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| ME 228: MATERIALS AND STRUCTURES |
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| ENERGY DISPERSIVE XRAY SPECTROSCOPY |

SUBMITTED BY

ANIRUDH R

ASHLIN AUGUSTY

A SANJAYAN

**ENERGY DISPERSIVE XRAY SPECTROSCOPY**

**1. Introduction**

***1.1 Principles of the technique***

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a

focused beam of electrons to obtain a localized chemical analysis. All elements from atomic

number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements (Z < 10). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition.

By scanning the beam in a television-like raster and displaying the intensity of a selected

X-ray line, element distribution images or 'maps' can be produced. Also, images produced by

electrons collected from the sample reveal surface topography or mean atomic number

differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, but can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. There is thus a considerable overlap in the functions of these instruments.

***1.2 Accuracy and sensitivity***

X-ray intensities are measured by counting photons and the precision obtainable is

limited by statistical error. For major elements it is usually not difficult to obtain a precision

(defined as 2σ) of better than ± 1% (relative), but the overall analytical accuracy is commonly nearer ± 2%, owing to other factors such as uncertainties in the compositions of the standards and errors in the various corrections which need to be applied to the raw data. As well as producing characteristic X-ray lines, the bombarding electrons also give rise to a continuous X-ray spectrum, which limits the detachability of small peaks, owing to the presence of 'background'. Using routine procedures, detection limits are typically about 1000 ppm (by weight) but can be reduced by using long counting times

***1.3 Spatial resolution***

Spatial resolution is governed by the penetration and spreading of the electron beam in the specimen (Figure 1). Since the electrons penetrate an approximately constant mass, spatial resolution is a function of density. In the case of silicates (density about 3 g cm-3), the nominal resolution is about 2 μm under typical conditions, but for quantitative analysis a minimum grain size of several micrometers is desirable.

Better spatial resolution is obtainable with ultra-thin (~100 nm) specimens, in which the beam does not have the opportunity to spread out so much. Such specimens can be analyzed in a transmission electron microscope (TEM) with an X-ray spectrometer attached, also known as an analytical electron microscope, or AEM.



**Figure 1** Simulated trajectories of electrons (energy 20 keV) in Si (rectangle = 1x2μm.

***1.4 Sample preparation***

Since the electron probe analyses only to a shallow depth, specimens should be well

polished so that surface roughness does not affect the results. Sample preparation is essentially as for reflected light microscopy, with the provision that only vacuum compatible materials must be used. Opaque samples may be embedded in epoxy resin blocks. For transmitted light viewing, polished thin sections on glass slides are prepared. In principle, specimens of any size and shape (within reasonable limits) can be analyzed. Holders are commonly provided for 25mm (1") diameter round specimens and for rectangular glass slides. Standards are either mounted individually in small mounts or in batches in normal sized mounts.

Many samples are electrically non-conducting and a conducting surface coat must be

applied to provide a path for the incident electrons to flow to ground. The usual coating material is vacuum-evaporated carbon (~10nm thick), which has a minimal influence on X-ray intensities on account of its low atomic number, and (unlike gold, which is commonly used for SEM specimens) does not add unwanted peaks to the X-ray spectrum. However, steps should be taken to maintain as constant a thickness as possible.

**2. X-ray spectroscopy**

**2.1 *Atomic structure***

According to the Rutherford-Bohr model of the atom. Electrons orbit around the positive nucleus. In the normal state the number of orbital electrons equals the number of protons in the nucleus (given by the atomic number, Z). Only certain orbital states with specific energies exist and these are defined by quantum numbers (see standard texts). With increasing Z, orbits are occupied on the basis of minimum energy, those nearest the nucleus, and therefore the most tightly bound, being filled first. Orbital energy is determined mainly by the principal quantum number (n). The shell closest to the nucleus (n = 1) is known as the K shell; the next is the L shell (n = 2), then the M shell (n = 3), etc. The L shell is split into three subshells designated L1, L2 and L3, which have different quantum configurations and slightly different energies (whereas the K shell is unitary). Similarly, the M shell has five subshells. This model of the inner structure of the atom is illustrated in Figure 2.

The populations of the inner shells are governed by the Pauli exclusion principle, which states that only one electron may possess a given set of quantum numbers. The maximum population of a shell is thus equal to the number of possible states possessing the relevant principal quantum number. In the case of the K shell this is 2, for the L shell 8, and for the M shell 18. Thus for Z ≥ 2 the K shell is full, and for Z ≥10 the L shell is full.

Electrons occupying outer orbits are usually not directly involved in the production of X-ray

spectra, which are therefore largely unaffected by chemical bonding etc.

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 **Figure 2.** Schematic diagram of inner atomic electron shells.

**2.2 *Origin of Characteristic X-rays***

'Characteristic' X-rays result from electron transitions between inner orbits, which are normally full. An electron must first be removed in order to create a vacancy into which another can 'fall' from an orbit further out. In electron probe analysis vacancies are produced by electron bombardment, which also applies to X-ray analysis in the TEM. X-ray lines are identified by a capital Roman letter indicating the shell containing the inner vacancy (K, L or M), a Greek letter specifying the group to which the line belongs in order of decreasing importance α, β**,** etc.), and a number denoting the intensity of the line within the group in descending order (1, 2, etc.). Thus the most intense K line is Kα**1** (The less intense Kα**2** line is usually not resolved, and the combined line is designated Kα**1,2** or just Kα). The mostintense L line is Lα**1.** Because of the splitting of the L shell into three subshells, the L spectrum is more complicated than the K spectrum and contains at least 12 lines, though many of these are weak.

Characteristic spectra may be understood by reference to the energy level diagram

(Figure 3), in which horizontal lines represent the energy of the atom with an electron removed from the shell (or subshell) concerned. An electron transition associated with X-ray emission can be considered as the transfer of a vacancy from one shell to another, the energy of the X-ray photon being equal to the energy difference between the levels concerned. For example, the Kα line results from a K-L3 transition (Figure 3).

Energies are measured in electron volts (eV), 1 eV being the energy corresponding to a

change of 1 V in the potential of an electron (= 1.602 x10**-19** J). This unit is applicable to both Xrays and electrons. X-ray energies of interest in electron probe analysis are mostly in the range 1- 10 keV.

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 **Figure 3**. Energy level diagram for Ag showing transitions responsible for main K and L

emission lines (arrows show direction of vacancy movement), energy of emission line indicated in brackets.

The 'critical excitation energy' (Ec) is the minimum energy which bombarding electrons (or other particles) must possess in order to create an initial vacancy. Figure 4 shows the dependence of Ec on Z for the principal shells. In electron probe analysis the incident electron energy (E0) must exceed Ec and should preferably be at least twice E**c** to give reasonably high excitation efficiency. For atomic numbers above about 35 it is usual to change from K to L lines to avoid the need for an excessively high electron beam energy (which has undesirable implications with respect to the penetration of the electrons in the sample, and in any case may exceed the maximum available accelerating voltage).

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**Figure 4.** Energies of principal characteristic lines (\_) and their excitation energies (----).

**2.3 *Wavelengths, energies and intensities of X-ray lines***

The preceding discussion treated X-rays as photons possessing a specific energy (E).

Sometimes it is more appropriate to describe X-rays by their wavelength (λ), which is related to energy by the expression:

 E λ = 12396

where E is in electron volts and λ is in **Å**, where 1**Å** = 10-10m.

Since X-ray lines originate in transitions between inner shells, the energy of a particular

line shows a smooth dependence on atomic number, varying approximately as Z2 (Moseley's law). The energies of the Kα**1**, Lα**1** and Mα**1** lines are plotted against Z in Figure 4. The total X-ray intensity for a particular shell is divided between several lines. In the case

of the K shell, more than 80% of the total intensity is contained in the combined Kα**1,2** line

(Figure 5). The relative intensity of the Kβ line decreases with decreasing atomic number, in

accordance with the electron occupancies of the relevant energy levels.



**Figure 5** Typical K spectra.

**2.4 *The continuous spectrum***

Electron bombardment not only produces characteristic X-ray lines resulting from

electron transitions between inner atomic shells but also a continuous X-ray spectrum or

(continuum', covering all energies from zero to E0 (the incident electron energy). This continuum arises from interactions between incident electrons and atomic nuclei. The intensity of the continuum decreases monotonically with increasing X-ray energy, and is approximately proportional to Z. The main significance of the continuum in the present context is that it contributes the 'backgrounds' upon which characteristic elemental lines are superimposed.

**3**. **Energy-dispersive spectrometers**

Energy-dispersive spectrometers (EDSs) employ pulse height analysis: a detector giving output pulses proportional in height to the X-ray photon energy is used in conjunction with a pulse height analyzer (in this case a multichannel type). A solid state detector is used because of its better energy resolution. Incident X-ray photons cause ionization in the detector, producing an electrical charge, which is amplified by a sensitive preamplifier located close to the detector. Both detector and preamplifier are cooled with liquid nitrogen to minimize electronic noise. Si(Li) or Si drift detectors (SDD) are commonly in use.

**3.1 *Energy resolution***

The ED spectrum is displayed in digitized form with the x-axis representing X-ray energy (usually in channels 10 or 20 eV wide) and the y-axis representing the number of counts per channel (Figure 6). An X-ray line (consisting of effectively mono-energetic photons) is broadened by the response of the system, producing a Gaussian profile. Energy resolution is defined as the full width of the peak at half maximum height (FWHM). Conventionally, this is specified for the Mn Kα peak at 5.89 keV. For Si(Li) and SDD detectors, values of 130-150 eV are typical (Ge detectors can achieve 115eV). The resolution of an EDS is about an order of magnitude worse than that of a WDS, but is good enough to separate the K lines of neighboring elements (Figure 6).



**Figure 6** ED spectrum of jadeite (part), showing K peaks of Na, A1 and Si.

**3.2 *Dead time and throughput***

In processing the pulses from a solid state detector prior to pulse-height analysis, it is

necessary to use certain integrating time to minimize noise. The system consequently has a

specific 'dead time', or period after the arrival of an X-ray photon during which the system is

unresponsive to further photons. This limits the rate at which pulses can be processed and added to the recorded spectrum. ‘Throughput' passes through a maximum above which it decreases with further increases in input count rate. The maximum throughput rate is a function of the integration time and the design of the system.

Energy resolution is determined partly by the statistics of the detection process and partly by noise fluctuations in the baseline upon which the pulses are superimposed. The longer the integration time, the more the noise is smoothed out, and the better the energy resolution. There is thus a 'tradeoff' between resolution and throughput. Hitherto, maximum throughput rates have been typically in the region of 20 000 counts s-1 for Si(Li) and 100 000 counts s-1 and above for SDD.

**4 Qualitative analysis**

**4.1 *Line identification***

The object of qualitative analysis is to find what elements are present in an 'unknown' specimen by identifying the lines in the X-ray spectrum using tables of energies or wavelengths. Ambiguities are rare and can invariably be resolved by taking into account additional lines as well as the main one.

**4.2 *Qualitative ED analysis***

The ED spectrometer is especially useful for qualitative analysis because a complete

spectrum can be obtained very quickly. Aids to identification are provided, such as facilities for superimposing the positions of the lines of a given element for comparison with the recorded spectrum (Figure 7).



**Figure 7** Line markers for S K and Ba L lines in the ED spectrum of barite.

Owing to the relatively poor resolution, there are cases where identification may not be

immediately obvious. An example showing unresolved S K and Pb M lines is given in Figure

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 **Figure 8** Unresolved peaks in an ED spectrum (PbS sample).

**5 Quantitative analysis – experimental**

***5.1 Counting statistics***

X-ray intensities are measured by counting pulses generated in the detector by X-ray

photons, which are emitted randomly from the sample. If the mean number of counts recorded in a given time is *n*, then the numbers recorded in a series of discrete measurements form a Gaussian distribution with a standard deviation (σ) of *n*1/2/*n*. A suitable measure of the statistical error in a single measurement is ±2σ. It follows that 40 000 counts must be collected to obtain a 2σ precision of ± 1% (relative). Such statistical considerations thus dictate the time required to measure intensities for quantitative analysis.

**5.2 *Choice of conditions***

The optimum choice of accelerating voltage is determined by the elements present in the specimen. The accelerating voltage (in kV) should be not less than twice the highest excitation energy Ec (in keV) of any element present, in order to obtain adequate intensity. For instance, in silicates, the element with the highest atomic number is commonly Fe, which also has the highest excitation energy (7.11 keV), hence the accelerating voltage should be at least 15 kV. Line intensities increase with accelerating voltage, but so does electron penetration, making spatial resolution worse and increasing the absorption suffered by the emerging X-rays.

The other important variable selected by the user is beam current. The higher the current the higher the X-ray intensity, but there are practical limitations. Some samples are prone to beam damage, which necessitates the use of a low current. In the case of ED analysis, the limited throughput capability of the system has to be considered and a current as low as a few nA may be appropriate.

**6 Quantitative analysis - data reduction**

**6.1 *Castaing's approximation***

As shown by Castaing (1951), the relative intensity of an X-ray line is approximately

proportional to the mass concentration of the element concerned. This relationship is due to the fact that the mass of the sample penetrated by the incident electrons is approximately constant regardless of composition. (The electrons are decelerated by interactions with bound electrons and the number of these per atom is equal to the atomic number, which, in turn, is approximately proportional to the atomic weight). Given this approximation, an 'apparent concentration' (C') can be derived using the following relationship:

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*Cst* where Isp and Ist are the intensities measured for specimen and standard respectively, and Cst is the concentration of the element concerned in the standard. To obtain the true concentration, certain corrections are required.

**7 Emerging technology**

There is a trend towards a newer EDS detector, called the [silicon drift detector](http://en.wikipedia.org/wiki/Silicon_drift_detector) (SDD). The SDD consists of a high-resistivity silicon chip where electrons are driven to a small collecting anode. The advantage lies in the extremely low capacitance of this anode, thereby utilizing shorter processing times and allowing very high throughput. Benefits of the SDD include:

1. High count rates and processing,
2. Better resolution than traditional Si(Li) detectors at high count rates,
3. Lower dead time (time spent on processing X-ray event),
4. Faster analytical capabilities and more precise X-ray maps or particle data collected in seconds,
5. Ability to be stored and operated at relatively high temperatures, eliminating the need for [liquid nitrogen](http://en.wikipedia.org/wiki/Liquid_nitrogen) cooling.

Because the capacitance of the SDD chip is independent of the active area of the detector, much larger SDD chips can be utilized (40 mm2 or more). This allows for even higher count rate collection. Further benefits of large area chips include:

1. Minimizing SEM beam current allowing for optimization of imaging under analytical conditions,
2. Reduced sample damage and
3. Smaller beam interaction and improved spatial resolution for high speed maps.

In recent years, a different type of EDS detector, based upon a [micro-calorimeter](http://en.wikipedia.org/wiki/Calorimeter), has become commercially available. This new model allegedly has the simultaneous detection capabilities of EDS as well as the high spectral resolution of WDS. The EDS micro-calorimeter relies highly on two components: an absorber, and a [thermistor](http://en.wikipedia.org/wiki/Thermistor). The former absorbs X-rays emitted from the sample and converts this energy into heat; the latter measures the subsequent change in temperature due to the influx of heat (in essence, a [thermometer](http://en.wikipedia.org/wiki/Thermometer)). The EDS micro-calorimeter has suffered from a number of drawbacks; including low count rates, poor collection efficiencies and small detector areas. The count rate is hampered by its reliance on the [time constant](http://en.wikipedia.org/wiki/Time_constant) of the calorimeter’s electrical circuit. The collection efficiency is a function of the absorber material and remains to be optimized. The detector area must be small in order to keep the [heat capacity](http://en.wikipedia.org/wiki/Heat_capacity) as small as possible and maximize thermal sensitivity ([resolution](http://en.wikipedia.org/wiki/Optical_resolution)).