An Introduction to Energy-Dispersive and Wavelength-Dispersive X-Ray Microanalysis

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INTRODUCTION

Electron probe X-ray microanalysis techniques – energy-dispersive X-ray spectroscopy (EDS) and wavelength-dispersive X-ray spectroscopy (WDS) – 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.

By contrast, with WDS the spectrum is acquired sequentially as the full wavelength range is scanned. Although it takes longer to acquire a full spectrum, the WDS 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.

ENERGY-DISPERSIVE X-RAY SPECTROSCOPY

An EDS system comprises three basic components that must be designed to work together to achieve optimum results: the X-ray detector or spectrometer, the pulse processor, and the analyzer (Figure 1).

The Energy-Dispersive Spectrometer

The ED spectrometer converts the energy of each individual X-ray into a voltage signal of proportional size. This is achieved through a three stage process. Firstly the X-ray is converted into a charge by the ionization of atoms in a semiconductor crystal. Secondly this charge is converted into the voltage signal by the FET preamplifier. Finally the voltage signal is input into the pulse processor for measurement. The output from the preamplifier is a voltage 'ramp' where each X-ray appears as a voltage step on the ramp. EDS detectors are designed to convert the X-ray energy into the voltage signal as accurately as possible. At the same time electronic noise must be minimized to allow detection of the lowest X-ray energies.

Components of the ED Spectrometer Collimator assembly

The collimator (Figure 1b) provides a limiting aperture through which X-rays must pass to reach the detector. This ensures that only Xrays from the area being excited by the electron beam are detected, and stray X-rays from other parts of the microscope chamber are not included in the analysis.

Electron trap

Electrons that enter the detector cause background artifacts and also overload the measurement chain. The electron trap (Figure 1b) is a pair of permanent magnets that strongly deflect any passing electrons. The trap is only required on detectors with thin polymer windows, as thicker beryllium windows efficiently absorb electrons below 20 keV in energy.

Window

The window (Figure 1b) provides a barrier to maintain vacuum within the detector whilst being as transparent as possible to low energy X-rays. There are two main types of window materials. Beryllium (Be) is highly robust, but strongly absorbs low energy X-rays meaning that only elements from sodium (Na) can be detected. Polymer-based thin windows can be made much thinner than Be windows and therefore are transparent to much lower energy X-rays, many allowing detection of Xrays down to 100 eV. Although these window materials are far less robust, by placing them on a supporting grid they can withstand the pressure difference between the detector vacuum and a vented microscope chamber at atmospheric pressure. The greater transmission of the polymer-based windows means that they have largely replaced Be as the material used for detector windows.

Crystal

The crystal (Figure 1b) is a semiconductor device that through the process of ionization converts an X-ray of particular energy into electric charge of proportional size. To achieve this a charge-free region within the device is created. Two main materials are used for the detecting crystal. The most common is silicon (Si), into which is drifted lithium (Li) to compensate for small levels of impurity. High purity germanium crystals (HPGe) are also used. Si(Li) was the first material used in EDS detectors and remains the most common choice today. HPGe offers performance advantages when measuring higher energy X-rays.

When an incident X-ray strikes the detector

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Figure 1:

Components of an EDS system. (a) The X-ray spectrometer detects and converts X-rays into electronic signals. 6. Cryostat. (b) Detail of the spectrometer arm showing the major components. 1. Collimator assembly. 2. Electron trap. 3. Window. 4. Crystal. 5. Field-effect transistor. (c) Schematic showing geometry of spectrometer arm, specimen and SEM pole piece (w: solid angle; d: distance of detector from specimen; a: take off angle of X-rays). (d) The pulse processor measures the electronic signals to determine the energy of each X-ray detected. (e) The analyzer interprets the X-ray data and displays an X-ray spectrum of the specimen.



Figure 2: Conversion of X-ray signals into a voltage 'ramp' by the EDS detector. (a) Generation of a characteristic X-ray in a sample by electron bombardment. (b) Generation and measurement of electron-hole pairs in the crystal. (c) Circuit diagram of the EDS detector.

crystal its energy is absorbed by a series of ionizations within the semiconductor to create a number of electron-hole pairs. The electrons are raised into the conduction band of the semiconductor and are free to move within the crystal lattice. When an electron is raised into the conduction band it leaves behind a 'hole', which behaves like a free positive charge within the crystal (Figure 2b). A high bias voltage, applied between electrical contacts on the front face and back of the crystal, then sweeps the electrons and holes to these opposite electrodes, producing a charge signal, the size of which is directly proportional to the energy of the incident X-ray.

EDS detectors are available with different sizes of crystals. The crystal size is often measured in area: 5 mm², 10 mm², 30 mm², 50 mm² etc. There is a trade off in performance; normally the larger the crystal, the worse will be its resolution, particularly at low energy.

Field-effect transistor

The field-effect transistor (FET) (Figure 1b) is positioned just behind the detecting crystal. It is the first stage of the amplification process that measures the charge liberated in the crystal by an incident X-ray and converts it to a voltage output.

The charge is converted to a voltage signal by the FET preamplifier (Figure 2c). During operation, charge is built up on the feedback capacitor. There are two sources of this charge, current leakage from the crystal caused by the bias voltage applied between its faces, and the X-ray induced charge that is to be measured. The output from the FET caused by this charge build-up is a steadily increasing voltage 'ramp' due to leakage current, onto which is superimposed sharp steps due to the charge created by each X-ray event (Figure 3a). This accumulating charge has to be periodically restored to prevent saturation of the preamplifier. Therefore at a predetermined charge level the capacitor is discharged, a process called restoration. Restoration can be achieved either by pulsed optical restore where light from an LED is shone onto the FET, or by using direct injection of charge into a specially designed FET.

The noise is strongly influenced by the FET, and noise determines the resolution of a detector particularly at low energies. Low noise is also required to distinguish low energy X-rays such as beryllium from noise fluctuations. Direct charge restoration via the FET introduces less noise than optical restore. At high count rates, the restoration periods limit the maximum output rate and any aftereffects of the restoration will affect pulse measurement. Direct charge restoration via the FET is considerably faster and avoids the aftereffects associated with optical restore so that noise and resolution are less likely to degrade with increasing count rate.

Cryostat

The charge signals generated by the detector are small and can only be separated from the electronic noise of the detector if the noise is reduced by cooling the crystal and FET. Most EDS detectors work at close to liquid nitrogen temperatures (90 K), and are cooled using a reservoir of liquid nitrogen held in a dewar (Figure 1a). The low temperatures required can also be achieved using mechanical cooling devices. However, these are more expensive to build and maintain, particularly if low vibration is essential, and so are normally used only where liquid nitrogen is difficult to obtain. The 'cold finger' that cools the crystal is insulated from the wall of the detector snout by a vacuum. The vacuum is maintained at a low enough level to prevent the condensation of molecules on the crystal.

Properties of X-ray Detectors

An intrinsic problem with all detectors is incomplete charge collection (ICC). If all the electron-hole pairs generated by an X-ray are not swept to the electrical contacts, the charge signal measured by the FET will be lower than expected, and the energy measured lower than the energy of the incident X-ray. This phenomenon is known as incomplete charge collection and results in counts appearing in the spectrum at lower energies than the energy of the X-ray which they represent, typically as a tail on the low-energy side of the peak. All detectors suffer from ICC to some extent. Low energy X-rays have a very shallow depth of penetration and ICC is usually poor near the front contact.

The resolution of a detector is typically specified by its performance using a set of standards such as Mn, F and C. Resolution is guoted as the width of a given peak at half its maximum height (FWHM). The lower the number the better the resolution a detector has and the better it will be at resolving peaks due to closely spaced X-ray lines. Good analytical performance requires good resolution at low energies. Mn resolution (5.9 keV) does not give a reliable indication of resolution at low energies because it is insensitive to ICC and does not separate noise and detector material components. F resolution (0.7 keV) is more sensitive to low energy noise and is a better guide to low energy performance. C resolution accounts for noise and is very sensitive to incomplete charge collection. An excellent resolution at carbon implies good resolution at all energies.



Figure 3: Accurate measurement of the voltage ramp is the role of the pulse processor. (a) Typical output voltage ramp showing events induced by Mn Kα X-rays. (b) Layout of a typical pulse processor showing the measurement and pulse pile-up inspector channels. (c) Output of the measured steps gives an X-ray spectrum showing number of counts versus energy.





A major cause of detector degradation over time is the build up of contaminants that absorb X-rays before they can be detected by the crystal. Common examples include the condensation of oil on the collimator or detector window and ice forming on the face of the crystal. These contaminants will cause preferential absorption and a drop-off in sensitivity for low energy X-rays.

The Role of the Pulse Processor

The charge liberated by an individual X-ray photon appears at the output of the preamplifier as a voltage step on a linearly increasing voltage ramp (Figure 3a). The fundamental job of the pulse processor is to accurately measure the energy of the incoming X-ray, and give it a digital number that is used to add a count to the corresponding channel in the computer (Figure 3b). It must also optimize the removal of noise present on the original X-ray signal. It needs to recognize quickly and accurately a wide range of energies of X-ray events from 110 eV up to 80 keV. It also needs to differentiate between events arriving in the detector very close together in time, otherwise the combination produces the spectrum artefact called pulse pile-up.

Comparing Different Pulse Processors

For accurate and efficient EDS analysis the performance of the pulse processor is as important as the detector. EDS detector specifications typically reveal the best possible performance that the detector can achieve. Any pulse processor will perform its best at very low count rates, when the voltage steps on the ramp are widely spaced and easy to measure. Therefore detector specifications are often quoted at 1000 cps. However, this count rate is well below what is required for efficient analysis and only the best designs of pulse processor will maintain good and stable detector performance as the input count rate is varied.

How does performance change when the count rate is increased? At more commonly used input rates between 2000 and 10000cps, processors may not be able to maintain the best resolution if resolution degrades with count rate, or process time is shortened to achieve a useful acquisition rate. Therefore one useful measure of how an EDS hardware system will perform is the resolution achieved when the input rate is at least 2500cps, and the acquisition rate is below the maximum for the process time chosen.

Figure 4:

Spectra collected from pure silicon at 1000, 2500, 5000 and 10000 cps input rates using a digital pulse processor measuring at the same process time. Even when displayed at 5 eV per channel no change in resolution or position can be seen for these four spectra.

Modern EDS software is designed to give reliable automatic identification of X-ray peaks and accurate standardless analysis.

This is a relatively straightforward task when peaks are well separated, but for overlapped peaks where there is no clear valley between the peaks, accurate energy calibration is vital. Some systems may appear to have stable performance with count rate because peaks do not move more than 5eV and X-ray line markers are always in the correct channel at 10eV/channel. However, when quantifying peaks about 35 eV apart (e.g. Si K α and W M α) only a 4 eV shift in energy calibration can introduce a 10 weight% error. If the resolution also varies and the width of peaks is wrongly predicted by the software then larger errors may occur.

The best method to test how energy calibrations and resolutions change over a useful operating count rate range, and how well these changes are compensated, is to analyze real samples at a useful range of input rates, for example 1000, 2500, 5000 and 10000 cps. By doing this the effect of any variation on the ability of a system to perform reliable analysis can be tested. Figure 4 shows four spectra collected from pure silicon at different input rates using a digital pulse processor where count rate stability is good.

WAVELENGTH-DISPERSIVE X-RAY SPECTROSCOPY

A WDS system comprises three basic components that must be designed to work together to achieve optimum results: an X-ray spectrometer, measurement electronics and analyzer software.



Wavelength-dispersive X-ray spectrometer.

The Wavelength-Dispersive Spectrometer

The WD spectrometer (Figure 5) 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 are 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 (Figures 5 and 6).

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

Several different diffracting crystals with different crystal lattice spacings (*d*) 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 lithium fluoride, pentaerythritol, and thallium acid phthalate.

Low energy (long wavelength) X-rays require larger *d*-spacing for diffraction and LSM (layered synthetic microstructure) crystals are often used for this purpose, e.g. W-Si, Ni-C and Mo-B₄C. 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.

Detectors

Detectors used in WDS are usually of the gas proportional counter type. 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 pho-



Figure 6: Rowland circle and Johansson geometry of a WD spectrometer.

ton that started the process. Electronic pulse height analysis is subsequently performed on the pulses to filter out noise.

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 (Figure 6). 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.

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.

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.

Resolution Comparison of EDS and WDS

Figure 7 shows how the improved resolution of WDS makes peak identification easy. The WD spectrum for MoS₂ has been acquired from an INCAWave spectrometer using INCAEnergy+ 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 the molybdenum L α line at 2.293 keV is severely overlapped by sulfur K α at 2.307 keV, but the WD spectrum (in blue) clearly resolves these lines.

Qualitative Microanalysis

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.

Figure 8a shows the ED spectrum from an alloy containing 0.15 wt% 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 (Figure 8b), the improvement in peak to background ratio means that there is no doubt that Si is present.

Quantitative Microanalysis

Figure 9 is an X-ray spectrum of a nickel-based superalloy containing AI, Ti, Cr, Co, Ta, W, Re and Mo in addition to Ni.

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

Combined ED/WD analysis is a very practical way of achieving reliable quantitative analysis.



Figure 9: Quantitative ED and WD microanalysis of nickel-based super alloy.





Figure 8:

Qualitative EDS and WDS analysis of alloy with 0.15 wt% silicon. (a) ED spectrum. (b) WD spectrum of silicon region.

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.

Conclusions

Although EDS is most commonly used for Xray 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.

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Figure 7: Comparison of EDS and WDS microanalysis of MoS₂.