

X-Ray Wavelength Spectrometers: Are They Still Needed?

*..or "The More Thing Change,
the More They Stay the Same"*

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During the early 1970's there was often heated debate over the quality of analytical performance attainable with Energy Dispersive (ED) systems using solid state detectors. Many scientists, particularly the more practical ones, were convinced that only WDX was reliable; while those with perhaps more imagination were convinced EDX was the future in microanalysis. At that time, both groups were right.

EDX has seen remarkable improvement since those early days. At that time ED spectrometers were limited to analysis of elements above atomic number 10, and state-of-the-art resolution was improving to about 155 eV at Mn. Overlaps were handled strictly in quantitative analysis routines and even then only by use of simple overlap factors. Wavelength Dispersive (WD) spectrometers, although slow and difficult to operate, were required for light element analysis, to perform analyses when overlaps were present or suspected, and to detect trace elements.

Today's Si(Li) detectors have resolution in the 130's, and even better resolution can be obtained with Ge detectors. Powerful computers only imagined in 1975 now enable sophisticated deconvolution programs to find peaks hidden under others and to graphically display their results. Detectors are provided with reliable thin windows able to transmit X-Rays down to Be. Have such improvements in EDX eliminated the need for WDX altogether?

For laboratories requiring only a quick overview analysis, the answer is probably yes. For other laboratories facing more complex analysis requirements, wavelength spectrometers must still be called upon to reform the very same tasks mentioned above, with only a difference in degree rather than kind:

1. As long as WDX resolution remains an order-of-magnitude better than EDX, WDX will be needed.
2. While ED system improvements were being achieved and highly advertised, WD advancements were also being made (but at a slower pace and not highly advertised).
3. Analytical requirements have become proportionately more demanding. Therefore, EDX, although much improved, is still being stretched to its performance limits.

In Part 1 of this two-part article, the benefit of high resolution will be illustrated through examples. Simply put, higher resolution means higher peak-to-background ratio (P/B) and the virtual elimination of peak overlap, resulting in higher sensitivity and more definitive analyses.

If sophisticated ED deconvolution routines could truly compensate for poor resolution, the on-going intense competition among EDX manufacturers to produce higher and higher resolution detectors (Si(Li) or Ge) would have stalled out years ago. Continued improvements would have been pointless.

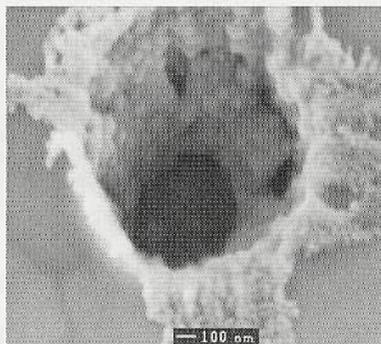
In cases of two overlapping peaks of relatively equal magnitude, or where there is an unoverlapped peak of the same line series to use as a basis for determining the height of the overlapped peak, deconvolution routines are reliable. There are many cases, however, which don't fit these criteria, and better resolution is the only answer. Some common analytical situations which require higher resolution (and its accompanying higher P/B) are:

1. The qualitative (and quantitative) analysis of trace elements (below the 0.5 % level);
2. The determination of predominantly single-line elements which, in EDX may be overlapped by multiple lines of another element or elements or where a small peak is buried within a large one (severe overlap);

Examples of such overlap cases include the determination of

- 1) oxygen in the presence of chromium;
- 2) silicon in the presence of Ta or W;
- 3) sulfur in the presence of Mo, Pb, or both;

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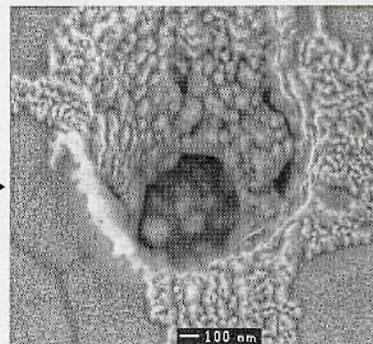
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4) analysis of clays or catalysts containing low levels (typically <0.5%) or V, Ba and/or rare earths in the presence of 2 % Ti.

3. The analysis of light elements at concentration levels below about 5%.

Before presenting examples of applications where WDX is needed, Table 1, which compares some salient characteristics of WDX and EDX, should be considered:

Table 1: Comparison of EDX vs. WDX

	EDX	WDX
Data Collection.	Parallel	Serial
Peak widths (eV):	80 - 160	2 - 20
Detection Limits:	1000 ppm - 1%	10 - 1000 ppm
Probe Currents Needed:	0.1 - 1nA	1 - 200mA
Count-rate Limits:	10 ⁴ cps over spectrum	10 ⁴ cps per element
Main Advantages:	Fast-parallel collection High solid angle Wide angle of collection	Resolution Sensitivity Light element analysis

It may be clear from the table why EDX has become the dominant method used for microanalysis: it's faster, easier, and more efficient.

- It's faster because it will collect X-Rays of all energies within its operating range essentially in parallel. WDX is serial.

- It's easier, in part because of the same reason, but also because it has a wide angle of collection (fewer mistakes can be made by the operator). WDX requires that the sample be at a specific working distance for proper operation.

- It's more efficient, which means that X-Ray data can be collected at specimen currents consistent with typical operating parameters used for imaging. WDX requires one or two orders of magnitude more specimen current.

Having reviewed the reasons why EDX is always the first X-Ray tool to be used to solve a problem, some examples where analysts are forced to turn to WDX will be presented ("Oh well, I guess I'll have to use WDX").

Trace Elements

WDX will give practical detection limits normally well below 0.1 % and down to as few ppm in favorable cases. If one needs to "see" a peak in a spectrum (wavelength scan) to be convinced, then concentrations in the 100 - 500 ppm range are detectable for most elements in reasonable time and in convincing fashion. Figure 1 shows a peak from Al, with a nominal 300 ppm concentration in brass. The scan took several minutes to collect (25 channels at 20 seconds per channel), but the presence of Al is clearly demonstrated.



Figure 1: 0.03% Al in brass

Severe EDS Overlaps

Figure 2a is a spectrum showing the presence of both oxygen and chromium in the sample. Specifically, the spectrum is from an oxidized Cr foil. Note that the oxygen peak lies between two strong Cr peaks separated by only 75 eV. It is commonly assumed that only the Lα is of concern with respect to O Kα overlap, but clearly the WDX spectrum shows otherwise. Actually, the peak labeled Lλ also contains the Lη.

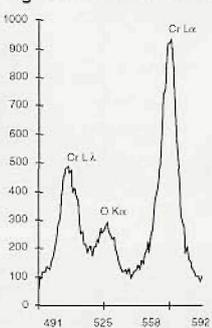


Figure 2a: Oxide on chromium foil

Figure 2b shows two spectra from oxidized stainless steel tubes. The left spectrum is from a very thin oxide, reported as 40Å; the spectrum on the right is from a thicker oxide. Note that the wavelength scan in these cases did not include the Cr Lα.

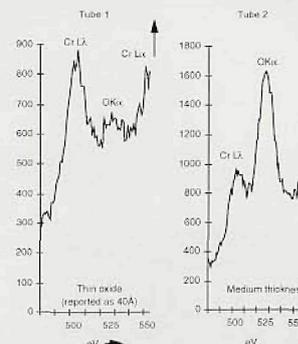


Figure 2b: Oxide layers of different thicknesses on stainless steel

Figure 3 shows a WD spectrum acquired at 10 kV from a thin film (1500 Å) of tantalum silicide (a film used in the semiconductor manufacturing process) on a Si substrate. If the Ta/Si ratio is to be determined, a low accelerating voltage is required to reduce the contribution to the Si peak from the underlying Si wafer. Therefore, the M lines of Ta must be used, and they severely overlap with the Si Kα. The outline of the ED spectrum (from a 149 eV detector) is shown overlaid on the WDX spectrum.

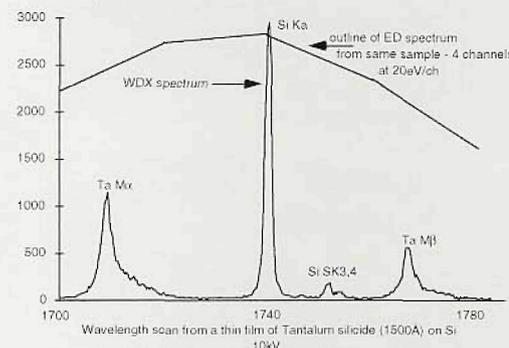


Figure 3: 1500Å Tantalum silicide film on Si substrate

Figure 4 is one in a family of many S/Pb/Mo overlaps that would fall into the severe category. In this case, the spectrum is from a leaded steel component used in an automobile engine. The average (bulk) concentrations of S and Pb are 0.3 and 0.1 % respectively. This spectrum also shows a phenomenon unique to WDS, that of a higher-order diffraction. Since the material is predominantly iron, even the Kβ of Fe is a strong peak, and its 3rd-order line presents an interference with the Pb Mα. To minimize this interference, an accelerating voltage of 10 kV was used to reduce the Fe K emissions, and the electronics (single-channel analyzer) were optimized for the detection of the Pb line at the expense of the much higher energy Fe Kβ (the 3rd order line is still the Fe Kβ, it just appears to be of lower energy).

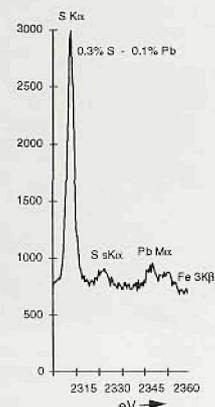


Figure 4: Spectrum from engine component (leaded steel)

Figure 5 shows spectra from two closely-related clays that can be uniquely identified only by their Ba concentrations. One type contains 2500 ppm (0.25 %) Ba, while the other contains only 400 ppm (0.04 %). There is approximately 2 % Ti in the clay. The Ba Lα and Ti Kα are separated by only 43 eV.

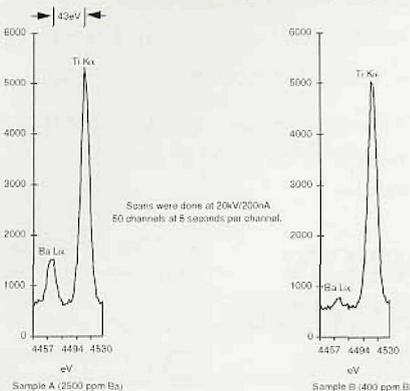


Figure 5: Low concentrations of Ba in the presence of 2% Ti (clay)

Continued on Page 12

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Analysis of Light Elements Present in Low Concentrations

Figure 6 is a carbon profile in a carburized steel, taken from the case to the core. The case concentration is 1% C, with the core being 0.3%.

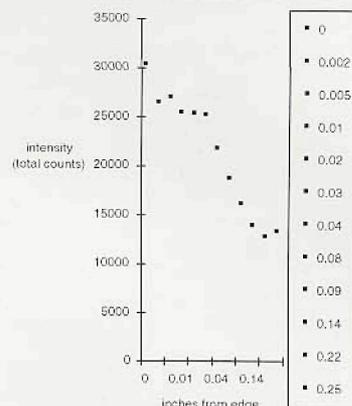


Figure 6: Carbon profile in carburized steel drill bit

Figure 7 is also a carbon profile, this one from a steel rod. The intent was to determine if the bulls-eye pattern which shows up in the etched cross-section of the rod correlated with carbon segregation. In order to eliminate the etching process from contributing to or masking the results, the segregation pattern was marked with micro-hardness indentations and then the sample repolished. The correlation between carbon segregation and the etching pattern is revealed.

Figure 8 shows a calibration curve of intensity vs. wt% B in BPSG films (an SiO₂ film containing B and P, used in the semiconductor manufacturing process). The B concentrations are typically between 1 and 5%. WDX is one of the common tools used in the industry to control BPSG film composition.

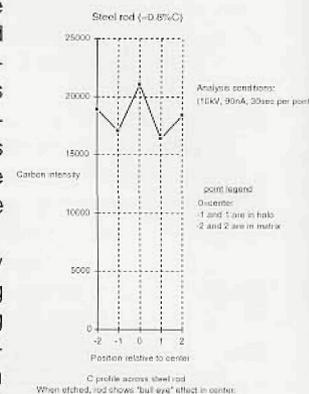


Figure 7: Carbon profile over steel rod showing apparent segregation

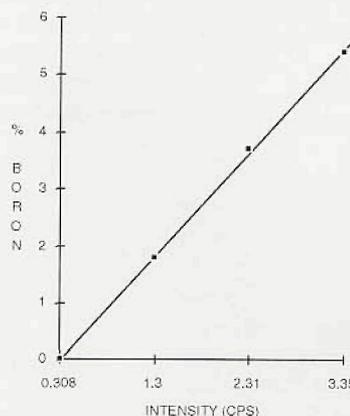


Figure 8: Calibration curve for wt% Boron in BPSG

In summary, this may be yet another example of "the more things change, the more they stay the same". If one were asked to define the role of the wavelength spectrometer in today's microanalysis laboratory, the answer would be to provide conclusive analyses of trace elements, to sort out severe EDS overlap situations, and to analyze light elements with better sensitivity than EDS can provide. The answer sounds very similar to that which would have been given in 1975.

Part 2 of the article will discuss some of the improvements made in WDX over the past 15 years, with particular emphasis on the dramatic change in the user interface. ■



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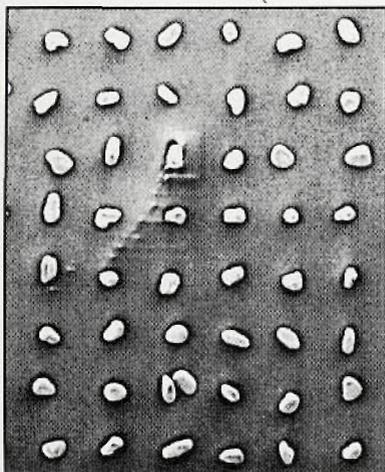
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100µm	1,000µm	02389-BA	02389-MB	02389-RA
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