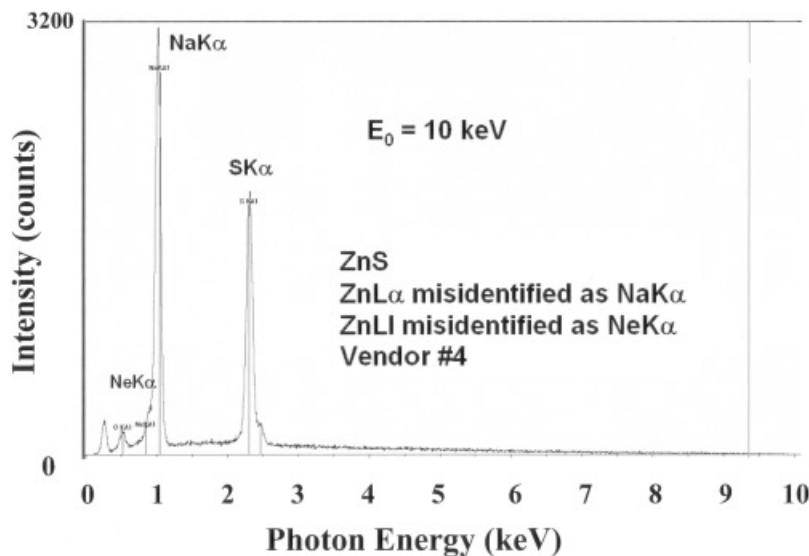


Figure 10. Automatic qualitative analysis peak identification of ZnS ($E_0 = 10$ keV) performed with the commercial software system of vendor 4. ZnL α is misidentified as NaK α . ZnLl is misidentified as NeK α .

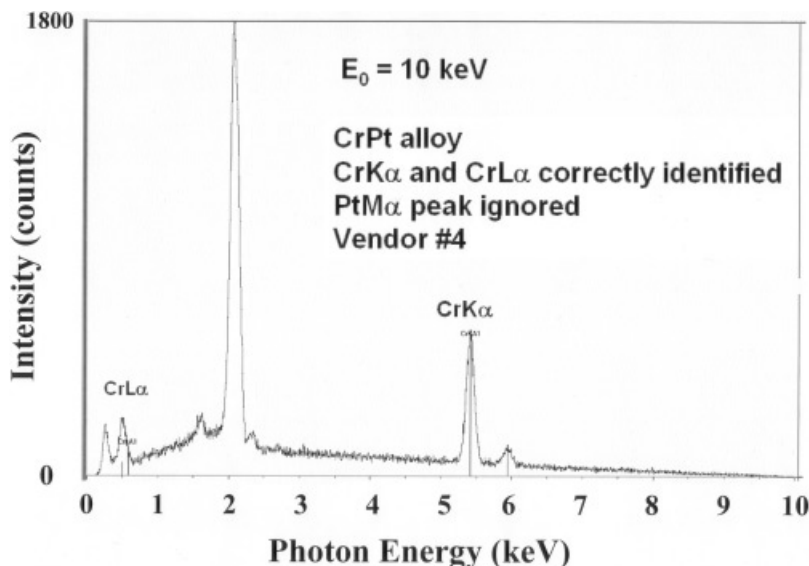


Figure 11. Automatic qualitative analysis peak identification of 75%Cr–25%Pt alloy ($E_0 = 20$ keV) performed with the commercial software system of vendor 4. The CrK α and CrL α peaks are correctly identified, but the PtM α peak, the highest intensity peak in the spectrum, is ignored.

erable length of time this situation has apparently been known, no literature references to this problem have been found.

To “minimize” the problem, some implementations of automatic qualitative analysis permit the user to exclude selected elements of the periodic table from the possibility of being identified. This might make sense for certain elements, such as the artificially synthesized radioactive elements technetium and promethium. In general, however, editing the periodic table is dangerous because it means that the user assumes perfect knowledge of the specimen constituents on the microscopic scale, and nature simply isn’t that tidy. Unusual and unexpected features are occasionally found in natural microstructures and even in artificially constructed microstructures, and we exclude at our peril information that might aid us in recognizing the unusual.

The possibility of blunders when identifying major constituents is so devastating as to demand that a quality measurement environment must always include close manual inspection of the results of automated qualitative analysis to ensure the validity of the peak identifications. Experienced, careful analysts who habitually examine peak identifications are not likely to be fooled by these automatic qualitative analysis blunders. When queried, manufacturers often indicate that they regard the automatic qualitative analysis function implemented in their software only as an aid to the analyst, who must make the final determination. However, the SEM/EDS community includes an increasing number of analysts who must operate in laboratories where they are responsible for several analytical techniques and for whom the SEM/EDS may only be of occasional use within a demanding schedule. These analysts often cannot invest the

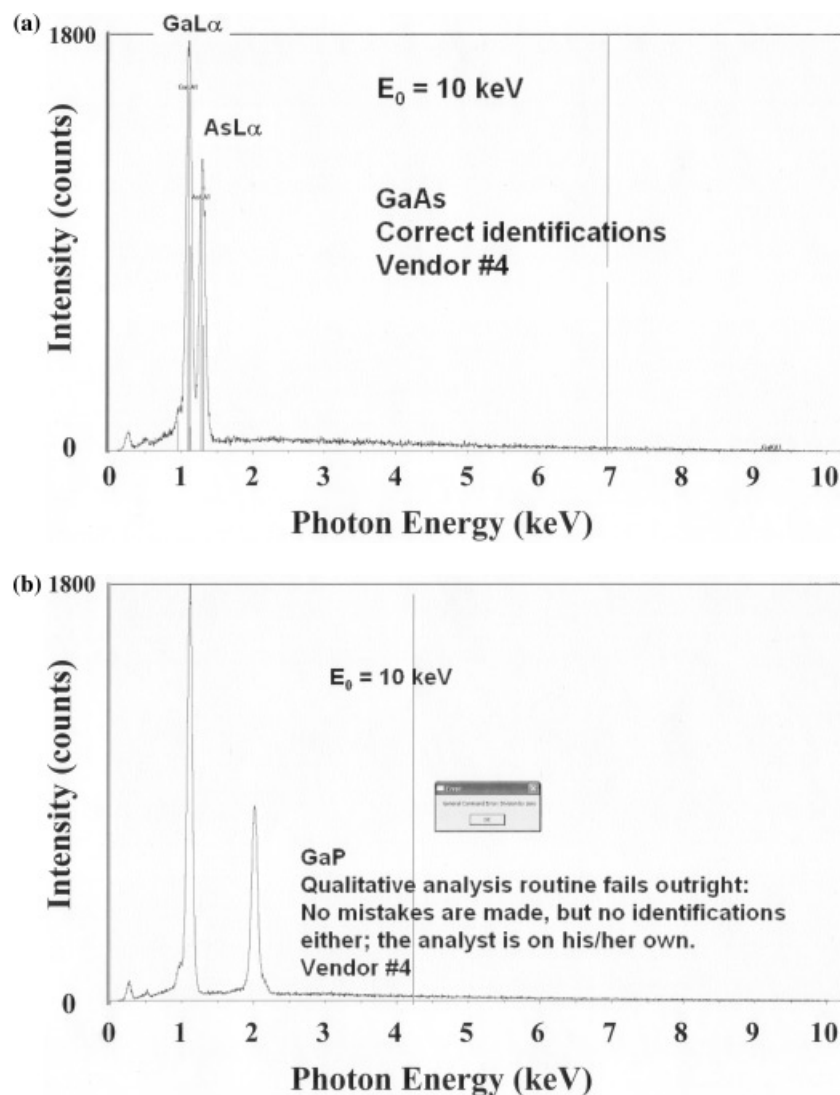


Figure 12. a: Automatic qualitative analysis peak identification of GaAs ($E_0 = 10$ keV) performed with the commercial software system of vendor 4. GaL α and AsL α are both correctly identified. b: Automatic qualitative analysis of GaP ($E_0 = 10$ keV) attempted immediately after the successful GaAs peak identifications. Both the GaL and the P K peaks are ignored.

time to become expert in every method. They necessarily come to rely on comprehensive analytical software that carries the results from automatic qualitative analysis, without careful manual confirmation, directly into the final report that is presented to the client. This is where peak identification blunders can do the most damage to the credibility not only of these individual analysts but eventually to the SEM/EDS community as a whole.

A Typical Strategy for Automatic Qualitative Analysis and Its Inherent Weakness

What is the strategy followed in the development of automatic qualitative analysis that leads to such blunders? The starting point for any automatic or manual approach to peak identification is a properly calibrated spectrum. Unless each peak position is found at the proper energy channel, the likelihood of successful, robust identification by any method is severely diminished. Thus the first step in any

qualitative analysis protocol that seeks to operate in a quality measurement environment is to check the calibration and perform an update if necessary. Calibration within 10 eV or better is desirable because of the multiplicity of X-ray peak possibilities that must be considered for intermediate and heavy elements. The calibration procedure is usually performed with an element such as copper that provides a low photon energy peak (e.g., nominally CuL α at 0.928 keV, although the measured L-peak is a convolution of CuL α and CuL β at 0.948 keV that produces a composite peak channel at approximately 0.935 keV, depending on detector energy resolution) and a high photon energy peak (e.g., CuK α at 8.040 keV). Alternatively, calibration may be established using the internal zero-strobe peak and a single externally measured peak such as a CuK α peak as reference. Having established calibration by following whatever method the manufacturer supplies, the careful analyst will check intermediate peaks (e.g., SiK α at 1.740 keV; TiK α at 4.508 keV; and FeK α at 6.400 keV) as well as peaks at high photon

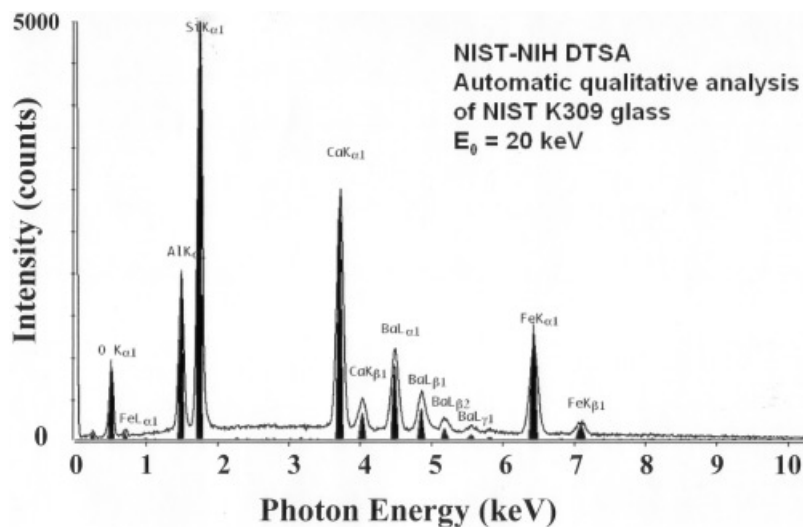


Figure 13. Automatic qualitative analysis of a complex, six-component glass, NIST K309, with NIST-NIH Desktop Spectrum Analyzer (DTSA) showing the original spectrum (line trace), the results of the peak finding algorithm (filled dark), and peak identifications. All peaks are identified correctly. $E_0 = 20$ keV.

energies ($E > 10$ keV, e.g., $\text{AsK}\alpha$ at 10.532 keV and $\text{ZrK}\alpha$ at 15.746 keV) and low photon energies ($E < 0.9$ keV, e.g., O K at 0.523 keV and C K at 0.282 keV). Even with a well-calibrated and linear energy response between 1 keV and 8 keV, low photon energy peaks in particular are likely to deviate from the proper peak position because of incomplete charge collection.

With energy calibration established, a typical basic approach to automatic qualitative analysis is to first locate the peak channel by processing the spectrum with a peak-finding algorithm. There is typically a user-selected software parameter that establishes a statistical threshold, based upon the counting statistics of the peak-to-background ratio (P/B), below which peaks are not considered detected and are ignored until the peak intensity is increased sufficiently to exceed this threshold. For those peaks that satisfy the P/B statistical threshold, the measured peak channel energies are then compared with a comprehensive X-ray energy database. This look-up scheme also typically includes a user-selected parameter for the energy width, ΔE , that constrains the range of the search, for example, $\Delta E = \pm 20$ eV. The larger the search range allowed, the greater the possibility of making an erroneous assignment.

It is generally not possible to say exactly what qualitative analysis peak identification procedures are actually being used in the “black box” commercial software. There is one open source analytical software system in which the qualitative analysis procedure can be scrutinized. NIST Desktop Spectrum Analyzer (DTSA) has a peak identification software tool that utilizes the basic peak-finder algorithm and look-up database approach (Fiori et al., 1991). Figure 13 shows an example of the spectrum (line trace) of a complex glass (NIST K309, which contains O, Al, Si, Ca, Fe, and Ba as major constituents), the peak channel finding solution (solid spectrum), and the peak identification solu-

tion derived from the database automatic search. Other examples of correct peak identifications with DTSA in complex specimens are shown in Figure 14. With a search range of ± 20 eV, the DTSA peak identification procedure is correct approximately 97% of the time for major element peaks, with about 3% “no solution” (i.e., no peak identification made) or incorrect identifications. What is the problem that leads to these failed identifications or misidentifications? Most peak identification failures occur for L- and M-peaks in the low photon energy range below 3.5 keV. For L- and M-peaks in this energy range, the energies of the α and β components are too close for the EDS to resolve the separate peaks. However, the effect of the inevitable peak broadening that occurs in EDS measurement is to convolve the closely spaced α and β components, which are in an approximate ratio of 2:1, into a composite peak. The peak channel of this composite peak differs from the $L\alpha$ or $M\alpha$ peak by several tens of electron volts, effectively moving the peak out of the search range. This peak convolution effect is seen in Figure 15a for the bismuth M-family of peaks in bismuth telluride measured with $E_0 = 10$ keV, where the tellurium L-series is properly identified, but the bismuth M-family is unidentified by the automatic peak identification procedure. (The Bi L-family is not excited under the low voltage conditions chosen because $E_{L3} = 13.424$ keV and thus only the Bi M-family ensemble is available for the identification.) The location of the Bi M-family members has been added manually in Figure 15a and is more obvious in the expanded peak seen in Figure 15b where the shift in the peak channel from $\text{BiM}\alpha$ can be seen.

This convolution problem is much less severe for K-shell peaks in the low energy range because the $K\alpha$ and $K\beta$ separation is less and the $K\alpha/K\beta$ ratio is much higher, at least 10/1 and approaching 50/1 for $\text{AlK}\alpha$ - $\text{AlK}\beta$, so that the $K\alpha$ peak dominates the composite $K\alpha/K\beta$ peak.

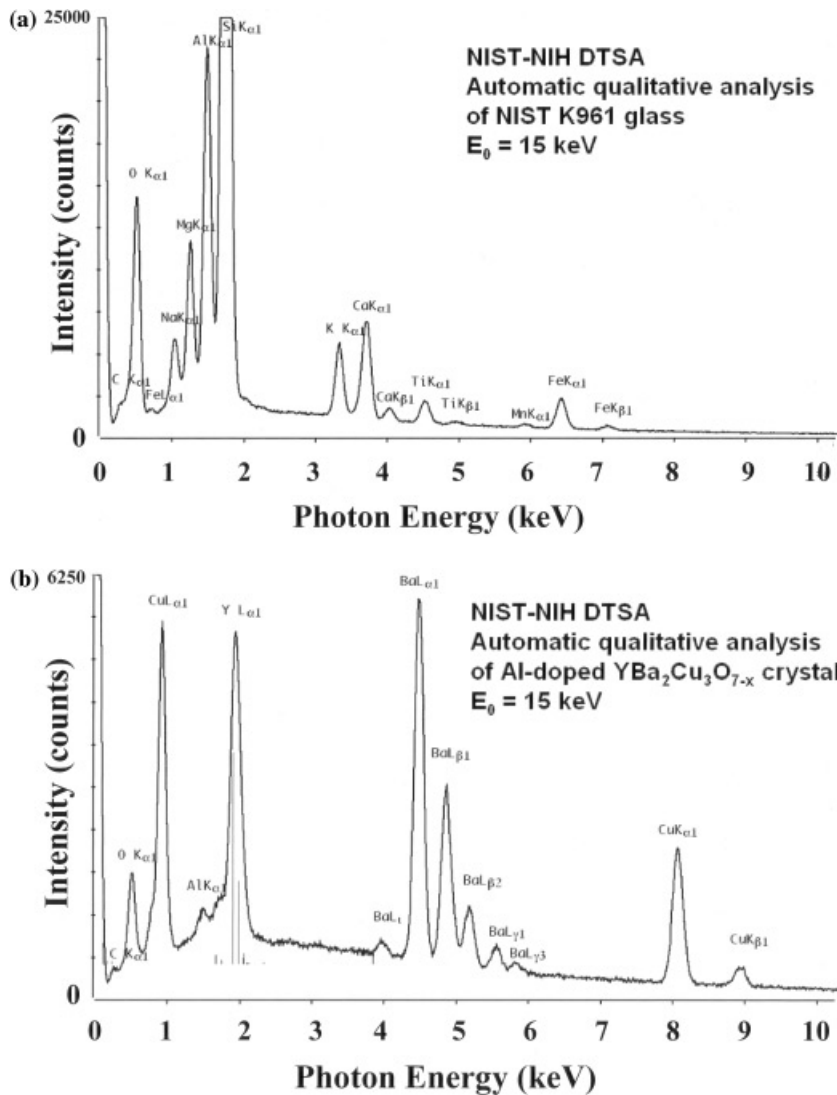


Figure 14. **a:** Automatic qualitative analysis of a complex, 10-component glass, NIST K961, with NIST-NIH Desktop Spectrum Analyzer (DTSA) showing the original spectrum (line trace) and peak identifications. All peaks are identified correctly. $E_0 = 15$ keV. **b:** Automatic qualitative analysis of Al-doped $YBa_2Cu_3O_{7-x}$ single crystal, with NIST-NIH Desktop Spectrum Analyzer (DTSA) showing the original spectrum (line trace) and peak identifications. All peaks are identified correctly. $E_0 = 15$ keV.

A Recommended Solution

Identification of X-ray peaks is sometimes assumed to be a trivial exercise: Anybody can do it manually by inspection, so surely a sophisticated automatic qualitative analysis computer program can do it without failure, especially when major constituents are involved. The examples of peak identification blunders by automatic qualitative analysis given above suggest that this line of thinking is dangerously naïve. In fact, qualitative analysis is a challenging problem that requires a careful strategy to properly solve a complex spectrum arising from a mixture of several elements. An analyst following an optimum strategy for manual qualitative analysis must actually make use of a combination of pattern recognition and physical rules that govern what X-ray peaks must be present in the spectrum (Fiori & Newbury, 1978; Goldstein et al., 2003). It is quite difficult to develop computer code for automatic qualitative analysis

that fully incorporates the rules by which a human operator solves a spectrum, especially the extended pattern recognition aspect.

A more sophisticated, second-level development of the peak-find/lookup method would bring into consideration those physical rules that define the multiplicity of X-ray peaks. One key rule is the existence of families of peaks (e.g., $K\alpha$ - $K\beta$; $L1$ - $L\alpha$ - $L\beta$ - $L\gamma$ - $L\eta$ (L_2 - M_1); $M\zeta$ - $M\alpha$ - $M\beta$ - $M\gamma$ - $M_{IV}N_{IV}$ (M_2 - N_4)) so that when a peak is identified as an alpha-peak of the K-, L-, or M-family, the other peak positions of that particular family must also be marked to avoid subsequent misidentification later in the procedure. The escape peak and sum peaks associated with the parent peak must also be located and marked. Similarly, when more than one family of X rays is excited, this information must be used to avoid later misidentification. For example, a $K\alpha$ peak above a photon energy of 2.5 keV must be accompanied by a lower-energy L-family within the measur-

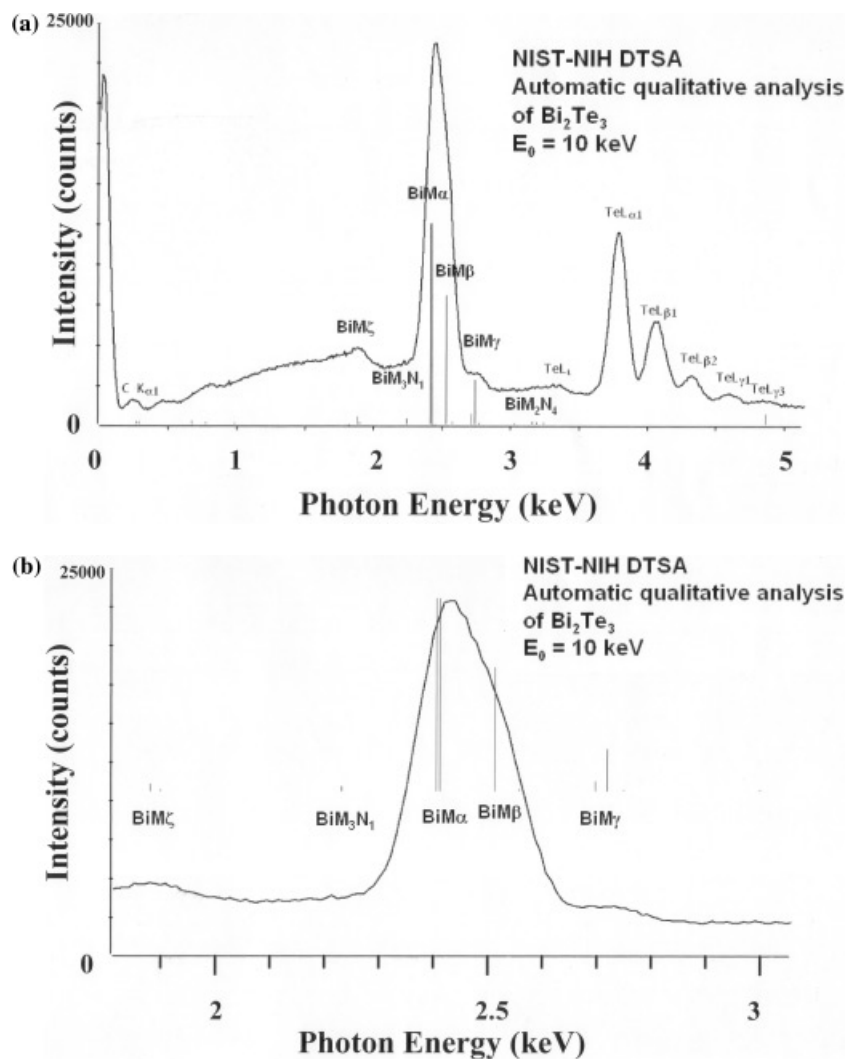


Figure 15. a: Automatic qualitative analysis of bismuth telluride with NIST-NIH Desktop Spectrum Analyzer (DTSA) showing the original spectrum (line trace) peak identifications, and location of Bi M-family peaks. $E_0 = 10$ keV. Note correct identification of Te L-family, but BiM peak, the highest peak in the spectrum is ignored. The Bi M-family peaks have been added manually by the analyst after the automatic analysis using the KLM markers. b: Expansion of a showing displacement of peak channel from BiM α and BiM β because of the peak convolution effect. The Bi M-family peaks have been added manually by the analyst.

able energy range above 100 eV. Whether this L-family is actually detectable depends on the exact circumstances of the element in question, the overall specimen composition, and the beam energy, but the possible presence of the L-family must not be neglected. Similarly an L α peak above a photon energy of 2 keV must be accompanied by a lower energy M-family; again the visibility of this low-energy family depends on exact circumstances. For K- and L-shell X-rays above 4 keV, the lower-energy L- and M-shell X-rays are very likely to be detectable.

The third and highest level of sophistication of the peak-find/lookup method would be achieved when the existence of the other peaks within a family or from a lower energy shell is actually confirmed in the recorded peak positions rather than just labeling their positions. Moreover, this additional information would be used to establish a figure of merit that could be used to justify the identification. The more of these minor peaks that can be recognized, the more robust the elemental identification. The need for high-count spectra is obvious when we require access to the minor family members to improve our confidence. Such a

careful and complete approach would also reduce the misidentification of low-relative-intensity members of a family as belonging to peaks of another element.

However, neither of the latter two refinements can deal effectively with the problem of low photon energy peaks, especially if the analysis is performed with low beam energy so that the identification of low-energy L- and M-shell peaks is not aided by the discovery of the corresponding high-photon-energy K- and L-shell peaks. A second difficulty arises when the number of counts accumulated in the spectrum is not sufficient to detect the minor, well-separated peaks such as Ll and M ζ . Instead, a different approach to peak identification is needed, an approach based upon fitting the entire family peak structure to the unknown. Thus, consider the problem of identifying peaks in the 2.3-keV photon energy range, where the possibilities include S K, MoL, and PbM. By applying multiple linear least squares fitting with locally measured, high-count peak references to the unknown, we can make use of the residuals after peak stripping to judge which elemental species best fits the measured peak. Figure 16 shows an example of

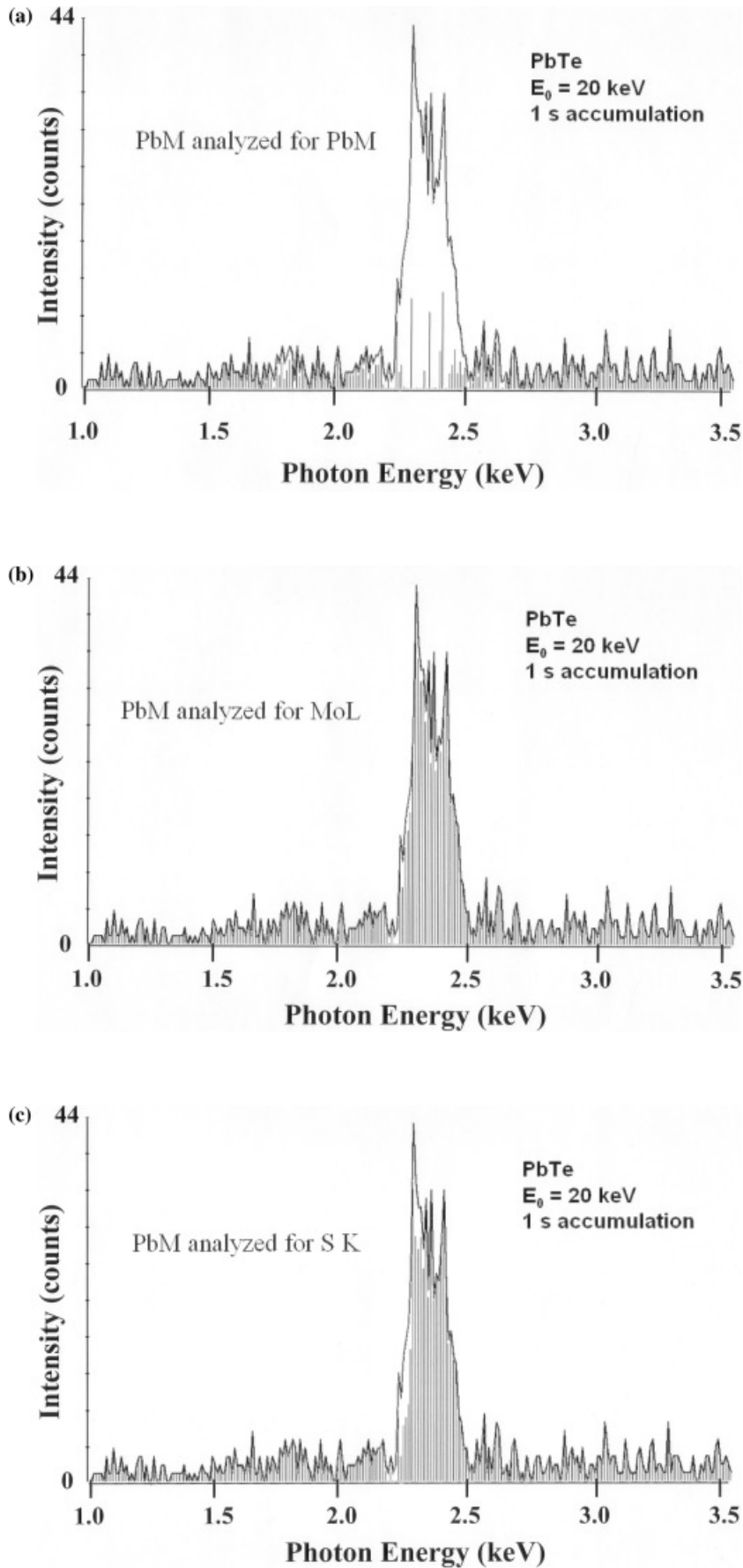


Figure 16. Spectrum of PbTe taken for 1 s at a count rate of 1000 cps with approximately 40 counts in the peak channel of the PbM peak. Multiple linear least squares fitting was applied with various peak references. The original peak is shown with the solid trace and the residuals after peak stripping are shown as vertical bars: (a) PbM stripped with a PbM reference peak from Pb metal; note excellent fit. (b) PbM stripped with a MoL reference peak from Mo metal; note poor fit. (c) PbM stripped with a S K reference peak from FeS_2 ; note poor fit.

multiple linear least squares fitting of a noisy, low-count spectrum for the PbM family (in PbTe) against peak references derived from high-count spectra of S K (from FeS₂), MoL (from Mo metal), and PbM (from Pb metal). The residuals after fitting are quite good for the correct reference, PbM, but very poor for the incorrect elements, S K and MoL. The noise conditions of this spectrum are much worse, by a factor of about 100, from any of the examples used in Figures 1–12, and yet it is clear from the residuals after fitting which peak identification is correct.

Some commercial implementations of automated qualitative analysis already include a peak fitting tool as a critical step for an “advanced” peak identification procedure, often embedded in “advanced quantitative analysis.” Clearly this is the direction to pursue for *all* automated qualitative analysis. As a community of analysts, we simply cannot accept “easy” but definitely fallible automated qualitative analysis methods, developed from the basic peak location/lookup procedure for “routine” analysis, and invoke the more elaborate, time-consuming, and demanding fitting methods for “difficult” problems only. All of our analytical problems must be regarded as difficult! The computing power certainly exists for an uncompromised approach that would fit all spectral peaks against peak references and use statistical methods to assign each proposed identification with a statistically based measure of confidence. Even with such an advanced system for qualitative analysis, the analyst bears final responsibility for achieving robust, high-confidence results, not the software, which must always be regarded as an aid.

CONCLUSIONS

Misidentifications of major constituents ($C > 0.1$ mass fraction, or 10 wt%) were found when analyzing certain binary compounds and alloys using the automatic qualitative analysis procedures embedded in commercial EDS systems of four different manufacturers. Although these misidentifications are generally only encountered in a few percent of analyses, the mistakes are not random. A particular misidentification made by a certain system is likely to be repeated indefinitely. The mistakes are so severe, for example, identifying gold as niobium, that they are likely to damage the credibility of the method and must be regarded as serious blunders.

The particular peak identification procedures used in commercial systems are generally not described by the manufacturers. The automatic peak identification procedure embedded in NIST Desktop Spectrum Analyzer (DTSA), which is based upon a strategy of peak channel location followed by database look-up, is found to be subject to misidentifications for certain L- and M-family peaks of intermediate and high atomic number elements. For these L- and M-shell peaks, the peak channel of the composite

peak created by the convolution imposed by the detector resolution function differs significantly from the peak energies of the component peaks. Another area of special difficulty is the low beam energy ($E_0 \leq 10$ keV) analysis case where X-ray peaks above a photon energy of 5 keV are excited inefficiently or not excited at all, depending on the exact choice of E_0 . The lack of the high photon energy K- and L-shell peaks means there is a loss of critical information that could make the identification of low photon energy L- and M-family peaks more robust.

In view of this situation, automatic qualitative analysis for peak identification in EDS should only be regarded as a useful aid that provides suggestions to the analyst. The ultimate responsibility resides with the analyst for assigning the peaks in an EDS spectrum to the correct elements. Aspiring analysts must be willing to spend the effort necessary to learn “how to read” X-ray spectra, that is, how to manually perform robust, high-confidence peak identification. Systematic study of pure elements and simple compounds, combined with a familiarity of the underlying physical rules that govern the appearance of X-ray peaks, enable the analyst to develop the experience needed to avoid mistakes when identifying peaks associated with major, minor, and trace constituents. Software tools are almost invariably provided in commercial systems that support manual inspection of automatic peak identification solutions. The analyst should systematically test the automatic peak identification of a commercial system to assess elements and peak families where failures are likely to occur.

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