

## Letter to the Editor: Accurate Element Identification is the Core Requirement for a Microanalysis System

We at Oxford Instruments were interested to read the article published in *Microscopy and Microanalysis* by Newbury (2005). Although our own views differ from those of Dr. Newbury in some respects, we do agree that this is an important matter. If this article generates an interest in the ability of a system and a user to accurately identify elements in a spectrum and encourages people to assess the quality of the qualitative analysis provided by a microanalysis system, then we believe this article has served a very useful purpose. After all, accurate element identification is the core requirement for a microanalysis system.

We are surprised at the rudimentary nature of the automatic peak identification algorithms reported in this article. Reliable identification requires more input parameters than knowledge of the position of X-ray lines. It is imperative to account for peak shape, in addition to intensity and position, for an algorithm to have any chance to be accurate in all cases. Identification routines that use top hat filtering and least squares peak deconvolution are required to ensure that elements are correctly identified in all situations, even where overlaps are severe. Using such algorithms allows manufacturers and users to adopt more robust philosophies where the system gives the same results no matter what the expertise of the user or the complexity of the X-ray lines in the spectrum.

The article by Newbury (2005) did not discuss the hardware aspects needed for automatic peak identification, and we believe that seeing this as a software problem alone understates the importance of electronic stability and calibration. The level of sophistication required for accurate automatic peak identification (and quantitative analysis) comes at a price. Peak deconvolution methods require an accurate knowledge of peak shape, resolution, and position. To meet this requirement, there are hardware requirements. Statham (2002), for example, has discussed the requirements for correctly deconvoluting two overlapping X-ray lines in terms of removing qualitative and quantitative errors. Hardware specifications can be used to help an analyst assess the suitability of hardware for accurate analysis. Examples of such specifications are (a) the ISO15632:2002 specification for resolution at a guaranteed count rate and (b) the stability of electronics for a particular process or

shaping time in terms of the change in resolution and peak position as count rate changes.

Although we were surprised by some of the mistakes reported, Oxford Instruments accepts that no system can automatically identify all of the elements in a sample (both major and minor) 100% of the time. For example, Statham (2002) explains limitations where lines are very close in energy. However, systems today should ideally be able to provide easy-to-use and intuitive tools to highlight where problems in peak identification may be present and to help users correct any errors. Such tools would immediately highlight to a trained (though not necessarily expert) user that the type of “blunder” described in the article had occurred.

The Newbury article, in particular, highlights issues where beam voltages of 10 keV or less are used. Here the lack of separated and high intensity X-ray lines makes the qualitative analysis task more difficult. For this reason a “check total” method has been developed (Statham, 2004, 2006) that uses highly accurate spectrum synthesis models (Duncumb et al. 2001; Duncumb & Statham, 2002) to check that the total peak to total background ratio of a spectrum is consistent with the constituent elements and collection parameters for that spectrum. This technique can highlight problems such as sample inhomogeneity and sample charging. It would also highlight to a user immediately that the type of misidentification described in the article had occurred. In the implementation of Statham (2004, 2006), the check total is reported as a number in “% terms.” If this number is less than 80% or more than 120%, then there is a major issue with the spectrum that the user should address. We have tested four of the examples highlighted in the Newbury paper, and in each case a “check total” tool would have warned the user that a mistake had been made:

- System #1 misidentified Ta as Si in a TaNb alloy at 10 keV: check total = 69%
- System #2 misidentified K as U and Sb in KBr at 20 keV: 51%
- System #3 misidentified Au as Nb and Rb in a CuAu alloy at 10 keV: 61%
- System #4 misidentified Zn as Na and Ne in ZnS alloy at 10 keV: 21%.

In each of these examples we corrected the peak identification and found that this changed the check total to a value within the allowed limit:

- Correctly identified Ta in a TaNb alloy at 10 keV: check total = 111%
- Correctly identified K in KBr at 20 keV: 99%
- Correctly identified Au in a CuAu alloy at 10 keV: 99%
- Correctly identified Zn in ZnS alloy at 10 keV: 113%.

It is no longer necessary for users to rely solely on the traditional methods of X-ray series recognition, line intensity, and position described in the article. Software tools are now available that can predict peak and background shapes based on the experimental conditions (normally directly read from the microscope) and the elements identified. These tools provide graphical “overlay” displays to compare spectra with the shape that would be generated if the elements identified by the software were present. If we examine any of the mistakes described in the article, such an overlay would show that all the peaks are not correctly identified. When the overlay is obviously incorrect, the user can use traditional tools, such as an element/line energy list, or simply use trial and error to add or remove elements from the list until the overlay is consistent with the observed spectrum. This type of overlay tool also highlights to a user if their system is not calibrated correctly because the fit between the overlay and the spectrum usually reveals any significant shift or broadening of peaks.

Where to next? We believe this is a serious issue and thank Dale Newbury for highlighting it. However, although perhaps not present on the particular systems used by Newbury, the type of automatic identification tools asked for in the article is already available from some vendors and has been available commercially in a number of forms for many years. Qualitative analysis is the core of every microanalysis system, but until Newbury’s article we had not seen

a systematic test of autoID performance for many years. Indeed, the samples described in Newbury’s article could provide a basis for such a test. We therefore suggest that Newbury might take his study to a more rigorous level and invite manufacturers and users to partake in a wider test of autoID and peak identification tools. This would help the community to determine if the crisis identified by Newbury is as serious as suggested and help users find and test tools that minimize their chance of making “blunders.”

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## Authors’ Response

I am pleased to respond to the letter from Simon Burgess commenting on my article, “Misidentification of Major Constituents by Automatic Qualitative Energy Dispersive X-ray Microanalysis: A Problem That Threatens the Credibility of the Analytical Community” (Newbury, 2005). First, I am grateful for the words of support for my article, even if inevitably qualified, expressed in Mr. Burgess’s letter. In response to his specific comments (in boldface), I offer the following:

### 1. **“We are surprised at the rudimentary nature . . .”**

As I noted in my article, much of commercial energy dispersive X-ray spectrometry (EDS) qualitative analysis (that is, peak identification) software is presented to the user as a “black box” of tools with no explanation of what is actually being done. It is not possible to identify the level of sophistication of the peak identification procedures embedded in this software. Thus, in describing the various routes that can be taken in implementing

EDS qualitative analysis, I chose to start with the simplest level (peak channel location and a lookup table, which constitutes a “single channel” solution). More sophisticated methods, such as full peak fitting involving all the peak channels and confirmation of all the X-ray family members that must be present, are described in the article as part of a recommended solution to the peak identification problem. I am convinced that a peak identification system based upon the recommended solution would not be vulnerable to blunders for the easiest case as tested in my article: high-intensity peaks with no significant peak interferences.

2. **“The article by Newbury did not discuss the hardware aspects needed for automatic peak identification . . .”**

My article was based upon testing the peak identification performance of actual commercial systems that have a variety of implementations of hardware. Certainly having properly operating EDS hardware is a fundamental requirement that determines the overall peak identification performance, and the measurement protocol included careful checking of the calibration. My article recognizes that the range of EDS instrumentation and software products is very wide and constantly changing. I chose to test recently installed commercial systems, all less than two years old, but these instruments inevitably represent only a subset of the EDS instrumentation and software in the field.

3. **“Although we were surprised by some of the mistakes reported . . . For example, Statham (2002) explains limitations where lines are very close in energy.”**

The mistakes reported in my article have nothing whatsoever to do with peaks that are very close in energy. The mistakes involved large peaks for which no interference could possibly exist because the test materials were carefully chosen with this possible problem in mind. Nevertheless, despite testing what should have been the easiest possible case for automatic peak identification, these analyses revealed peak identifications where elements that constituted as much as half of the specimen were misidentified!

4. **“The Newbury article in particular highlights issues where beam voltages of 10 kV or less are used.”**

I applaud the development of advanced tools that aid the analyst by providing a check on the tentative peak identification result, including tools that model the spectrum based upon the current estimate of the composition and the known spectrometer performance parameters. Such tools will be especially useful for “low voltage analysis” where the reduced beam energy inevitably means that important higher photon energy peaks (e.g., peaks at energies greater than 5 keV) are either weakly excited or not excited at all, thus eliminating the valuable redundancy of being able to identify an element with more than one family of X-ray peaks, for example, K-L or L-M, that is possible for many elements. Without commenting on the efficacy of any particular EDS analysis system, I think it is

**Table 1.** EDS Spectral Challenges

Photon energy range (keV)	Candidate elements (energy of principal peak in range)
0.390–0.395	N K (0.392); ScL $\alpha$ (0.395)
0.510–0.525	O K (0.523); V L $\alpha$ (0.511)
0.670–0.710	F K (0.677); FeL $\alpha$ (0.705)
0.845–0.855	NeK $\alpha$ (0.848); NiL $\alpha$ (0.851)
1.00–1.05	NaK $\alpha$ (1.041); ZnL $\alpha$ (1.012); PmM $\alpha$ (1.032)
1.20–1.30	MgK $\alpha$ (1.253); AsL $\alpha$ (1.282); TbM $\alpha$ (1.246)
1.45–1.55	AlK $\alpha$ (1.487); BrL $\alpha$ (1.480); YbM $\alpha$ (1.521)
1.70–1.80	SiK $\alpha$ (1.740); TaM $\alpha$ (1.709); W M $\alpha$ (1.774)
2.00–2.05	PK $\alpha$ (2.013); ZrL $\alpha$ (2.042); PtM $\alpha$ (2.048)
2.10–2.20	NbL $\alpha$ (2.166); AuM $\alpha$ (2.120); HgM $\alpha$ (2.191)
2.28–2.35	S K $\alpha$ (2.307); MoL $\alpha$ (2.293); PbM $\alpha$ (2.342)
2.40–2.45	TcL $\alpha$ (2.424); BiM $\alpha$ (2.419)
2.60–2.70	ClK $\alpha$ (2.621); RhL $\alpha$ (2.696)
2.95–3.00	ArK $\alpha$ (2.956); AgL $\alpha$ (2.983); ThM $\alpha$ (2.996)
3.10–3.20	CdL $\alpha$ (3.132); U M $\alpha$ (3.170)
3.25–3.35	K K $\alpha$ (3.312); InL $\alpha$ (3.285); U M $\beta$ (3.336)

a fair question to ask the manufacturers if these sophisticated analytical tools for peak identification are *always* brought into operation when determining peak identification results. The first reported peak identifications may be accepted uncritically by a naïve user without further review, no matter what sophisticated tools are available to examine the first results. Are the peak identification confirmation tools implemented in a manner that essentially forces the analyst to examine possible mistaken peak identifications without easily ignoring any red flags that may be raised? Can the advanced, sophisticated peak identification and/or confirmation tools be turned “off” to “simplify” the system? Support tools that can be turned “off” in the software menu or ignored because they require the user to delve deeply into software windows to find and operate the tool are not likely to be used by novice analysts. Peak identification is a complicated problem, and the full set of tools must always be brought to bear in any results reported to the user.

5. **“Where to next?”**

Mr. Burgess’s proposal to develop a set of specimens to challenge automated peak identification procedures is a good one. While the limited sample set used for the study in my article is a possible starting point, there are actually many possible peak ambiguities when the full periodic table is in play (stable elements and long-lived isotopes, e.g., Th and U), more of which should be included in a comprehensive study of the peak identification problem. Table 1 presents a partial list of these spectral trouble spots, considering where the principal K-, L-, and M-peaks occur near the same photon energy.

Since writing this article, I have served as a national tour speaker for the Microbeam Analysis Society, presenting

the EDS peak identification blunders topic to several regional Microscopy and Microanalysis Society audiences, and I have also presented the topic at other scientific conferences. At *every* presentation, one or more members of the audience have come forward to describe their own, often painful, encounters with EDS peak identification blunders. This experience convinces me even more firmly that as an analytical community we have a serious problem with automated peak identification. While the evolution of advanced peak identification software tools as described by Mr. Burgess is certainly the proper route to ultimately correcting this situation, we must also acknowledge a structural situation that unfortunately guarantees that the peak identification blunders problem will be with us for a long time to come. Thanks to the diligent efforts of the commercial manufacturers in what is now a mature industry with 35 years of experience, EDS instrumentation is highly reliable and typically has a lifetime of well over 10 years. In fact, the lifetime is often determined by the longevity of the computer platform rather than the EDS instrumentation. While we obviously benefit from this outstanding EDS reliability, it does mean that older software systems that have not been updated with new tools and which are

vulnerable to peak identification blunders will remain in place and will continue to haunt us. As new, inexperienced users come into our analytical community, especially those who inherit older EDS software systems, we need to warn them of the possibility of EDS peak identification blunders.

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