Energy Dispersive X-ray Spectrometry and X-ray Microanalysis
X-ray Microanalysis

- X-ray Microanalysis in the electron microscope is the process of using characteristic x-rays, generated in a specimen by the electron beam, to determine the element composition of the specimen.
X-ray Microanalysis

- X-rays were discovered in 1895 by Wilhelm Roentgen (German scientist).
- Henry Moseley (British scientist) in 1914 showed the relationship between wavelength of characteristic x-rays emitted from an element and its atomic number Z. \( Z = \lambda^{-1/2} \)
- Energy is related to wavelength. \( E = \frac{hc}{\lambda} \) or \( E = \frac{12.4}{\lambda} \)
- From there it was found that energy levels in electron shells varied in discrete fashion with atomic number.
- By the 1920s characteristic patterns had been recorded for most elements.
- X-ray spectrometers - x-rays generating x-rays - large area.
- 1940s - Electron microanalyzer - electrons generating x-rays.
X-ray Microanalysis

• In 1948 a prototype wavelength dispersive spectrometer was developed.
• In 1949 the first microprobe was built by Raymond Castaing, the father of x-ray microanalysis.
• 1956 - first commercial Electron Probe Microanalyzer (EPMA) was developed in France - static electron probe.
• 1956 - scanning EPMA developed in England.
• Late 1960s development of solid (SiLi) state EDS detectors.
• Late 1960s EDS detector attached to an SEM.
X-ray Microanalysis

• There are two kinds of x-ray microanalysis.
  – Wavelength Dispersive Spectrometry (WDS) uses the wavelength of x-rays.
  – Energy Dispersive Spectrometry (EDS) uses the energy of the x-rays.
• They are related by the formulas:
  \[ E = \frac{hc}{\lambda} \]
  \[ E = \frac{12.396}{\lambda} \]
• We will discuss only EDS.
X-ray Microanalysis

- Incident electron beam
- Ejected electron
- M shell
- White radiation (continuum)
- X-ray (characteristic radiation)
- Nucleus
X-ray Microanalysis - Electron Transitions
X-ray Microanalysis

[Graph depicting energy levels and atomic numbers for various elements]
Critical Excitation Energy

• The orbital electron of an atom is held in place by something called its binding energy.
• To ionize an atom, the energy of the incoming electron must be great enough to knock out the orbital electron.
• That is, the energy of the electron beam must be greater than the binding energy of the shell.
• This beam energy is called the Critical Excitation Energy.
• Each shell and subshell has its own binding energy; therefore there are many Critical Excitation Energies.
• Inner shells have lower binding energies than outer shells.
A Titanium EDS Spectrum
X-ray Microanalysis
320 stainless steel with titanium inclusion
320 stainless steel with titanium inclusion
320 stainless steel with titanium inclusion
X-ray Mapping
How are elements distributed?

• Start with a backscatter image to obtain atomic number contrast.

• “Prospect” by probing different gray levels with EDS in the spot mode to find the elements in the image.

• Designate which elements you want to map.
X-ray Mapping

How are elements distributed?
Energy Dispersive X-Ray Spectrometer

EDX detector and its operation principle:

**Figure 5.21.** (a) Physical appearance of a retractable detector and associated preamplifier electronics. (b) Detail of Si(Li) mounting assembly.
• The lithium-drifted silicon crystal is mounted on a cold finger connected to a liquid-nitrogen reservoir stored in the Dewar.
• Low temperature is needed to limit the mobility of the lithium ions initially introduced in the silicon crystal and to reduce the noise.
• Since the detecting crystal is light sensitive, it is essential to block visible radiation by using an opaque window. Windowless and ultra thin-window EDS can be used if the specimen chamber is light tight.
• The window is also used to seal the detector chamber under vacuum condition and both to prevent contamination from the specimen region (especially when the specimen chamber is brought to air pressure) and to maintain the low temperature essential for reducing noise.
• As we can see that under no conditions should the bias be applied to a non-cooled detector.
Figure 5.20. Schematic representation of an energy-dispersive spectrometer and its associated electronics.
The Detection Process

• When x-ray photons are captured by the detection crystal they create electron-hole pairs. These electron-hole pairs are formed charge pulse by the applied bias and they are further converted to voltage pulse by a charge-to-voltage converter (preamplifier).

• The signals further amplified and shaped by a linear amplifier and finally passed to a computer x-ray analyzer (CXA), where the data is displayed as a histogram of intensity by voltage (energy).

• The key to understanding how an energy-dispersive X-ray spectrometer (EDS) works is to recognize that each voltage pulse is proportional to the energy of the incoming x-ray photon.
X-ray Detection Process in the Si(Li) Detector

Figure 5.22. The x-ray detection process in the Si(Li) detector.
Artifacts of the Detection process

Six types of major artifacts may possibly be generated during the detecting process:

5. Peak Broadening
6. Peak distortion
7. Silicon x-ray escape peaks
8. Sum peaks
9. Silicon and gold absorption edges
10. Silicon internal fluorescence peak
1. Peak Broadening:

- The natural width of an x-ray peak is energy dependent and is on the order of 2-10 eV measured using the full width at half the maximum of the peak intensity (FWHM).

- The measured peak width from the Si(Li) spectrometer is degraded by the convolution of the detector-system response function with the natural line width to a typical value of 150 eV for Mn (manganese) or 2.5% of the peak energy.

- For manganese Kα₁ radiation (5.898 keV), the natural FWHM is approximately 2.3 eV, which makes the natural width about 0.039% of the peak energy.
Figure 5.34. Gaussian peak shape representation for x-ray peaks above 1 keV.
Fig. 5.35. Redistribution of peak counts for Mn Kα with 150-eV resolution at FWHM.
• **Key Points**

• The immediate consequence of the peak broadening associated with the detection process is a reduction in the height of the peak, as compared to the natural peak, and an accompanying decrease in the peak-to-background ratio as measured at a given energy.

• A related effect is shown in Fig. 5.36, which is a computer simulation of a series of peaks containing equal numbers of counts measured at different energies. In this case, the variation of FWHM results in a variation of peak heights. This suggests the potential danger of estimating relative elemental concentrations by comparing peak heights between elements.
Figure 5.36. Resolution and peak intensity as a function of energy; Mn $K\alpha$ has a resolution of 150 eV.
2. Peak Distortion – Deviation from a Gaussian shape on the low-energy side of a peak.

- The collection of charge carriers created in certain regions of the detector near the faces and sides is imperfect due to trapping and recombination of the electron-hole pairs, leading to a reduction in measured value for the incident photon. The resulting distortion of the low-energy side of the peak is known as incomplete charge collection.

- As shown in Fig. 5.37, for example, comparing the chlorine K\(\alpha\) and potassium K\(\alpha\) peaks, the chlorine K\(\alpha\) peak (overlapped with Cl K\(\beta\)) shows more distortion than that of potassium, which are separated by an atomic number difference of only 2.
Figure 5.37. EDS spectrum of KCl illustrating peak overlap: K $K\alpha$, K $K\beta$, are nearly resolved. The solid line is a Gaussian fit to the data points. The shaded area represents the deviation caused by incomplete charge collection.
3. Silicon X-Ray Escape Peaks:

• The generation of a photoelectron leaves the silicon atom in the detector in an ionized state. In the case of K-shell ionization, relaxation of an L-shell electron results in the emission of either a Si K-series x-ray photon or an Auger electron. But most Auger electrons are reabsorbed due to their low energy.

• If the Si K x-ray photon (generated during the de-excitation) escapes from the detector, the total number of electron-hole pairs generated will depend on the energy:

\[ E' = (E - E_{\text{SiK} \alpha}) = (E - 1.74 \text{ keV}) \] instead of \( E \)

Where \( E \) is the total deposited energy, \( E_{\text{SiK} \alpha} \) (1.74 keV) is the silicon K\( \alpha \) x-ray photon energy.
• The reduction in the number of electron-hole pairs produced when an escape event takes place leads to the creation of an artifact peak called an “escape peak”.

• The escape peak appears at an energy equal to the energy of the parent line minus that of the silicon Kα, 1.74 keV.

• In principle, both Si Kα and Si Kβ escape peaks are formed, but the probability for Kβ formation is about 2% of the Kα; hence only one escape peak is usually observed per parent peak.

• Silicon x-ray escape peaks cannot occur for radiation below the excitation energy of the silicon K shell (1.838 keV).

• Escape peaks are illustrated in Fig. 5.38 and 5.39.
**Figure 5.38.** EDS spectrum derived from $^{55}$Fe radioactive source (emits Mn $K$ radiation). The background shelf is easily observable at energies below Mn $K\alpha$ down to the threshold at 300 eV. The Mn $K\alpha$ and $K\beta$ silicon escape peaks are noted. Extraneous characteristic peaks from the source holder are observed.
**Figure 5.39.** Electron-excited EDS spectrum of titanium. The Ti $K\alpha$ and $K\beta$ silicon x-ray escape peaks and the 2 $K\alpha$ and ($K\alpha + K\beta$) sum peaks are noted. Extraneous peaks from the specimen chamber are also observed. Hatched area is contribution due to incomplete charge collection.
Figure 5.28. (a) Electron-excited EDS spectrum of silicon showing sum peak. (b) Electron-excited spectrum of magnesium showing pileup continuum and sum peaks.
4. Absorption Edges

- The X-ray photons emitted from the specimen have to penetrate several layers of window materials before it arrives in the active part of the detector. During this process, absorption occurs.

- In the case of 7.6 μm beryllium protective windows, nearly all x-rays below about 600 eV are eliminated due to absorption effects.

- Above 2 keV, almost all x-rays are transmitted. Between these limits, the absorption increases with decreasing energy such that at 1.5 keV about 70% of the x-rays are transmitted, while for an energy of 1 keV, the transmission is 45%.

- It is important to realize that photoelectric absorption refers to a process in which x-rays are diminished in number but do not lose energy; thus, the energies of the observed spectral line are not altered while passing through the windows.
Figure 5.41. (a) Transmission curve for a "windowless" detector with a 0.01-\(\mu\)m Au contact and a 0.1-\(\mu\)m silicon dead layer. The energies of the light element K lines are shown along the energy axis. (b) Transmission curve for several commercially available window materials. The energies of the light-element K lines are shown along the energy axis. The actual transmission of x rays into the active part of the detector is a combination of the transmission characteristics shown in parts (a) and (b) of this figure. Quantum window = 0.25 \(\mu\)m; diamond window = 0.4 \(\mu\)m.
What is Sum Peak?

If a photon arrives at the detector before the linear amplifier has finished processing the preceding photon a pulse pileup occurs. This effect will appear as an increased output pulse height for the second photon because it is riding on the tail of the first as shown in Fig. 5.24.

Pulse pileup can also appear as a single large pulse representing the combined voltages of two pulses, if the second photon arrives before the pulse from the first has reached its maximum value. In the most extreme case, two photons arrive at the detector almost simultaneously, and the output is a single combined pulse corresponding to the sum of the two photon energies.
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Figure 5.24. EDS main amplifier pulse shapes for different time constants (T.C.).
Figure 5.29. Relationship of output and input count rates for three different values of pulse width and resolution.
6. Internal fluorescence Peak of Silicon

- The photoelectric absorption of x-rays by the silicon dead layer results in the emission of Si K x-rays from this layer into the active volume of the detector. These silicon x-rays, which do not originate in the sample, appear in the spectrum as a small silicon peak, the so called silicon internal fluorescence peak.

- An example of this effect is shown in the spectrum of pure carbon, Fig. 5.42, which also contains a significant silicon absorption edge.

- For many quantitative-analysis situations, this fluorescence peak corresponds to an apparent concentration of approximately 0.2 wt% or less silicon in the specimen.
**Figure 5.42.** Electron-excited EDS spectrum from carbon. The silicon and gold absorption edges are illustrated. The solid line represents a theoretical fit to the continuum. $E_0 = 10$ keV. The silicon peak arises from internal fluorescence.
Figure 5.56. Electron-excited spectrum of carbon from an unsatisfactory detector with a thick silicon dead layer producing a silicon absorption edge of a very significant size.
Figure 5.46. Transmission through three thicknesses of ice, which can easily form on the front surface of many Si (Li) detectors.
Figure 5.49. Possible sources of remote x-ray excitation in an electron-beam–EDS system. Solid lines, electron paths; dashed lines, x-ray paths: (1) Excitation of polepiece; (2) Remote excitation of sample by backscattered electron; (3) Remote excitation of sample by electron scattered by aperture; (4) Remote excitation of sample by x rays produced at aperture.