Wavelength Dispersive X-ray Microanalysis

Explained

OXFORD
INSTRUMENTS

Introduction

Electron probe X-ray microanalysis techniques (Wavelength Dispersive X-ray and Energy Dispersive X-ray Spectrometries WDS and EDS, respectively) use the characteristic X-rays generated from a sample bombarded with electrons to identify the elemental constituents comprising the sample. Both techniques generate a spectrum in which the peaks correspond to specific X-ray lines and the elements can be easily identified. Quantitative data can also be obtained by comparing peak heights or areas in the unknown with a standard material.

Of the two methods, EDS is more commonly employed. Data collection and analysis with EDS is a relatively quick and simple process because the complete spectrum of energies is acquired simultaneously. Using WDS, the spectrum is acquired sequentially as the full wavelength range is scanned. Although it takes longer to acquire a full spectrum, the WD technique has much improved resolution compared to EDS. Typical resolution of an ED detector is 70 to 130 eV (depending on the element), whereas peak widths in WD are 2 to 20 eV. The combination of better resolution and the ability to deal with higher count rates allows WDS to detect elements at typically an order of magnitude lower concentration than EDS.

While the WDS technique has always been appreciated for its higher resolution and trace element capability, it has been traditionally viewed as more complex to set up, and WDS data more tedious to obtain and interpret than EDS.

And, in the past, it was.

Evolution of the WDS technique

The development of WD spectrometers goes back long before ED detectors became widely available in the early 1970s.

The first electron probe microanalyzer (EPMA) was developed during the 1940s and used an optical microscope to observe the position and focus of the electron beam on the sample. Later, WD spectrometers were fitted to SEMs which allowed the specimen to be positioned more precisely under the electron beam and also made possible a visual picture of the distribution of a chosen element – the X-ray map.

On early commercial WDS spectrometers, all of the spectrometer mechanisms had to be moved by hand, and the operator had to physically exchange the crystals to cover the spectrum. The output from counters, recorded against time was sent to a chart recorder, and all the peak identification, peak and background measurements, and matrix corrections were done by hand. The advent of desktop computers and precision stepper motors in the late 1970s made possible the mechanization of the spectrometer and the SEM stage. With these changes, WDS analysis became significantly less cumbersome. However, the initial setup for an analysis and the entire data reduction process were still tedious and time-consuming. Analysis parameters had to be optimized for each element and type of sample. Computers of that generation were not particularly user-friendly. Data for ED and WD were beginning to be combined, but automatic peak identification of the ED spectrum was not routine, and combined ED and WD analyses were unduly complicated. The situation changed somewhat in the mid-1980s, when data processing became fully automated. However, setup for the analysis remained virtually unchanged. The current generation of WDS spectrometers with their advanced control and analysis software make the technique considerably easier to use. Multi-crystal spectrometers now change crystals on-the-fly rather than first moving to a specified position on the Rowland circle, flipping to the appropriate crystal, and moving back to the correct position on the circle for analysis of the

desired element. Software has been developed for quick, easy qualitative analysis by WDS. Operating parameters for the detectors have been optimized and entered into the software so that analysis setup is quick for the vast majority of samples. Comparing WD and ED spectra and combining WD and ED analysis is now routine and easy.
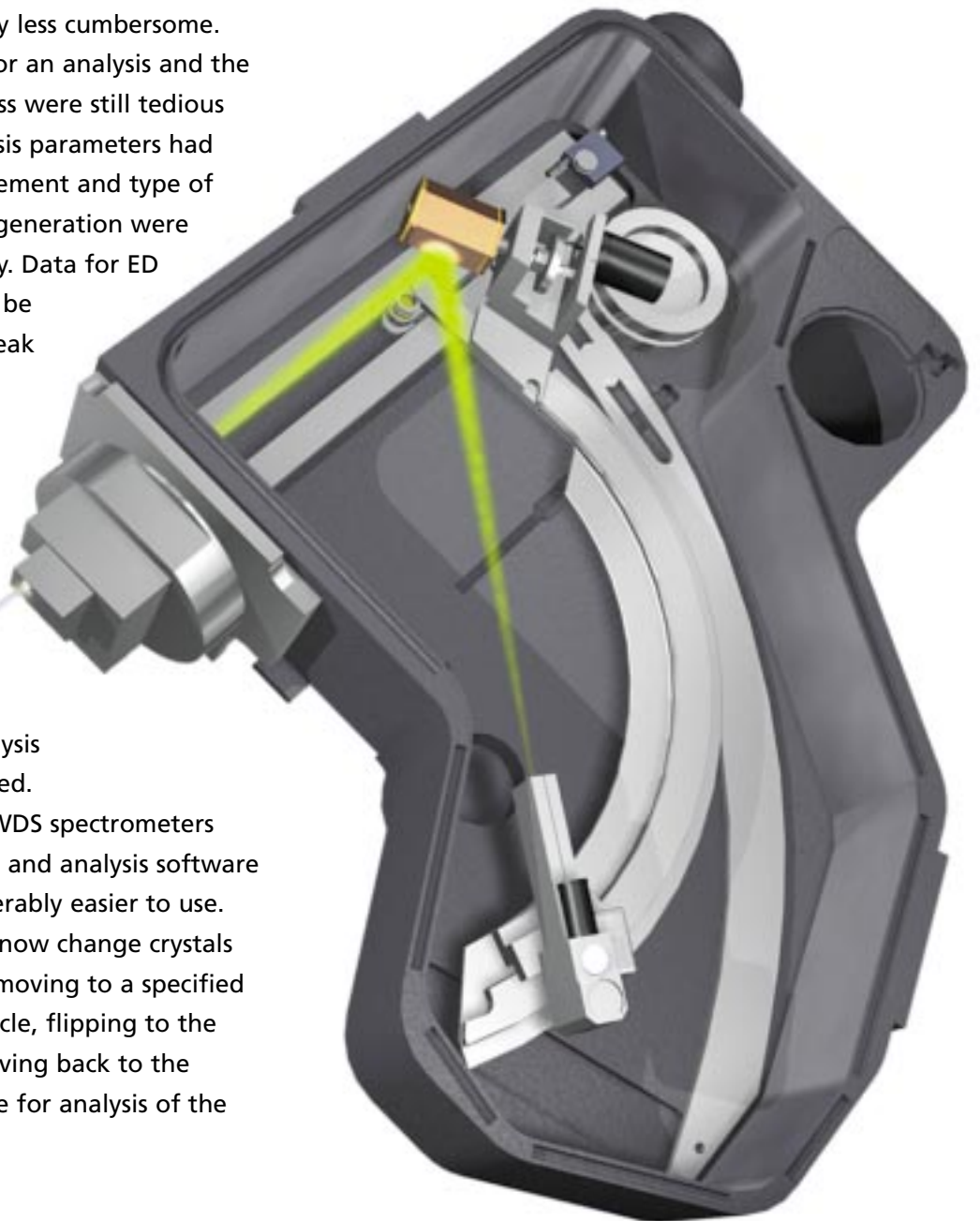
Basics of WDS

The WD spectrometer is fitted on a port of the SEM, usually at an angle inclined to the horizontal so that it provides an identical X-ray take off angle to the ED detector. Although the WD technique often requires a higher SEM beam current than is typically used for ED, the X-ray data is usually acquired from ED and WD simultaneously. If the ED detector is fitted with a variable collimator there is no compromise in performance for either technique.

Diffraction

Inside the spectrometer, analyzing crystals of specific lattice spacing are used to diffract the characteristic X-rays from the sample into the detector (Fig. 1).
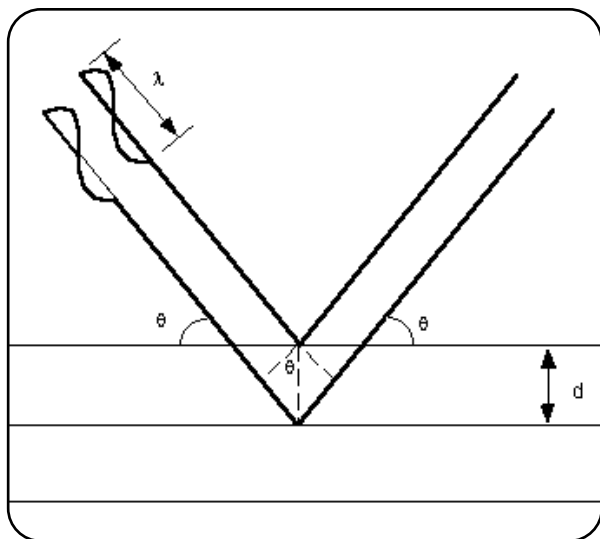

Figure 1

The wavelength of the X-rays diffracted into the detector may be selected by varying the position of the analyzing crystal with respect to the sample, according to Bragg's law ($n\lambda=2d \sin\theta$), where n is an integer referring to the order of the reflection; λ is the wavelength of the characteristic X-ray; d is the lattice spacing of the diffracting material; and θ is the angle between the X-ray and the diffractor's surface.
A diffracted beam occurs only when this condition is met and therefore interference from peaks from other elements in the sample is inherently reduced. However, X-rays from only one element at a time may be measured on the spectrometer and the position of the crystal must be changed to tune to another element.

Crystals

There are two types of crystal geometry in use today. In the first, called Johann geometry, the diffracting crystal is bent to a radius of 2R, where R is the radius of the focusing circle, called the Rowland circle (Fig. 2a). The second, called Johansson geometry, is more precise. It has the crystal bent to radius 2R and then ground to radius R, so that all of the points of reflection lie on the Rowland circle (Fig. 2b). The result of this geometry is that all of the X-rays originating from the point source on the sample are diffracted over a greater percentage of the crystal surface and are brought to focus at the same point on the detector, thus maximizing the collection efficiency of the spectrometer.

Several different diffracting crystals with different crystal lattice spacings are normally used for WDS, in order to cover all of the wavelengths (energies) of interest, as well as to optimize performance in the different wavelength ranges. Some of the crystals commonly in use are listed in Table 1. Of these crystals, only the LIF is naturally occurring. Low energy (long wavelength) X-rays require larger d-spacing for diffraction and LSM (layered synthetic microstructure) crystals are often used for this purpose. These pseudo-crystals are built up by physical vapor deposition of alternating layers of heavy and light elements. The elements are chosen to maximize scattering efficiency, and the effective d-spacing is dictated by the thickness of the alternating layers.
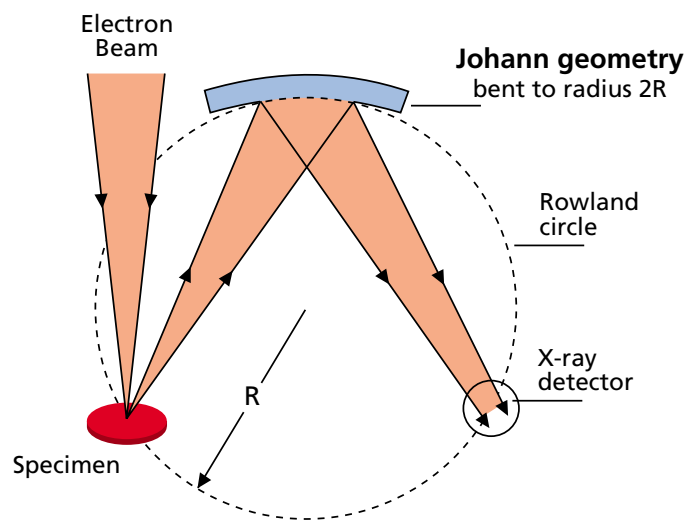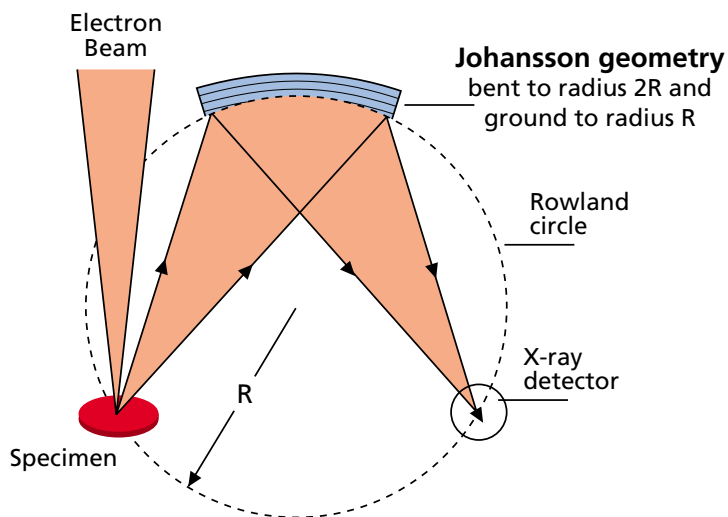

Figure 2a

Figure 2b

Table 1 – Common diffracting crystals used for WDS

Crystal Designation	Crystal Type	2d Spacing, Å	Analyzing Range, Å	Analyzing Range, eV	Element Range Kα
LIF(220)	Lithium Fluoride	2.8473	0.8087 - 2.6306	15,330 - 4,712	V to Y
LIF(200)	Lithium Fluoride	4.0267	1.1436 - 3.7202	10,841 - 3,332	Ca to Ge
PET	Pentaerythritol	8.74	2.4827 - 8.0765	4,994 - 1,535	Si to Ti
TAP	Thallium acid phthalate	25.75	7.3130 - 23.79	1,695 - 521.2	O to Si
LSM-060	W-Si	~61	~17 - ~56	~729 - ~221	C to F
LSM-080	Ni-C	~78	~22 - ~72	~564 - ~172	B to O
LSM-200	Mo-B_4C	~204	~58 - ~190	~214 - ~65	Be and B

Detectors

Detectors used in WDS are usually of the gas proportional counter type (Fig. 3). Generally, X-ray photons are diffracted into the detector through a collimator (receiving slit), entering the counter through a thin window. They are then absorbed by atoms of the counter gas. A photoelectron is ejected from each atom absorbing an X-ray. The photoelectrons are accelerated to the central wire causing further ionization events in the gas, so that an "avalanche" of electrons drawn to the wire produces an electrical pulse. The detector potential is set so that the amplitude of this pulse is proportional to the energy of the X-ray photon that started the process. Electronic pulse height analysis is subsequently performed on the pulses to filter out noise.
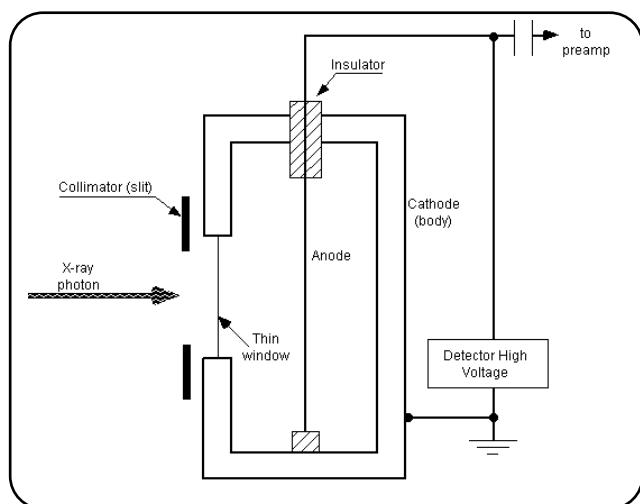

Figure 3

There are two types of gas proportional counters: sealed (SPC) and gas flow (FPC). Generally, SPCs are used for high-energy X-ray lines, while FPCs are used for low energy lines. Sealed proportional counters have a relatively thick window (i.e. beryllium, ~50μm thick), in order to prevent leakage of the gas (usually xenon or a xenon-CO_2 mixture) which is sealed into the detector. Gas flow proportional counters commonly use ultra-thin (0.5 -1μm thick) mylar or polypropylene windows, and the counter gas (usually P-10: argon with 10% methane) flows through the detector at a constant rate.

Spectrometer geometry

To maintain the correct geometrical relationship between specimen, crystal and detector for the full range of diffracted angles, it is necessary to maintain all three on the Rowland circle. This is accomplished by a mechanical goniometer which moves the crystal and detector so that correct diffraction conditions are maintained. If a spectrometer is mounted with the Rowland circle vertical (as is typical on dedicated microprobes), it is necessary to position the sample height very accurately to maintain diffraction geometry. This is achieved by adjusting the height of the sample and observing focus using an optical microscope. In the SEM, accurate vertical positioning is not critical because the spectrometer is mounted with the Rowland circle horizontal and inclined, thus eliminating the need for an optical microscope.

To analyze for a particular element it is important that the crystal and detector are positioned accurately and associated counting electronics are set up correctly. In the past this was a tedious and complex procedure, but automation and PC control have made WD operation very straightforward, routine and reliable.

Comparison of EDS and WDS

Using EDS, all of the energies of the characteristic X-rays incident on the detector are measured simultaneously and data acquisition is therefore very rapid across the entire spectrum. However, the resolution of an EDS detector is considerably worse than that of a WDS spectrometer.

The WDS spectrometer can acquire the high count rate of X-rays produced at high beam currents, because it measures a single wavelength at a time. This is important for trace element analysis. The resolution of the EDS detector is such that situations may arise in which overlap of adjacent peaks becomes a problem. Many of the overlaps can be handled through deconvolution of the peaks. Others, however, are more difficult, particularly if there is only a small amount of one of the overlapped elements. Examples of these more difficult overlap situations are listed in Table 2.

In practice it is advantageous to use the speed of EDS for an initial survey of an unknown sample because major elements will be rapidly identified. However, if trace elements are present they will not be identified, and it may be difficult to interpret complex overlaps. Following the initial ED survey, WD can be used to check for overlaps and to increase sensitivity for trace elements.

Common Peak Overlaps in EDS Microanalysis
S Kα - Mo Lα – Pb Mα
Na Kα - Zn Lα
Ni Lα - La Mα
Zr Lα - Pt Mα - P Kα - Ir Mα
Nb Lα - Hg Mα
Si Kα - W Mα – Ta Mα - Rb Lα
Al Kα - Br Lα
Y Lα- Os Mα
O Kα - V Lα
Mn Lα - Fe Lα - F Kα

Table 2

Resolution comparison between EDS and WDS

The following two examples show how the improved resolution of WDS make peak identification easy.

MoS$_2$

The WD spectrum for MoS$_2$ has been acquired from the **INCA**Wave spectrometer using **INCA**Energy+ software. Using this application, the WD spectrum acquisition is initiated by highlighting part of the ED spectrum. The two spectra are then superimposed automatically to illustrate the difference in resolution.

In the yellow ED spectrum (fig. 4), the molybdenum Lα line at 2.293 keV is severely overlapped by sulfur Kα at 2.307 keV, but the WD spectrum (in blue) clearly resolves these lines and SKβ and MoLβ.
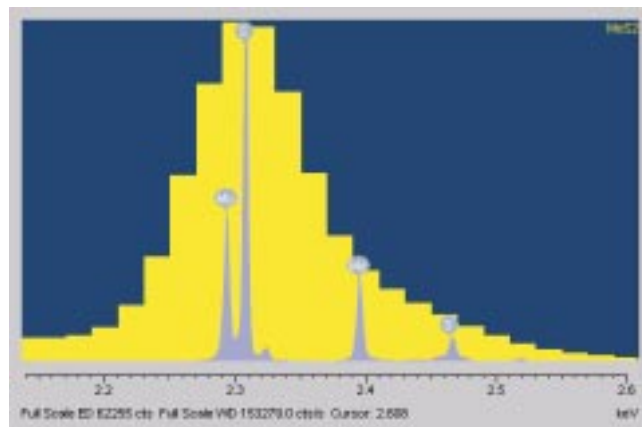

Figure 4

Si, Nb, Mo, W Containing Precipitates

Sub-micron precipitates in an alloy sample require analysis at relatively low beam voltages to eliminate possible X-ray contribution from surrounding phases. This means that L lines for tungsten (8.3977 keV) which are clearly visible in the ED spectrum, are not efficiently excited and so are unsuitable for characterizing composition. In such circumstances, the M-lines of W must be used. Since the M lines for W are not resolvable from Si K lines by EDS in this case (WMα at 1.774 keV and Si Kα at 1.740 keV), the use of WDS is preferred.

The spectra in Fig. 5 illustrate this point. Again, **INCA**Energy+ was used to obtain a WD spectrum overlaid on the ED spectrum (scaled to the WD spectrum). The presence of tungsten in the ED spectrum is masked by the Si K lines while the two are clearly distinguishable in the WD spectrum.
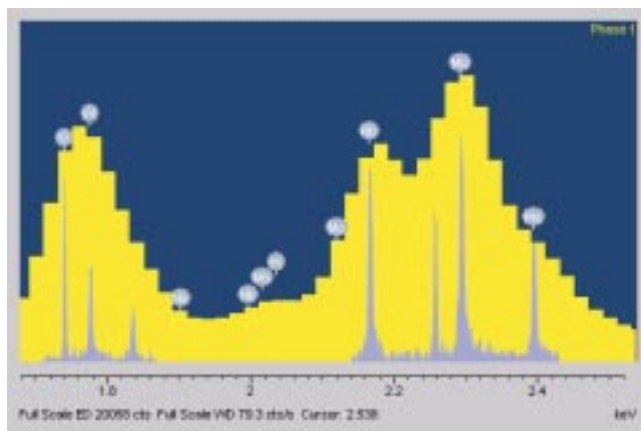

Figure 5

Qualitative analysis

Using normal ED operating conditions it is not always easy to positively identify peaks due to trace elements. However, by increasing the beam current and slowly scanning over the peak position using the WD spectrometer, trace elements can be reliably identified.

Fig 6. shows the ED spectrum from an alloy containing 0.15wt% Si. The red line shows the expected peak position for Si, but it is difficult to be positive about reliable identification. In the WD spectrum (fig 7), the improvement in peak to background ratio means that there is no doubt that Si is present .
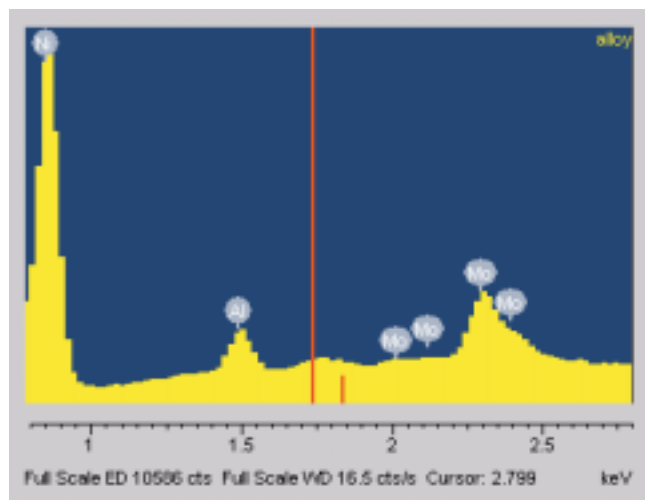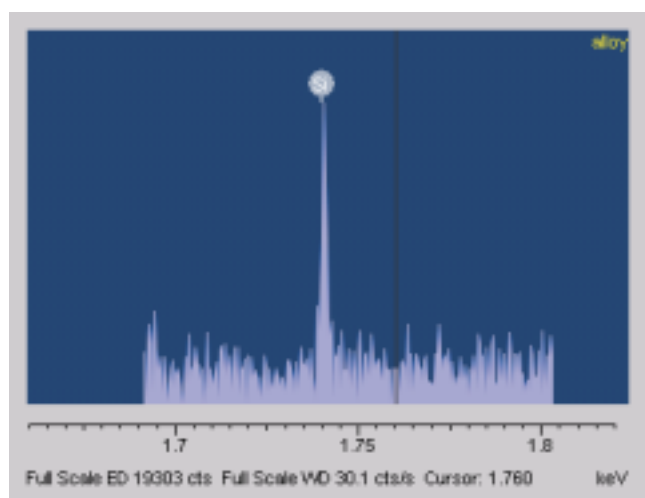

Figure 6

Figure 7

Quantitative analysis

Nickel-based superalloy

The nickel-based superalloy analyzed here contains Al, Ti, Cr, Co, Ta, W, Re and Mo in addition to Ni.

While the W, Ta, and Re contribute to the ED spectrum, identification by ED is complicated by the presence of the large Ni Kβ line at 8.264 keV, along with several other L-family lines associated with Ta, W, and Re in the spectrum. The WD spectrum (Fig. 8), shows the lines from W, Ta, and Re, all clearly separated.

Quantitative results taken on this specimen are listed in Table 3. The alloy has first been analyzed using only EDS. Note that the standard deviations for Ta, W and Re are relatively high because of poor statistics and severe peak overlaps.

The second set of results is a combination of ED and WD data. Using **INCA**Energy+, WD data is acquired simultaneously with the ED spectrum. Hence the total analysis time may not need to be increased. For trace elements and peaks that are severely overlapped in the ED spectrum, a large improvement in statistical precision can be obtained by using WD.
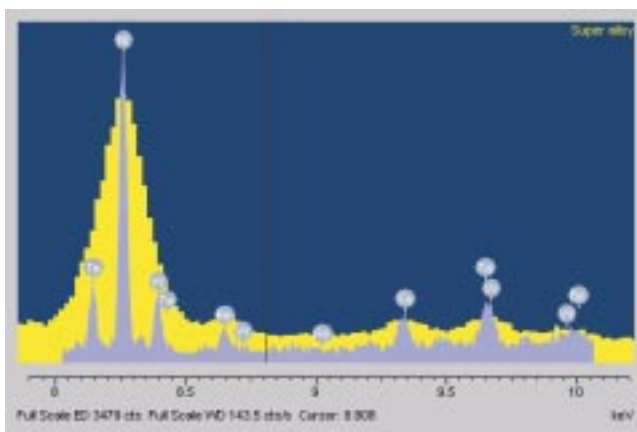
In general, statistical errors in the WD results can be much less than for ED quantitative analysis. This is because higher currents can be used, the peaks are not overlapped and have a better peak to background ratio.

Combined ED/WD analysis is a very practical way of achieving reliable quantitative analysis. ED can be used for accurate quantification of the elements present in relatively large amounts, and WD can be used for accurate quantification of elements present in amounts below 1 wt%. By using both techniques, the analyst exploits the speed of EDS analysis and the sensitivity of the WDS technique.

	ED Only		ED & WD		
	analyzed wt%	std. dev. wt%	analyzed wt%	std dev wt%	method
Al	4.87	0.09	4.83	0.09	ED
Ti	1.007	0.05	1.011	0.05	ED
Cr	6.469	0.09	6.406	0.09	ED
Co	9.62	0.151	9.55	0.153	ED
Ni	59.377	0.35	58.86	0.35	ED
Mo	0.629	0.11	0.533	0.01	WD
Ta	7.03	0.48	7.136	0.078	WD
W	6.393	0.55	6.585	0.077	WD
Re	3.264	0.443	3.099	0.05	WD

Table 3

Figure 8

BPSG film

Borophosphosilicate (BPSG) films are used as a passivation layer for silicon devices in the semi-conductor industry and the concentrations of boron and phosphorus affect the properties of these films.

Quantitative analysis of boron is virtually impossible using ED analysis because of the relatively poor peak to background ratio of the boron peak. However, using modern LSM crystals (in this case the LSM-200) it is possible to achieve excellent count rates with relatively low electron beam currents. Quantitative results are shown in table 4.

Counting precision, even for a very light element such as boron, is excellent and the WD technique is a viable method for analysis of BPSG films.

	wt %	sigma wt %	at %
B	2.35	0.04	4.22
P	3.77	0.06	2.36
Si	37.6	0.38	25.98
O	54.6	0.36	66.23
N	0.87	0.19	1.21

Table 4

Mapping

When the spectrometer is positioned on a peak, the output pulses can be used for mapping. Although only one element can be mapped at a time, the significant benefit of using the WD signal is its much improved peak to background ratio. The analyst needs to be aware of the limitations of WD mapping at low magnification. If the beam is scanned over a large area, there will be some positions near the edge of the field where the conditions for diffraction are not met. This will result in lost intensity which could result in misinterpretation of the map. In practice, the effect is not noticeable provided the magnification is 500x or above.
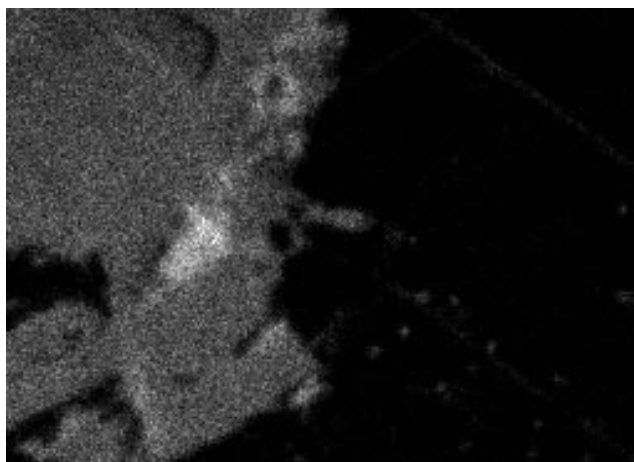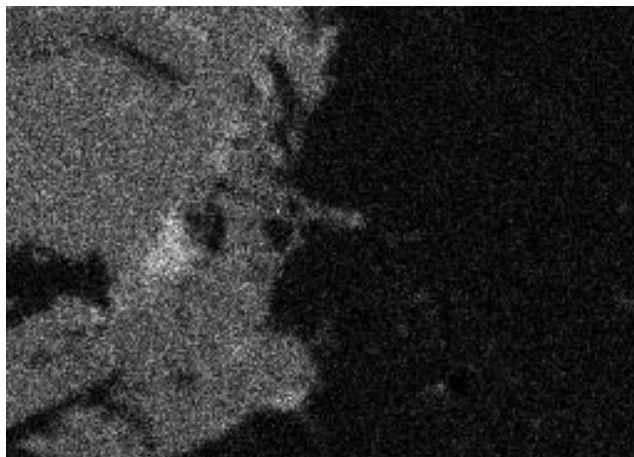

Figure 9a – WD map

Figure 9b – ED map

These two maps for aluminum were acquired simultaneously from a geological sample containing silicate minerals

Summary

Although EDS is most commonly used for X-ray microanalysis, there are undeniable benefits in using a wavelength spectrometer to provide increased sensitivity and peak separation.

The increased resolution of WDS allows easy identification of peaks with complete confidence compared with the potential overlaps in the EDS spectrum. Also, WDS can deal with much higher X-ray intensities and achieve detection limits significantly better than EDS, which is important for trace element analysis.

In practice, the techniques of EDS and WDS are complementary. The speed of EDS is used for the initial survey of a sample, and the resolution and dynamic range of WD is used to check for overlaps and increase sensitivity for trace elements.

In the past WDS spectrometers were complex to set up correctly, but modern software now makes WD straightforward. Comparing WD and ED spectra and combining results is now routine and easy.

General References on WDS:

Goldstein, J. I., et al., Scanning Electron Microscopy and X-ray Microanalysis, 2nd ed., Plenum Press, New York (1992).

Scott, V. D., Love, G., and Reed, S. J. B., Quantitative Electron-Probe Microanalysis, 2nd ed., Ellis Horwood Limited, Hemel Hempstead, Hertfordshire, England (1995).

Reed, S. J. B., Electron Probe Microanalysis, 2nd ed., Cambridge University Press (1993).

Chandler, J. A., X-ray Microanalysis in the Electron Microscope, Elsevier/North Holland Biomedical Press, Amsterdam (1977).

Oxford Instruments
Analytical

UK
Halifax Road, High Wycombe
Bucks, HP12 3SE England
Tel: +44 (0) 1494 442255
Fax: +44 (0) 1494 461033
Email: analytical@oxinst.co.uk

Australia
Sydney, N.S.W. 1715
Tel: +61 2 9484 6108
Fax: +61 2 9484 1667
Email: oisydney@ozemail.com.au

Austria
A – 1030 Wien
Tel: +43 (0) 1 710 61 98
Fax: +43 (0) 1 710 61 98
Email: rob.wills@oxinst.at

China
Beijing
Tel: +86 (0) 10 6833 0336/5/4
Fax: +86 (0) 10 6833 0337
Email: oiadmin@oxford-instruments.com.cn

France
Saclay, Cedex
Tel: +33 (0) 1 69 85 25 21/24
Fax: +33 (0) 1 69 41 86 80
Email: analytical-info@oxford-instruments.fr

Germany
Wiesbaden
Tel: +49 (0) 6122 937 176
Fax: +49 (0) 6122 937 178
Email: analytical@oxford.de

Japan
Tokyo
Tel: +81 (0) 3 5245 3591
Fax: +81 (0) 3 5245 4466/4477
Email: yoda@oxford-instruments.ne.jp

Latin America
Clearwater FL
Tel: +1 727 538 7702
Fax +1 727 538 4205
Email: oxford@gate.net

Scandinavia
Link Nordiska AB
Lidigö, Sweden
Tel: +46 8 590 725 50
Fax: +46 8 590 725 58
Email: info@linknord.se
Web: www.linknord.se

Singapore
Tel: +65 6337 6848
Fax: +65 6337 6386
Email: analytical.sales@oxford-instruments.com.sg

USA
Concord MA
Tel: +1 978 369 9933
Toll Free: +1 800 447 4717
Fax: +1 978 369 8287
Email: info@ma.oxinst.com

www.oxford-instruments.com

Ref: OIA/011/B/0502

PATENTS
EP 0325383
EP 0302716
US 4931650
GB 2192091
US 5170229
US 5357110
JP 2557692
JP 2581597
EU 0568351

BSI REGISTERED

UKAS QUALITY MANAGEMENT
003

CERTIFICATE NUMBER FM29142

OXFORD
INSTRUMENTS