

Energy Dispersive Spectroscopy on the SEM: A Primer

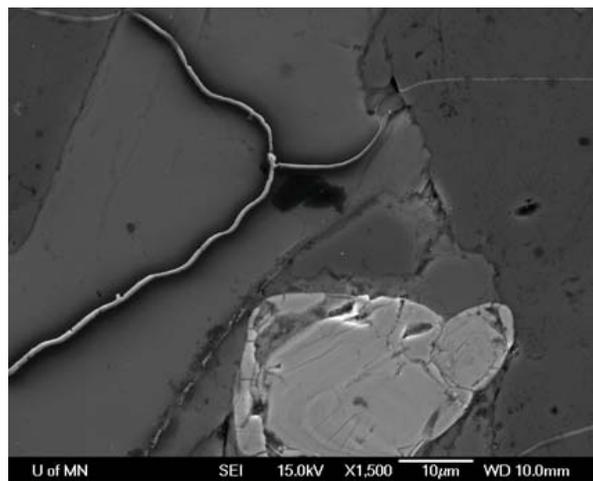
Bob Hafner

This primer is intended as background for the “EDS Analysis on the SEM” course offered by the University of Minnesota’s Characterization Facility. You must learn this material **prior to** the hands-on training sessions. It is also assumed that you have a working familiarity with the content in the “Scanning Electron Microscopy Primer”. Good sources for further information are: “Scanning Electron Microscopy and X-Ray Microanalysis” by Joseph Goldstein et al; and, “X-ray and Image Analysis in Electron Microscopy” by John J. Friel.

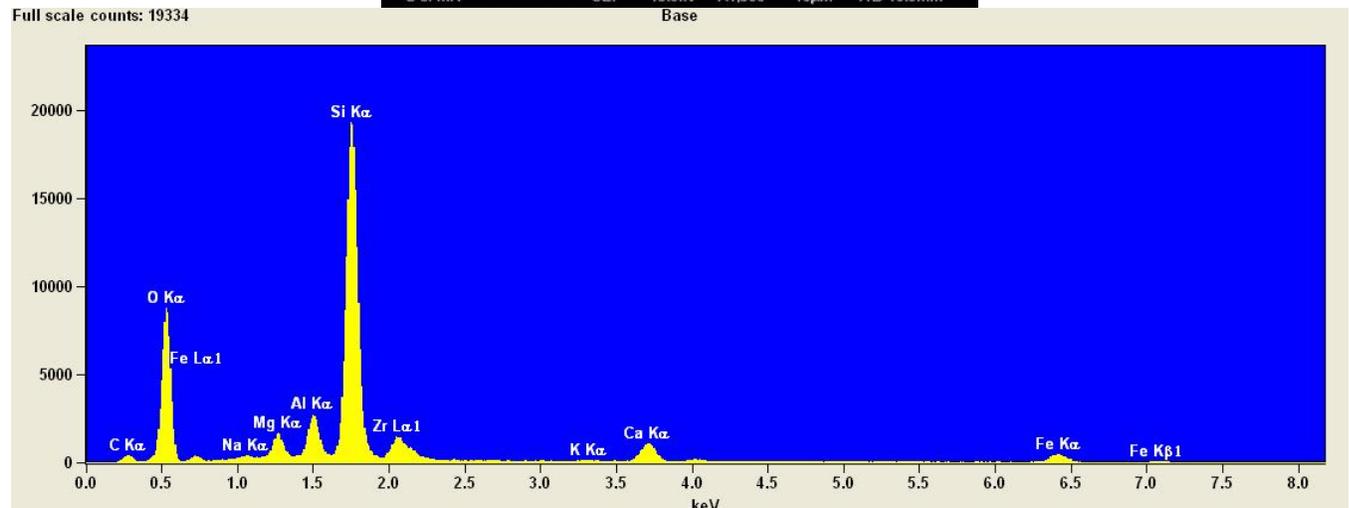
The Big Picture

Backscattered electron images in the SEM display compositional contrast that results from different atomic number elements and their distribution. Energy Dispersive Spectroscopy (EDS) allows one to identify what those particular elements are and their relative proportions (Atomic % for example).

Initial EDS analysis usually involves the generation of an X-ray spectrum from the entire scan area of the SEM. Below is a secondary electron image of a polished geological specimen and the corresponding X-ray spectra that was generated from the entire scan area. The Y-axis shows the counts (number of X-rays received and processed by the detector) and the X-axis shows the energy level of those counts. The EDS software we have, “Noran System Six” (NSS), is quite good at associating the energy level of the X-rays with the elements and shell levels that generated them.

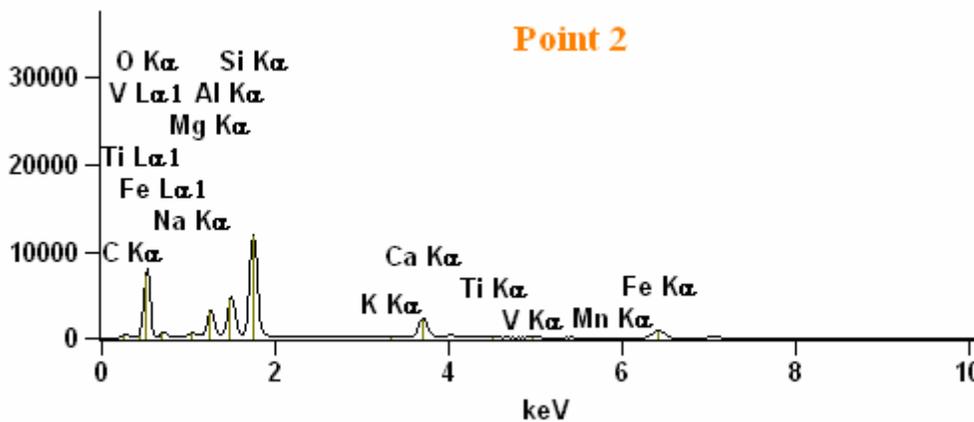
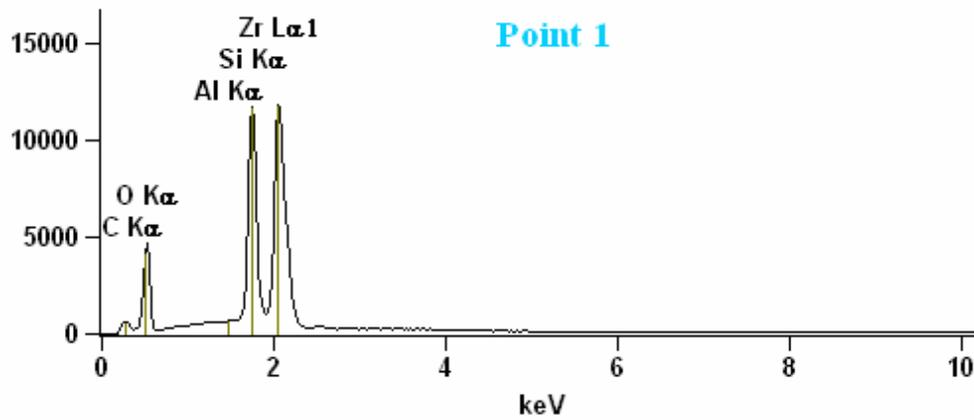
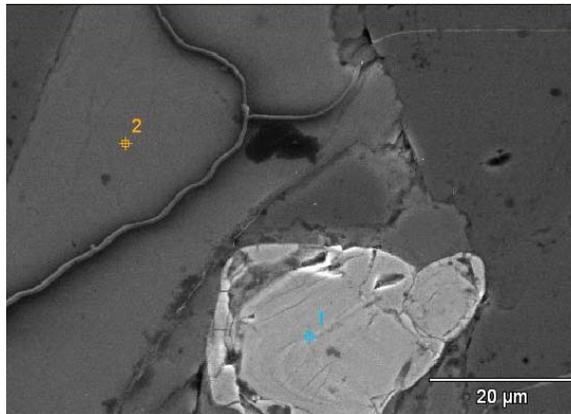


Full scale counts: 19334

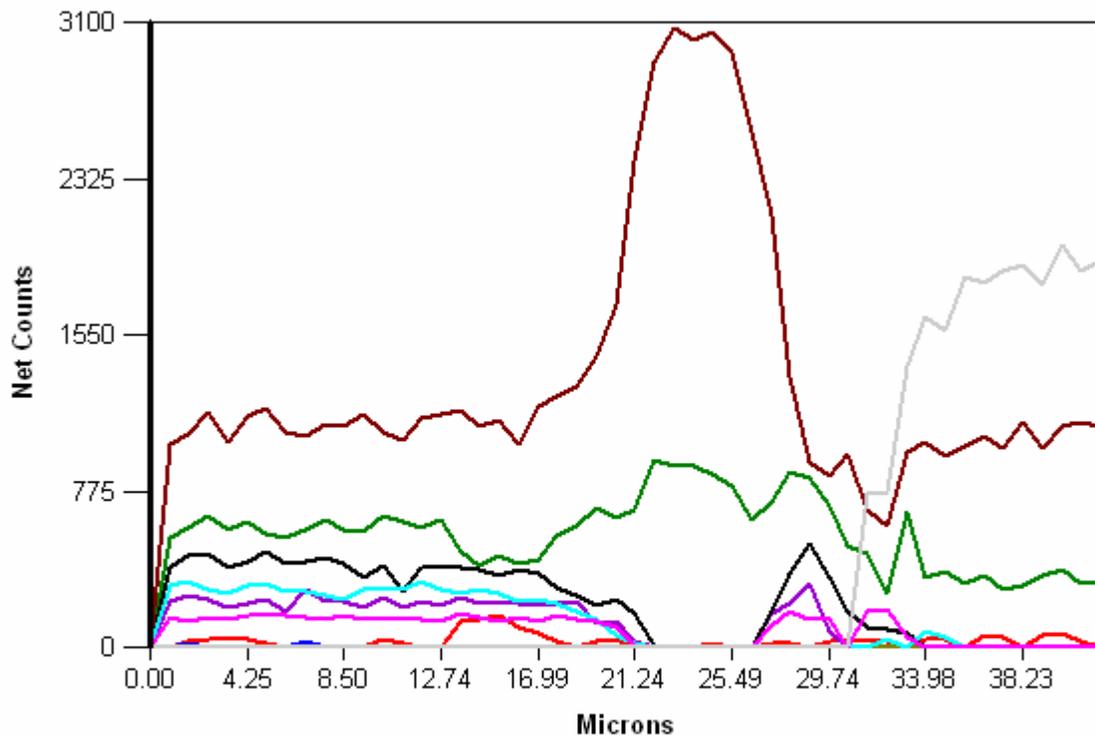
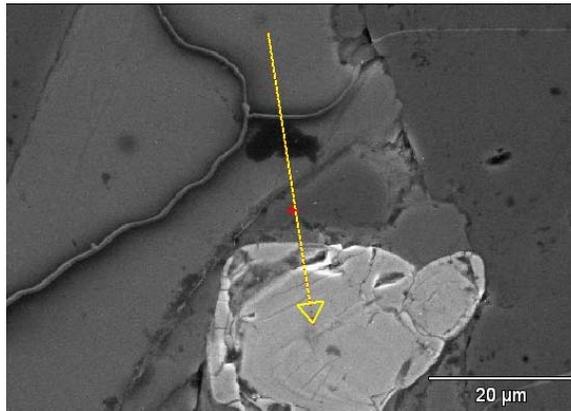


The NSS software allows one to obtain/display elemental data in a number of additional ways. One can:

- keep the electron beam stationary on a spot or series of spots and generate spectra that will provide more localized elemental information.

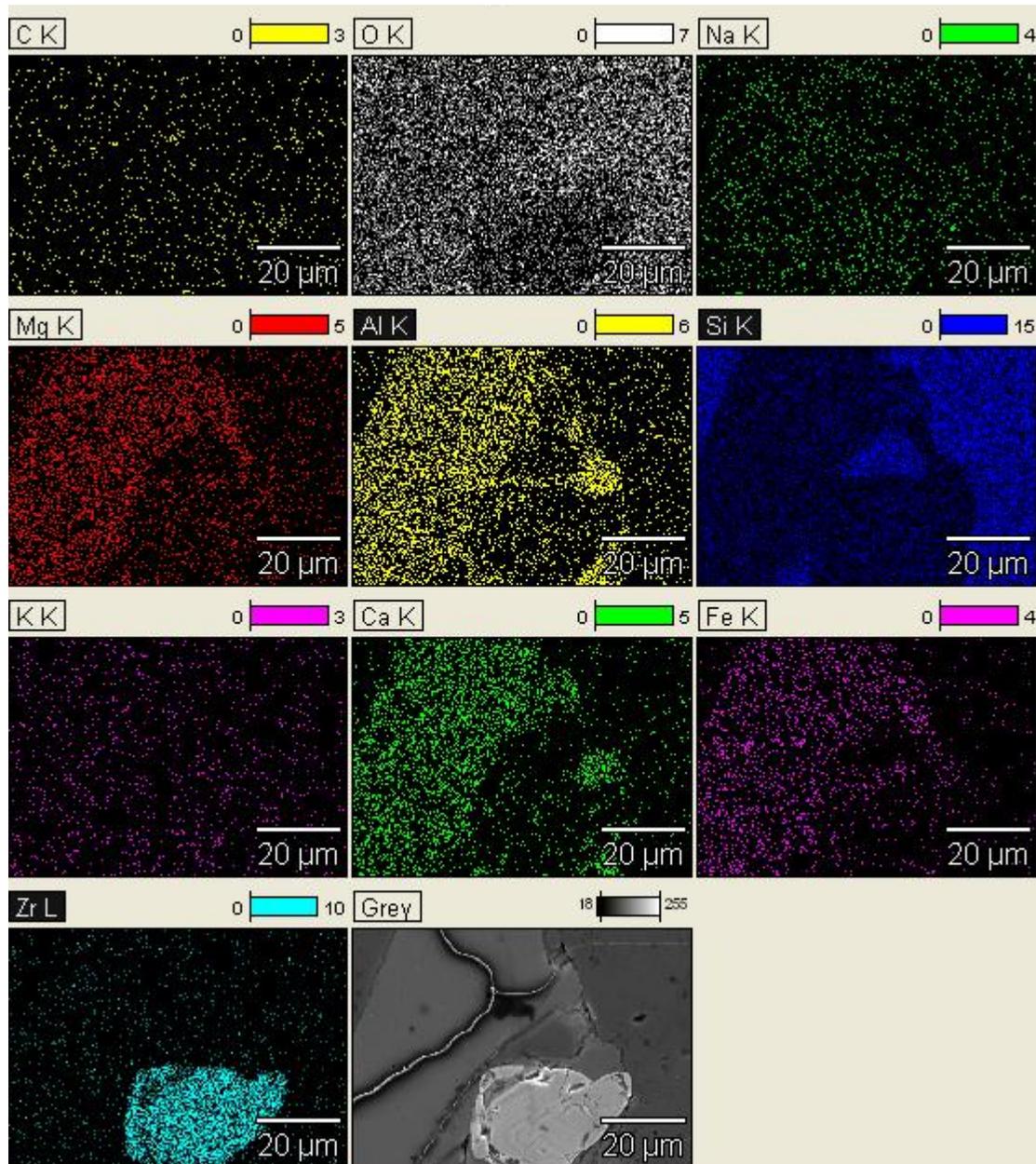


- have the electron beam follow a line drawn on the sample image and generate a plot of the relative proportions of previously identified elements along that spatial gradient.



C K: 0	O K: 0	Na K: 0	Mg K: 0
Al K: 0	Si K: 0	K K: 0	Ca K: 0
Fe K: 0	Zr L: 0		

- map the distribution and relative proportion (intensity) of previously defined elements over the scanned area.



These are powerful and useful forms of elemental analysis. However, as with any technique, there are constraints with which you should be familiar. Below is a list [1] of some of those.

- Energy resolution: 130 eV (Full Width Half Max) at Mn K α
- Limit of detection: 1000 – 3000 ppm; >10% wt%
- Elements identified: elements heavier than Beryllium
- Spatial resolution: Low atomic number (Z): 1-5 μm^3 ; High Z: 0.2 – 1 μm^3
- Precision (the closeness of agreement between randomly selected individual measurements): approaching $\pm 0.1\%$
- Accuracy (the closeness of agreement between an observed value and an accepted reference value): (95% analysis).
 - $\pm 1\%$ for polished bulk target, pure standards on site
 - $\pm 2\%$ for polished bulk target, standards collected on another SEM and then corrected for the geometry and settings of the present microscope (NBS terms this “without standards”).
 - $\pm 5\%$ for particles and rough surfaces “without standards”

Obviously all of these constraints are important to understand; however, spatial resolution of the signal is often surprising to newcomers. The units of spatial resolution are microns -- not nanometers. This is due to the fact that X-rays are generated from very deep in the interaction volume. Also, it is common to use intermediate (15—20 keV) accelerating voltages to ensure the peaks one wishes to record. The size of the interaction volume increases with accelerating voltage. EDS is certainly not a surface analysis technique. It doesn't take much magnification in the SEM to reach the point where the pixel size on the specimen approaches this dimension.

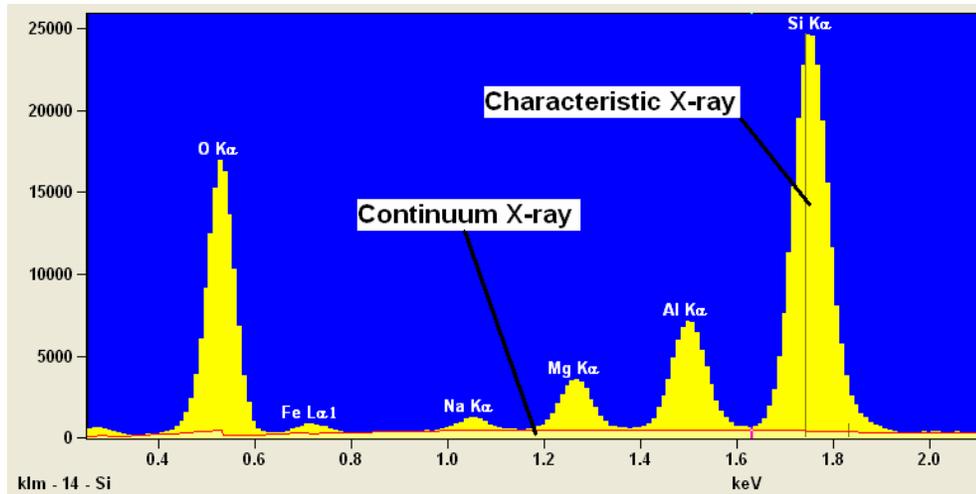
You may want to consider Wavelength Dispersive Spectroscopy if you are in need of better: limits of detection (30—300 ppm; 1% wt%); performance for light elements; energy resolution (10 eV [FWHM] at Mn K α); precision and accuracy.

X-ray Generation

Two basic types of X-rays are produced on inelastic interaction of the electron beam with the specimen atoms in the SEM:

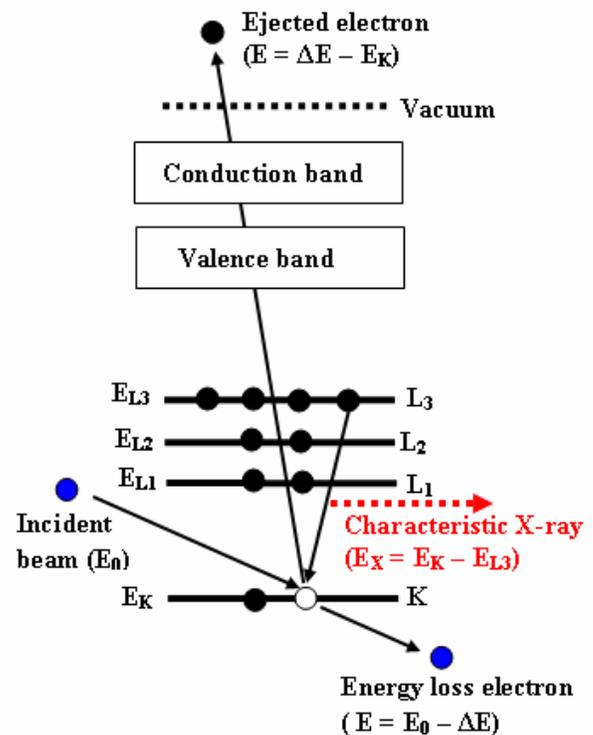
- **Characteristic X-rays** result when the beam electrons eject inner shell electrons of the specimen atoms.
- **Continuum (Bremsstrahlung) X-rays** result when the beam electrons interact with the nucleus of the specimen atoms.

Characteristic X-rays reveal themselves as peaks imposed upon a background of Continuum X-rays.



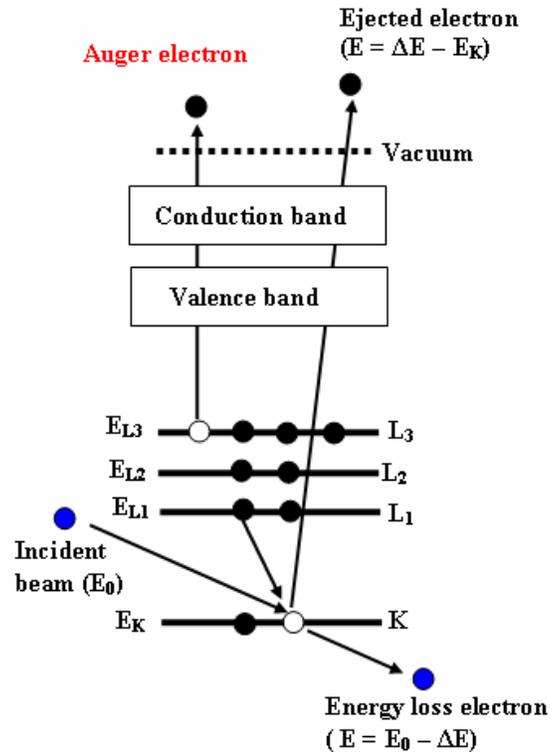
Characteristic X-ray production [2]:

A hole in an inner shell (here: K shell) of the specimen atom is generated by an incident high-energy electron (E_0) that loses the corresponding energy (E) transferred to the ejected electron. The hole in the K shell is subsequently filled by an electron from an outer shell (here: L3). The superfluous energy is emitted as a characteristic X-ray quantum. The energy of the X-ray is characteristic of the specimen atomic number from which it is derived.



Another sequence of events is possible following the ionization of the specimen atom [2]. The hole in the K shell is filled by an electron from an outer shell (here: L_1). The superfluous energy is transferred to another electron (here: L_3) which is subsequently ejected as **Auger electron**. Auger electrons have an energy range of 50 – 2500 eV and mean free paths within the specimen of 0.1 – 2 nm. This means that only Auger electrons escaping from a depth of 0.1 – 2 nm (5-10 atomic layers) will not have undergone additional inelastic interactions with specimen atoms after their generation. Auger spectroscopy is a true surface analysis methodology.

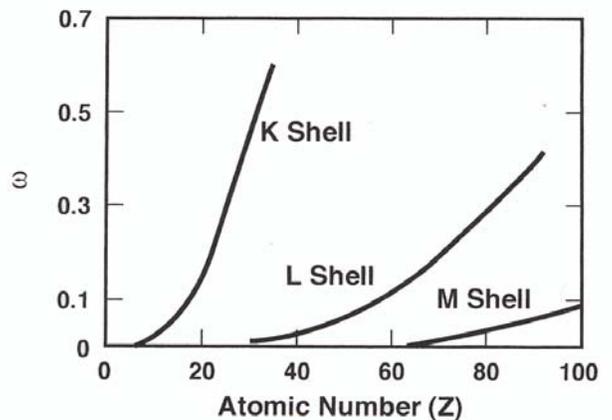
The energy of the Auger electron, like the X-ray, is characteristic of the specimen atomic number from which it was derived. Auger electron production is favored for low atomic number elements; characteristic X-ray production dominates for high atomic number elements.



Fluorescence Yield (ω):

$\omega = \# \text{ X-ray photons produced} / \# \text{ shell ionizations}$ [1].

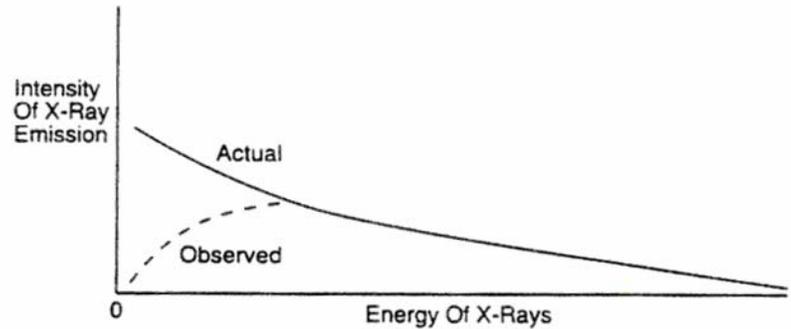
The sum of the fluorescence yield and Auger yield is unity. Note that, within a given series of lines, ω increases with atomic number and, for a given atomic number, is greatest for K shells and progressively less for L and M shells (K, L and M are the shells where the initial ionization occurred—more on this later).



Continuum X-rays production:

Continuum X-rays represent the background on which the characteristic X-ray peaks are imposed. They are considered a nuisance by the microscopist because the characteristic X-rays used for elemental identification need to be differentiated from them. A good peak-to-background ratio is essential for proper identification of elements using their characteristic X-ray peaks. The continuum X-rays result when beam electrons interact with the coulomb (electrical) field of the nucleus of the specimen atom. On interaction, the beam electron loses energy that can be given off as continuum X-rays. The distribution of this energy loss is continuous and not characteristic of the specimen atomic number.

The closer the beam electron comes to the nucleus of the specimen atom, the stronger is the interaction between it and the coulomb field of the nucleus, the more energy is lost by the beam electron, and the more energetic is the X-ray photon that is emitted. Wide misses of the specimen atomic nucleus by the beam electron are more probable. The result is more continuum X-rays at lower energies.



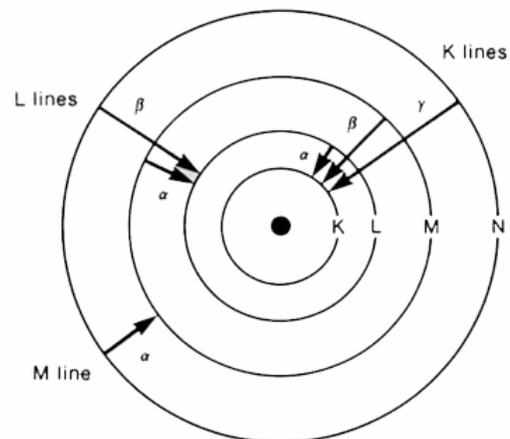
The difference between the actual and observed intensity of X-ray emission in the adjacent diagram is due to absorption by a “window” in the detector that emitted X-rays must pass through in order to be detected (more on this later).

The energy and wavelength of an X-ray are related by the following equation: λ (nm) = 1.2398 / E (keV). The most energetic continuum X-rays will have the minimum wavelength, termed the Duane-Hunt limit. The Duane-Hunt limit is the energy value where the X-ray continuum background goes to zero.

The intensity of the continuum background increases with probe current, atomic number and accelerating voltage.

Characteristic X-ray nomenclature [3]:

The characteristic X-ray lines are named according to the shell in which the initial vacancy occurs and the shell from which an electron drops to fill that vacancy. For instance, if the initial vacancy occurs in the K shell and the vacancy filling electron drops from the adjacent (L) shell, a $K\alpha$ x-ray is emitted. If the electron drops from the M shell (two shells away), the emitted x-ray is a $K\beta$ x-ray. Similarly, if an L-shell electron is ejected and an electron from the M-shell fills the vacancy, $L\alpha$ radiation will be emitted.



Within a given shell, there may be electrons in orbitals differing in energy due to bonding effects.

Thus the $K\alpha$ peak actually comprises the $K\alpha_1$ and $K\alpha_2$ X-rays. These are very close together and unresolved in an EDS system so that a $K\alpha_{1,2}$ doublet is seen as the $K\alpha$ peak at an energy between the two individual components and an intensity corresponding to a weighted average.

The most probable transition when a K-shell vacancy is created is the L to K transition, because these are adjacent energy shells. Therefore $K\alpha$ radiation will always be more intense than $K\beta$ radiation. It also follows that $K\beta$ radiation will be of higher energy than $K\alpha$ radiation, in as much as the energy difference between the M and K shells ($K\beta$ radiation) is greater than the energy difference between the L and K shells ($K\alpha$ radiation).

The energy difference between adjacent electron shells becomes less, progressing outward from the nucleus. It follows that the energy released upon electron transitions between adjacent shells in the outer shells is less than that released for inner shell transitions. That is, for a given atom, $M\alpha$ radiation will be of lower energy than $L\alpha$ radiation, which in turn will be of lower energy than $K\alpha$ radiation.

To ionize an atom, the incoming electron or ionizing radiation must possess a minimum amount of energy. That energy is the binding energy of the particular inner shell electron, which is a specific, characteristic energy for each electron in the atom. The binding energy for a K-shell electron, for example, is greater than that of an L-shell electron, since the K-shell electron is closer to the nucleus and more tightly bound. Therefore, if sufficient energy exists in the incident beam to excite K X-rays, L and M X-rays will also be excited if these shells and the one above them are occupied. Likewise, if sufficient energy exists in the incident beam to produce $K\alpha$ X-rays, $K\beta$ X-rays should be produced as well.

The following common “families of lines” can be used by the microscopist in peak identification:

- $K\alpha : K\beta = 10 : 1$
- $L\alpha : L\beta_1 : L\beta_2 : L\gamma = 10 : 7 : 2 : 1$
- $M\alpha : M\beta = 10 : 6$

For example, if a $K\alpha$ line is identified in a spectra then a $K\beta$ line should exist as well and have approximately one tenth the counts of the $K\alpha$ line.

The beam energy necessary for ionization is always slightly greater in energy than the corresponding X-ray emission line and is termed the **critical ionization energy**. In practice, one must exceed this critical ionization energy by a comfortable margin, preferably by a factor of 1.5 to 3, to efficiently excite the X-ray line with an electron beam. The term for this factor is “**overvoltage**”.

Moseley’s Law

The energy of the characteristic radiation within a given series of lines varies monotonically with atomic number. This is Moseley’s Law:

$$E = C_1 (Z - C_2)^2 \text{ where:}$$

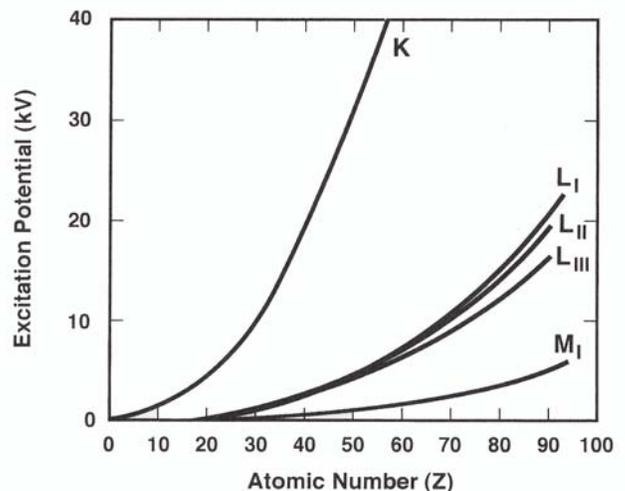
E = energy of the emission line for a given X-ray series (e.g. $K\alpha$)

Z = atomic number of the emitter

C_1 and C_2 are constants

Moseley’s Law is the basis for elemental analysis with EDS. If the energy of a given K, L or M line is measured, then the atomic number of the element producing that line can be determined.

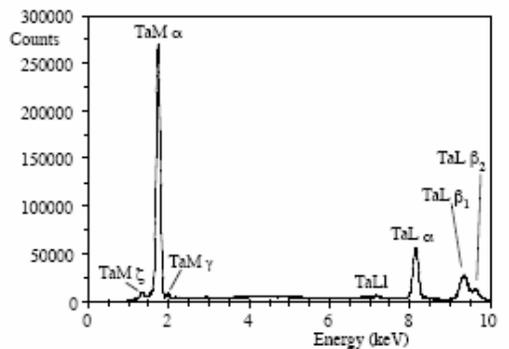
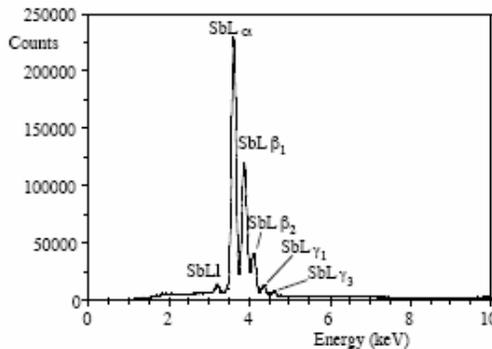
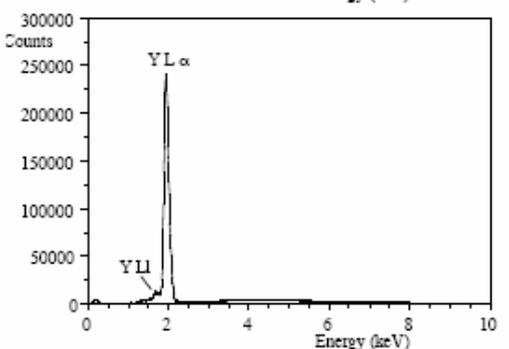
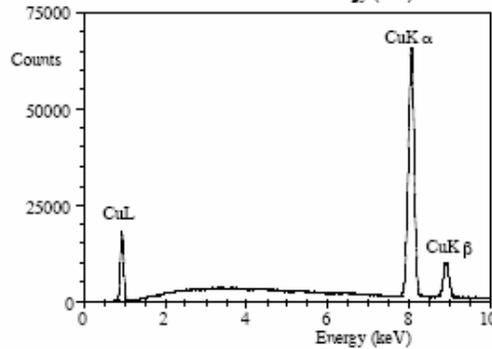
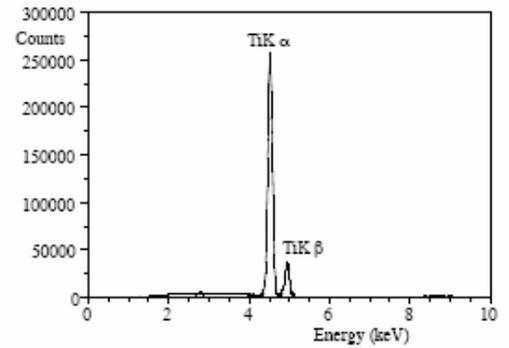
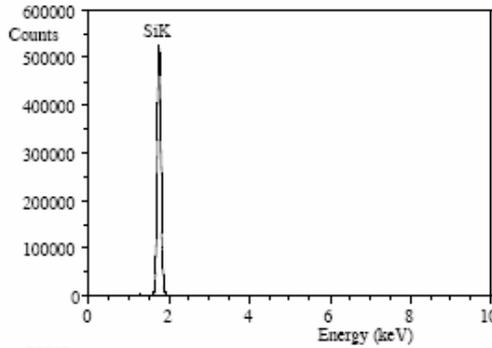
The K, L and M series X-rays increase in energy with increasing atomic number [1].



Within a “normal” accelerating voltage range (15-20 keV) used for EDS analysis [4]:

- light elements will emit X-rays of the K series only;
- intermediate elements will emit X-rays of the L series or K and L series;
- heavy elements will emit X-rays of the M series or L and M series.

Thus one can simultaneously record a wide range of elements during a given scan.



Peak to Background Ratio (P/B): The most important factor in determining the limits of detection in EDS analysis is the presence of the continuum background [1].

$$P/B = 1/Z [(E_0 - E_C) / E_C]^{n-1} \quad \text{where:}$$

E_C = critical ionization energy;

E_0 = accelerating voltage;

Z = atomic number;

N = constant for a particular element and shell with a normal range of 1.5 – 2.

This equation would seem to imply that the best P/B would occur at the highest accelerating voltages. However, very high accelerating voltages not only decrease spatial resolution, they also increase the absorption of X-rays within the specimen before they are measured by the detector (more on this below). An overvoltage of 1.5 - 3 is a good compromise.

Spatial Resolution

X-rays can derive from deeper in the sample than both secondary and backscatter electrons. Backscattered electrons originate from a volume more closely approximating that of X-rays, and therefore are a useful imaging signal to correlate with the X-ray analysis. In fact, the BSE signal is the signal of choice for correlation with X-ray maps.

X-ray spatial resolution depends only on the specimen density and overvoltage. The following equation [3] has been shown to give a good practical estimate of X-ray interaction with actual samples:

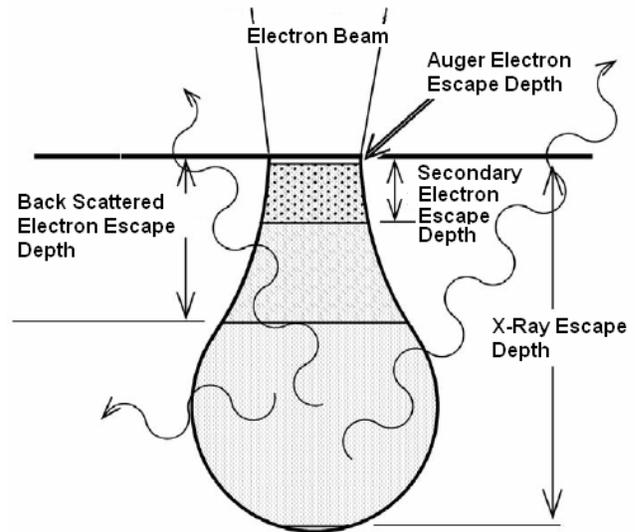
$$R = 0.064 (E_0^{1.68} - E_C^{1.68}) / \rho \quad \text{where:}$$

R = spatial resolution in μm ;

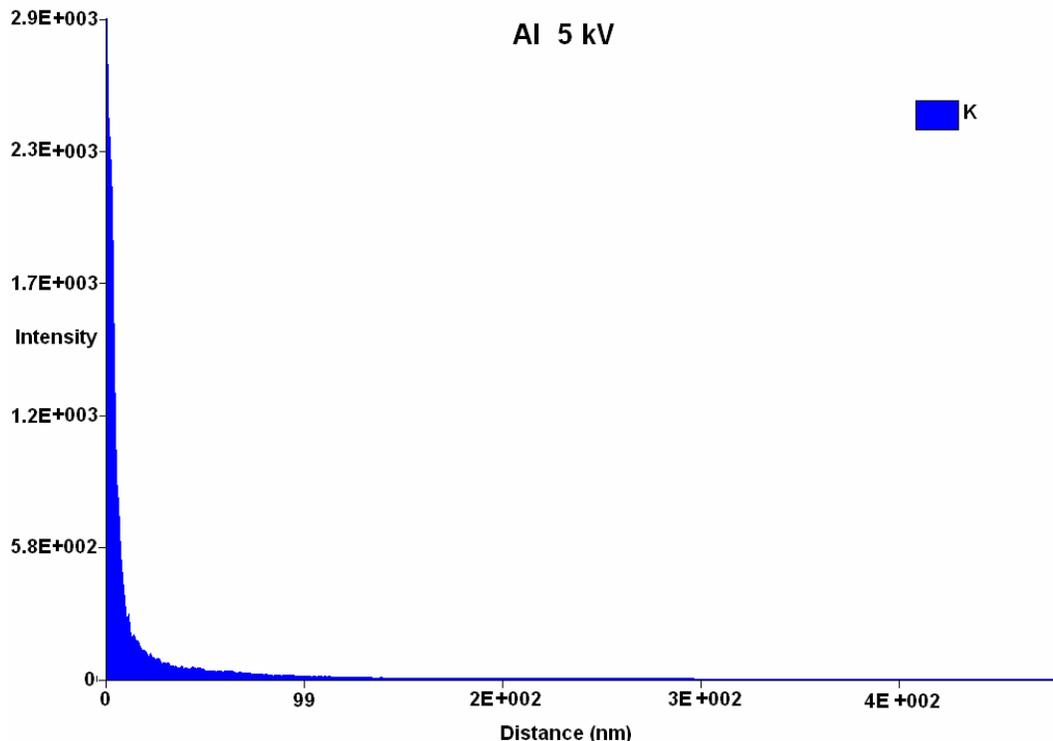
E_0 = accelerating voltage in keV;

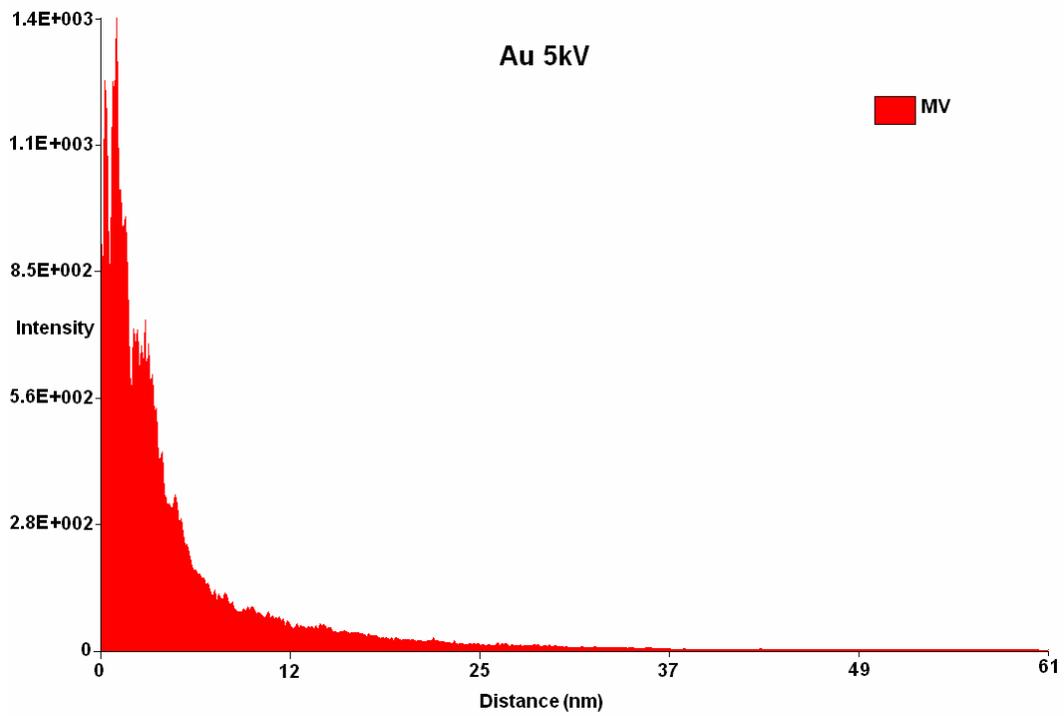
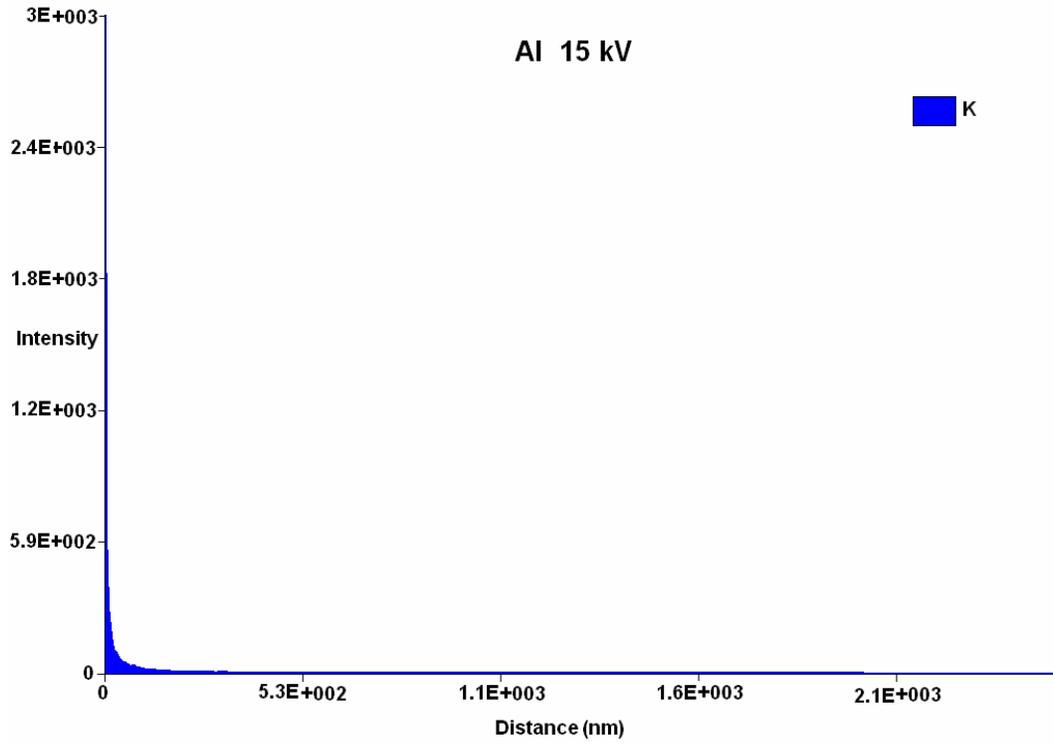
E_C = critical excitation energy in keV;

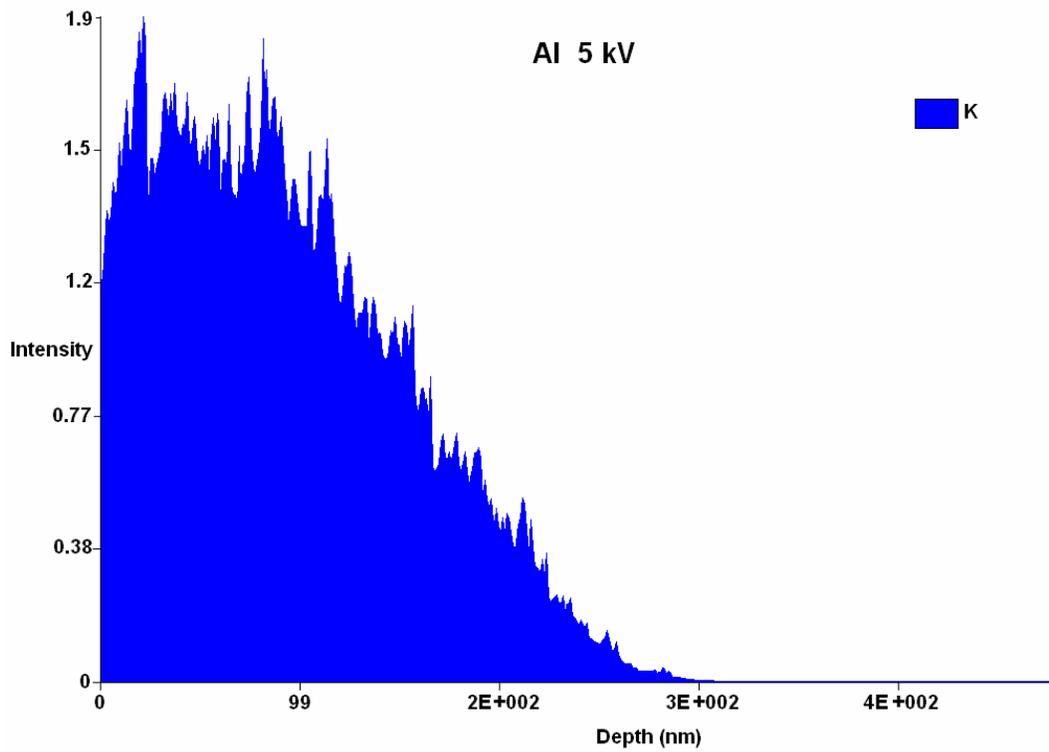
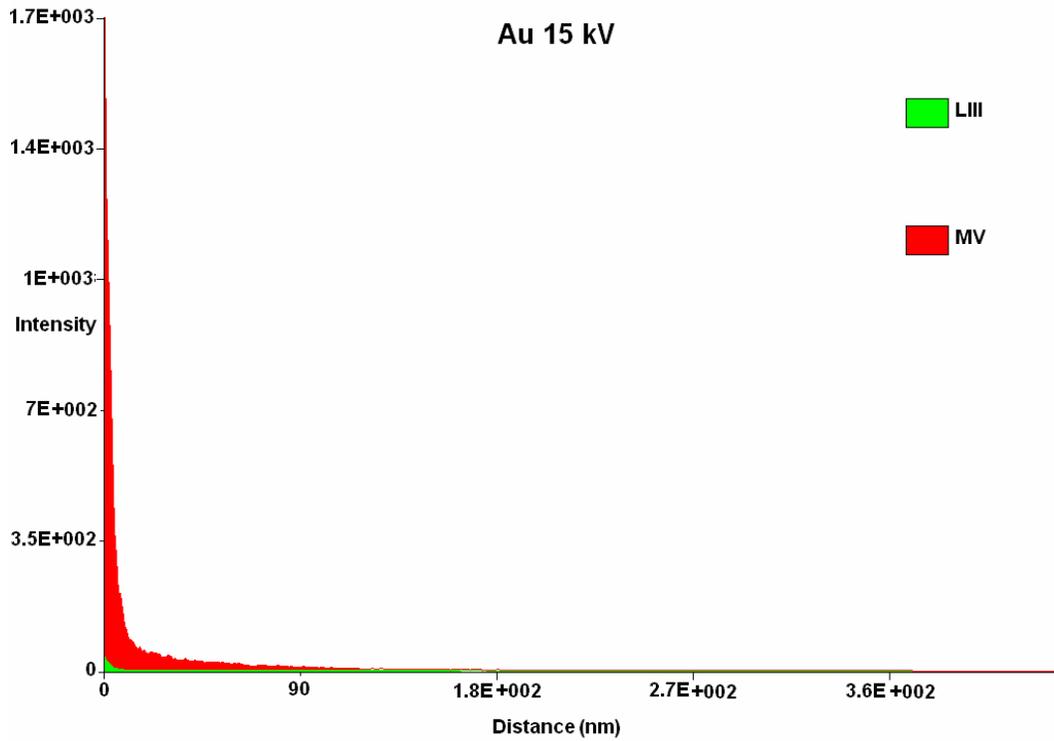
ρ = mean specimen density in g/cc.

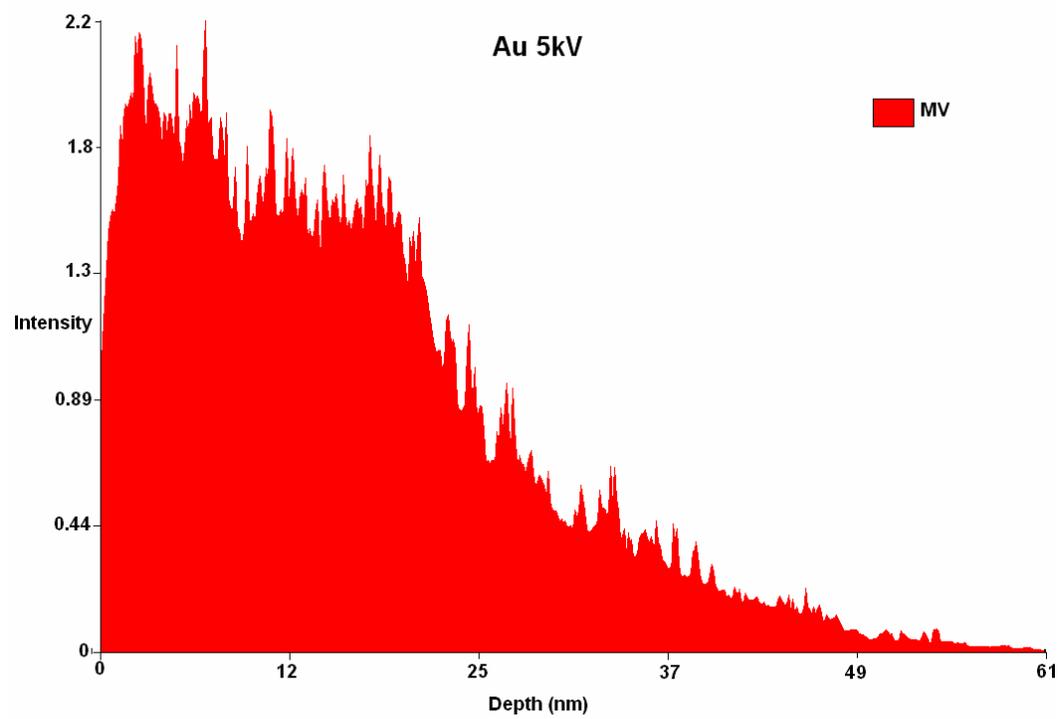
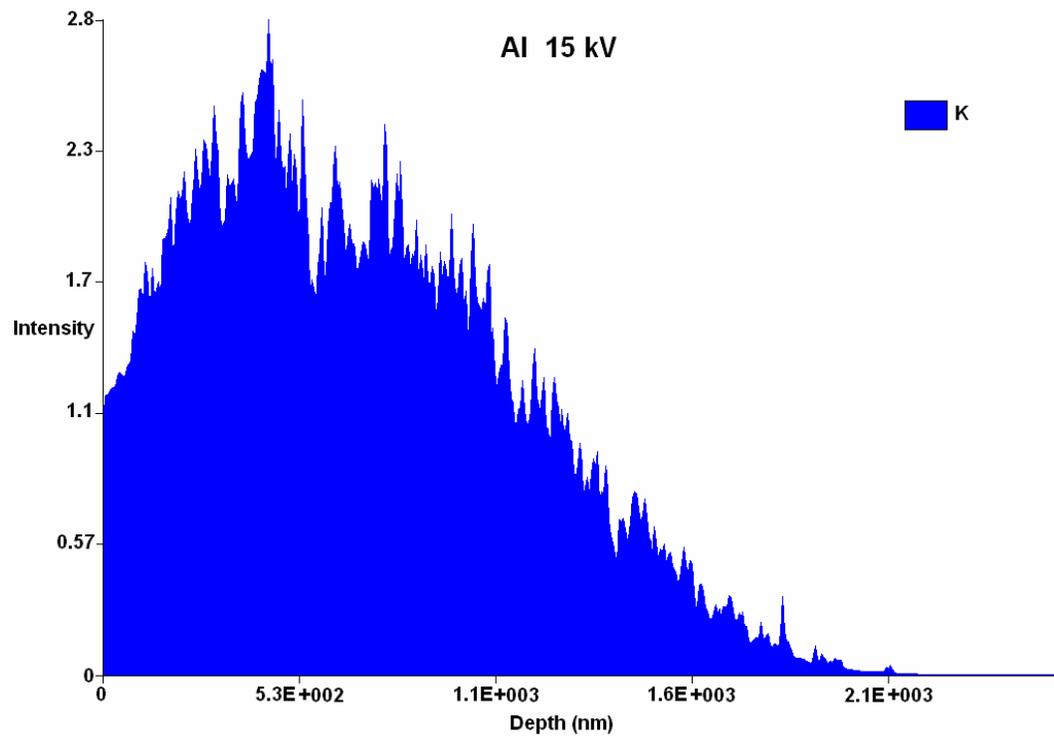


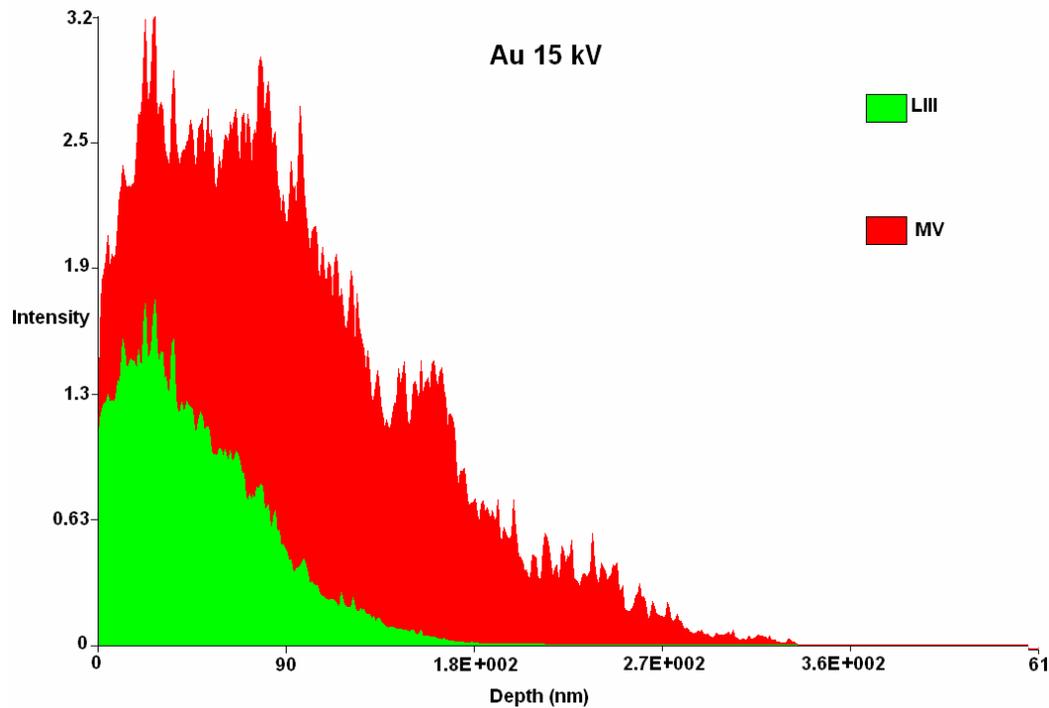
The Figures [4] below show the spatial resolution (distance from incident beam from which the signal is derived) and depth of signal for the elements Aluminum and Gold at the accelerating voltages of 5 kV and 15 kV. Take some time to put the relationships together between: incident beam energy; accelerating voltage; and, atomic number. Or better yet download a free electron flight simulator program such as “Casino”[5] and experiment on your own.





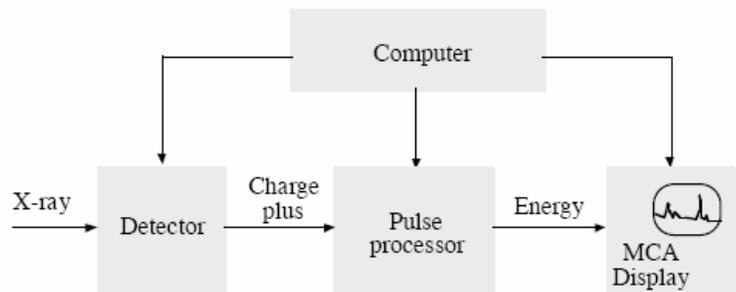






X-ray Spectral Measurement

The absorption of an individual X-ray photon by the detector leads to the ejection of a photoelectron which gives up its energy to the formation of electron-hole pairs. The electron-hole pairs in turn are swept away by an applied bias to form a charge pulse. The charge pulse is converted to a voltage pulse by a preamplifier. The signal is further amplified and “shaped” by a linear amplifier (pulse processor) and then passed on to a multi channel analyzer where the data is displayed as a histogram of intensity vs voltage.



The important point here is that **the voltage pulse produced is proportional to the energy of the incoming X-ray photon.**

The EDS system is comprised of three basic components [6]:

- an **X-ray Detector** which detects and converts X-ray into electronic signals;
- a **Pulse Processor** which measures the electronic signals to determine the energy of each X-ray detected; and,
- a **Multiple Channel Analyzer** which displays and interprets the X-ray data.

X-ray Detector:

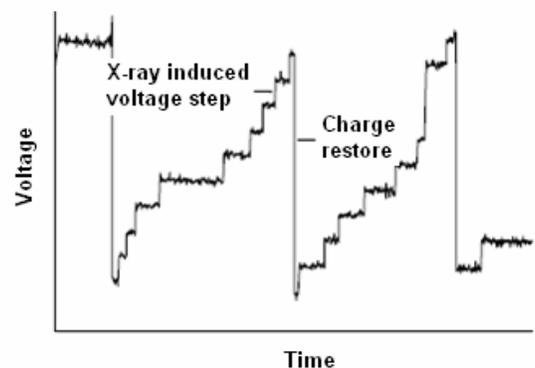
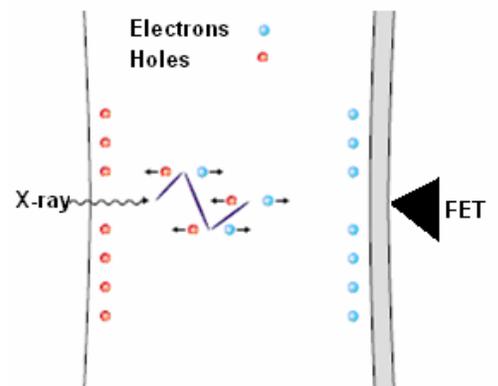
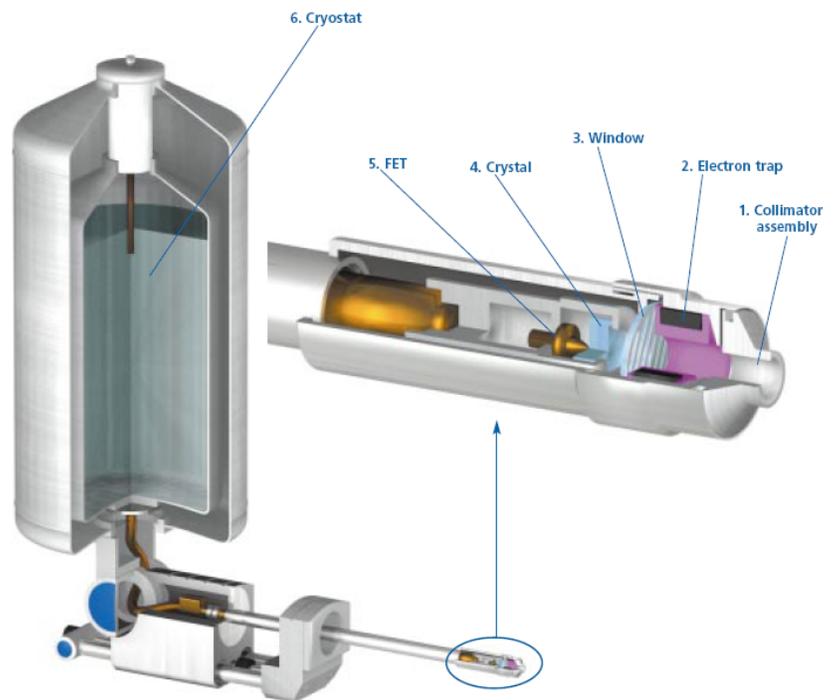
1. Collimator assembly: The collimator provides a limiting aperture through which X-rays must pass to reach the detector. This ensures that only X-rays from the area being excited by the electron beam are detected.

2. Electron trap: Electrons that penetrate the detector cause background artifacts. The electron trap is a pair of permanent magnets that strongly deflect any passing electrons that could cause background artifacts.

3. Window: The window provides a barrier to maintain vacuum within the detector whilst being as transparent as possible to low energy X-rays. CharFac has a polymer-based thin window that can transmit X-rays from elements heavier than Beryllium.

4. Crystal: The material used for the crystal is silicon (Si), into which is drifted lithium (Li) to compensate for small levels of impurity. When an incident X-ray strikes the detector crystal its energy is absorbed by a series of ionizations within the semiconductor to create a number of electron-hole pairs. An electron-hole pair is created for every 3.76 eV of incoming X radiation. Thus, for example, a Ni K α X-ray photon (7,471 eV) will produce a current of 1,966 electrons. 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. 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.

5. FET: The Field Effect Transistor 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. During operation, charge is built up on the feedback capacitor. The sharp steps on the voltage buildup are due to the charge created by each X-ray event. The voltage step size is proportional to the incident X-ray energy. This accumulating charge has to be periodically restored to prevent saturation of the preamplifier.



6. 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. The noise determines the resolution of a detector particularly at low energies. The natural width (FWHM) of an X-ray peak is on the order of 2-10 eV. The actual FWHM is at least an order of magnitude greater than this due to noise in the system. The EDS detector is cooled using a reservoir of liquid nitrogen held in a dewar. The vacuum is maintained at a low enough level to prevent the condensation of molecules on the crystal.

Pulse Processor

The signal (voltage step) from the preamplifier is transformed into a voltage pulse that is suitable for the multi channel analyzer. Shaping and noise reduction of the signal are achieved by digital computation. The noise on the voltage ramp from the detector is effectively filtered out by averaging the signal. The time over which the waveform is averaged is called the process time (T_p). T_p is under control of the operator. The longer the T_p , the lower the noise. If noise is minimized, the resolution of the peak displayed in the spectrum is improved, and it becomes easier to separate or resolve, from another peak that is close in energy.

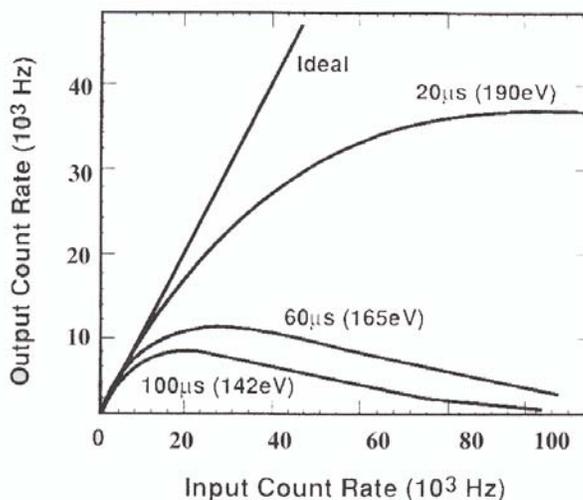
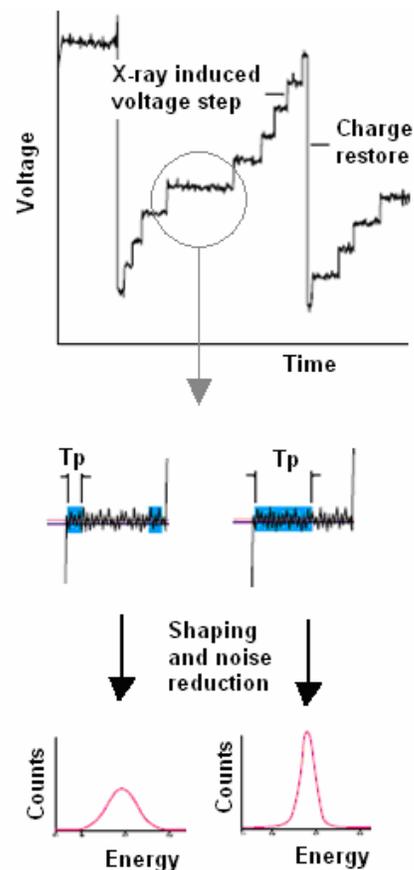
However, there is a trade-off between the process time that is used, and the speed at which data can be measured. The longer the process time, the more time is spent measuring each X-ray, and the fewer events that can be measured.

Productivity depends on the rate of counts measured, called the output count (acquisition) rate, rather than the input count rate into the detector [1]. Only at very low count rates are the two proportional. As the input rate increases so will the acquisition rate, but an increasing number of events are rejected because they arrive in a shorter time period than the T_p . This phenomenon is termed “pulse pileup”. If input rates increase sufficiently, the proportion rejected will exceed the increase in measured events and the acquisition rate will start to decrease with further increases in input rate. This situation is most dramatic for the longer process times.

The way to avoid/minimize this is to ensure a certain percentage of “dead time” – time during which pulses are not measured.

$$\text{Deadtime} = (1 - \text{Output rate}/\text{Input rate}) \times 100.$$

Deadtimes of 30-60% will tend to maximize output. The operator can and should maximize output rates for a given sample and process time by controlling probe current/spot size.



Perhaps the following “bucket analogy” will be useful:

Water = X-ray data;

Bucket = computer;

Hole in bucket = processor;

Size of hole = process time;

Rate of water pouring out of the bucket = output count rate;

Rate of water pouring into the bucket = input count rate controlled by spot size.

By controlling the rate of water pouring into the bucket (spot size) you are controlling deadtime.

The analogy breaks down concerning why the output rate would actually decrease after a given input rate and not be constant—but hopefully you get the point.

Multi Channel Analyzer (MCA)

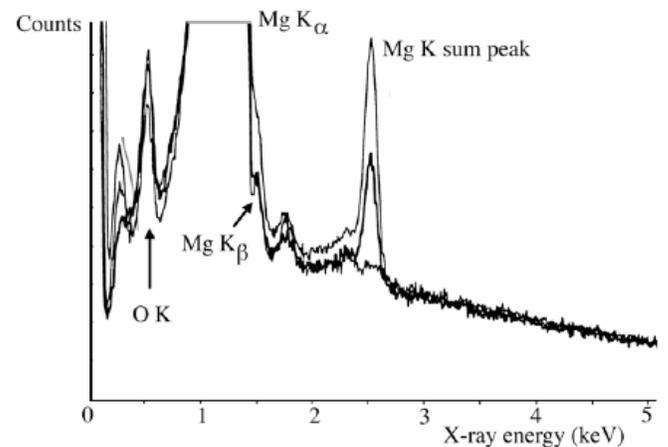
The MCA takes the data from the pulse processor and displays it as a histogram of intensity (number of counts) vs voltage. The voltage range (for ex., 20 keV) displayed on the x-axis is divided into a number (1024, 2048, etc) of channels each corresponding to a given energy range (for example, 5,280 eV –5,300 eV). The MCA takes the peak height of each voltage pulse, converts it into a digital value, and puts it into the appropriate channel. Thus a count is registered at that energy level.

Spectral Artifacts

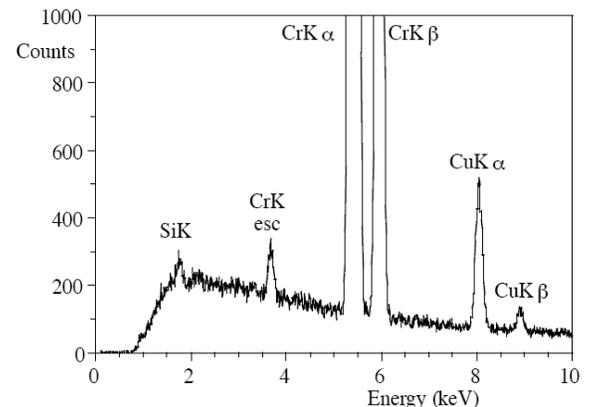
There are a number of artifacts possible with EDS, but most of them are related to detector electronics and are rarely seen in a properly functioning system. Two artifacts that are commonly seen are pulse pileup (sum) peaks and escape peaks [4]. We can choose to show/not show these with our NSS software

Sum peaks occur when X-ray photons reach the detector at nearly the same time, and the pulse processing electronics erroneously record the sum of their energies rather than each one individually. Lowering the beam current lowers the count rate and usually eliminates the problem.

Alternatively, the process time can be decreased; this action will allow pulses to be processed faster, but at the expense of degraded spectral resolution. The sum peak should be invisible if the count rate is < 10,000 cps and the deadtime is < 60%



Escape peaks occur when the detecting crystal is ionized and emits an X-ray that escapes the crystal. The result is a peak at 1.74 keV below the parent peak for Si(Li) detectors. Thus the total number of electron hole pairs created in the detector changes creating an energy loss..



Operator Control

Geometry of the Detector

The geometry of the beam--specimen—detector is such that maximum signal is obtained from the specimen at 10 mm working distance. In our system there is not much “play” with this geometry. You need to be focused and aligned at 10.0 mm – not 10.1 mm. The infrared chamber camera should be turned off as it will contribute unwanted signal.

Accelerating voltage:

One must exceed the critical ionization energy of the element(s) of interest by a factor of 1.5 to 3 to efficiently excite the X-ray line(s) with an electron beam. Exploratory analysis is often conducted with an accelerating voltage in the 15—20 keV range since a broad array of elements will be detected. An addition spectrum collected at 5-10 keV could help to avoid missing low atomic number elements at low concentrations. The accelerating voltage can subsequently be tailored to the elements and shell levels of your specimen. Keep in mind that accelerating voltage and atomic number are two factors that determine the spatial resolution of and depth of signal from your specimen.

Process time:

There are a range of available process times to select from on the NSS software. These are referred to as “Pulse Processor Time Constants” and can be found in the “Acquisition Properties” dialogue box. The range is: high resolution/low throughput (65 us time constant) --high throughput/low resolution (4 us time constant).

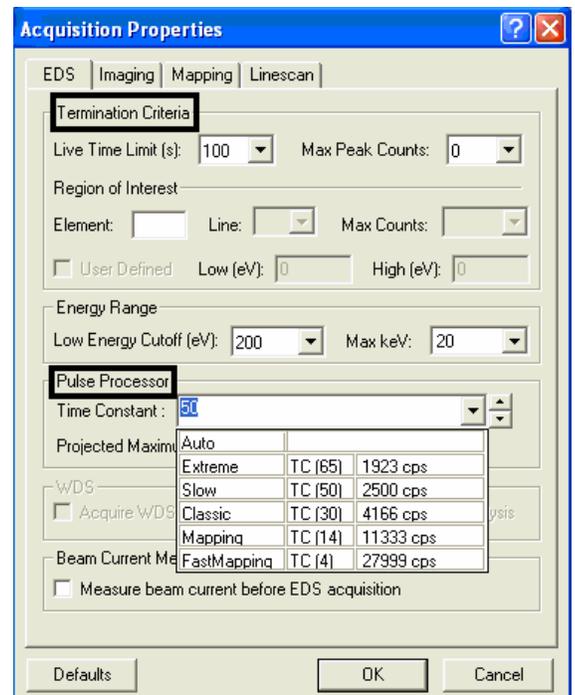
Duration of signal acquisition:

There are a number of ways to obtain a statistically significant number of counts and thus good peak/background ratios. Within the “Termination Criteria” section of the “Acquisition Properties” dialogue box one can:

- set a “live time” limit. The system will automatically compensate for the deadtime value;
- set a “maximum peak count”. Acquisition will terminate when the spectral vertical scale reaches this value;
- select of region of interest (energy range) and terminate acquisition when a set number of counts have been accumulated within that region.

Probe current:

The probe current can be adjusted to maximize the throughput at a given time constant for a given specimen. Deadtimes in the 30-50 % range should work well. Remember that changing probe currents will necessitate realignment of the microscope.



Qualitative X-ray Analysis

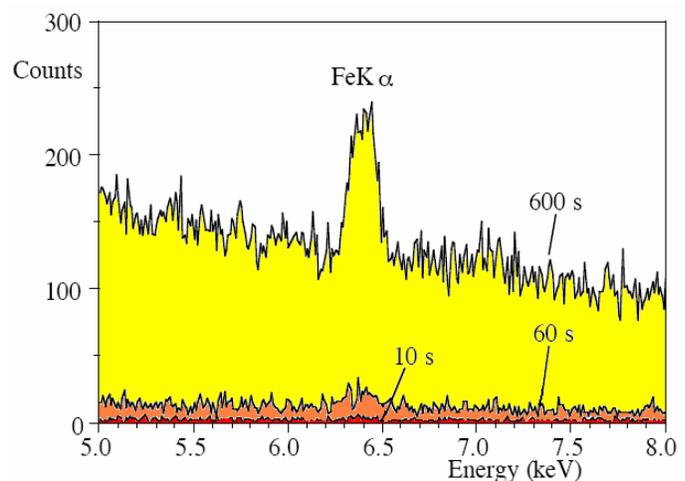
Qualitative analysis involves the identification of the elements present and is a prerequisite for quantitative analysis. The NSS automatic qualitative analysis capabilities are quite good when the system is properly calibrated with standards (peaks within 10 eV of their actual energies). The program does background subtraction and peak deconvolution, and then applies an intelligent method of identification within constraints set by the operator. However, the operator should use his/her knowledge of chemical principles and of the specimen to manually check the results.

Three broad categories are used when referring to the concentrations of elements present in a sample:

1. Major Components - More than 10 wt %;
2. Minor Components - 1-10 wt %;
3. Trace Elements - Less than 1 wt %.

General Guidelines for EDS Qualitative Analysis:

- Only peaks which are statistically significant should be considered for identification. The minimum size of the peak should be 3 times the standard deviation of the background at the peak position [$P > 3(B)^{1/2}$]. The operator must ensure a statistically significant number of counts in order to decide if a peak is present or absent. The adjacent Figure [4] shows the separation of peak to background signal as the acquisition time increases from 10 to 600 seconds.



- The apparent weights of peak members in a family provide an important source of information in identifying elements.

K family: $K\alpha$ (1) : $K\beta$ (0.1)

L family: $L\alpha$ (1) : $L\beta_1$ (0.7) : $L\beta_2$ (0.2) : $L\beta_3$ (0.08) : $L\beta_4$ (0.05) : $L\gamma_1$ (0.08) : $L\gamma_3$ (0.03) : $L\iota$ (0.04)

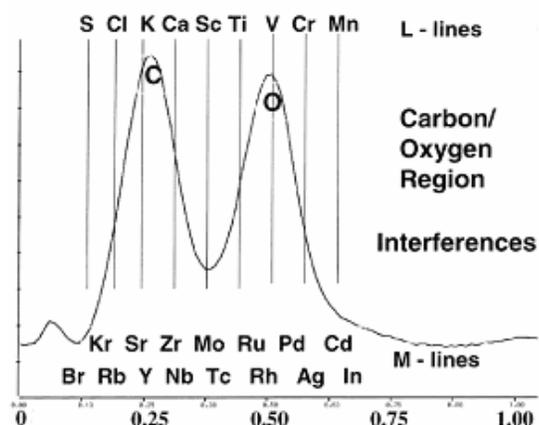
M family: $M\alpha$ (1) : $M\beta$ (0.6) : $M\gamma$ (0.05) : $M\xi$ (0.06)

- Begin with the most intense line towards the high-energy region of the spectrum where lines within a family are well separated. If it is above 3.5 keV, it must be either a K or L line. Using the KLM markers, compare the location of the peak to that of the marker. Check the relative intensities. If you identified a $K\alpha$ line, then the $K\beta$ line should be about 10% of the $K\alpha$ intensity. $K\alpha$ and $K\beta$ lines are typically resolved at sulfur and above. Below that, $K\beta$ is so small that $K\alpha$ and $K\beta$ collectively show themselves as one symmetrical peak. If a K line is identified, look for L lines, if they occur for that element. This will aid in identifying the lines at low energy later.
- If the line chosen does not correspond to a K line, try an L series. If the line is identified as the $L\alpha$, several other lines both above and below the $L\alpha$ should be present and correspond to the element. The EDS system should be able to display them at their correct relative intensities. M lines do not exist above 3.2 keV, so one would not look for them at this point.

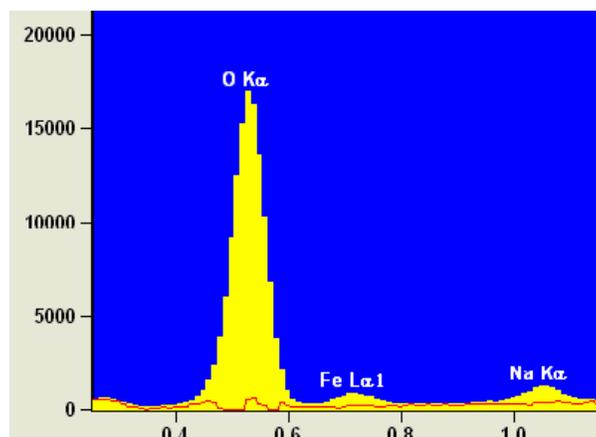
- While working with the most intense line, look for escape and sum peaks. If they are not found for this line, they are unlikely to cause interferences. If they are present, keep looking for them after other identifications.
- If (1) a peak is displaced relative to its marker, (2) relative intensities are wrong, or (3) there is a distortion in the peak shape, then there is an overlapping element. All three conditions will be present in an overlap situation. If one condition is seen, look for the others, and identify the second element. When looking for overlaps in the spectrum, one should always expand the energy scale and usually the vertical scale. The adjacent Figure and Table show overlaps commonly seen in EDS spectra [1].

Element	Interferes with
Ti K β	V K α
V K β	Cr K α
Cr K β	Mn K α
Mn K β	Fe K α
Fe K β	Co K α
Co K β	Ni K α
S K α & K β	Mo L α , Pb M α
W M α & M β	Si K α & K β
Ta M α & M β	Ni K α & K β
Ti K α	Ba L α
As K α	Pb L α
Sr L α	Si K α
Y L α	P K α

- Continue to identify lines while working towards lower energies and consider the possibility of M lines. The lines of an M series are generally not all resolved but contribute to an asymmetrical peak. In fact, M lines can often be recognized by this distortion, but beware of overlaps that may look similar.



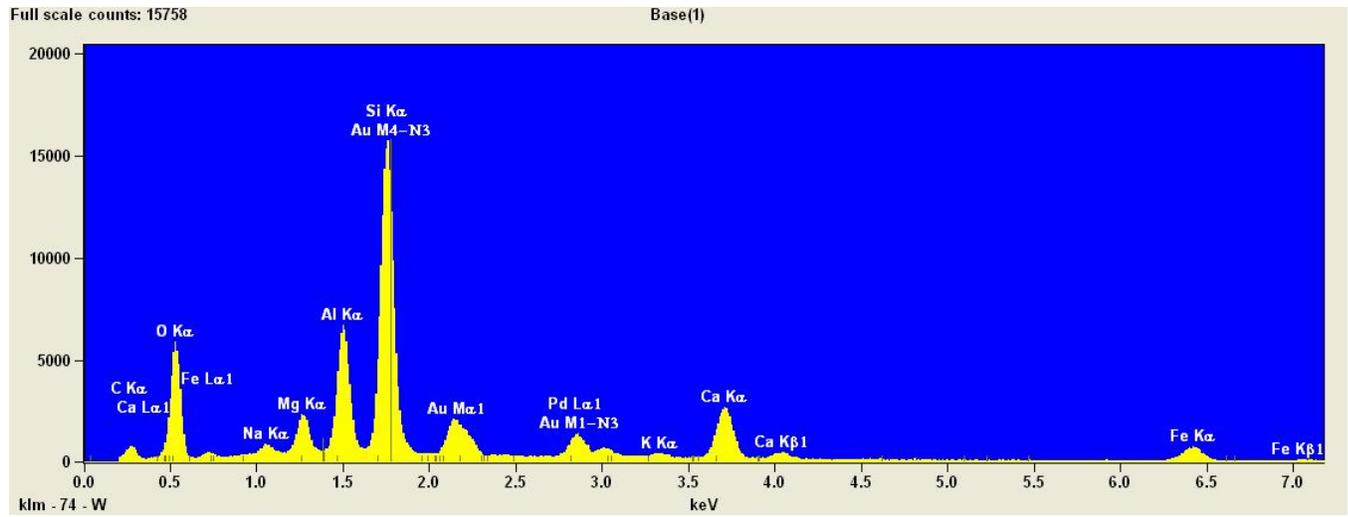
- When all high-energy lines and low-energy L and M lines are identified, light elements can be attempted. These will be K lines and may be overlapped with L lines from heavier elements. If it is not possible to distinguish them, peak deconvolution software or peak stripping may be necessary. Peak stripping is a mathematical process that allows the analyst to remove identified peak structures to reveal possible hidden peaks if they exist. The Noran system has a “residual spectrum” feature to accomplish this. The residual spectrum is shown in red in the adjacent Figure.



- After all major and minor peaks are located, trace elements can be attempted. In this case, the problem is to confidently find a peak above background. Only the major peak of a series will be visible, and that may be lost in the background. If a peak cannot be identified with some certainty, the first step is to collect more counts. If it still cannot be confirmed, it is either not present or present below the limits of detectability and WDS is warranted.

Quantitative X-Ray Analysis

Below is a spectrum from a geologic specimen and a subset of quantitative data associated with that spectrum. I recorded the maximum number of counts from the spectrum for a range of elements. The NSS software derived the Atomic percentages. For both of these data types I've included (in parentheses) the proportions of the elements relative to Silicon—the most abundant. One might expect the relative proportions for both data types to align with one another—i.e., there should be a close parallel between number of counts and atomic percentage. And that is indeed the case for a number of the elements. However, a couple of the elements (Ca and Fe) show a significant discrepancy. What to make of this?



Element	Maximum # of counts	Atomic %
Na	890 (0.06)	1.0 (0.01)
Mg	2315 (0.15)	2.63 (0.12)
Al	6720 (0.43)	8.38 (0.39)
Si	15760 (1.0)	21.64 (1.0)
Ca	2690 (0.17)	6.42 (0.30)
Fe	790 (0.05)	4.05 (0.19)

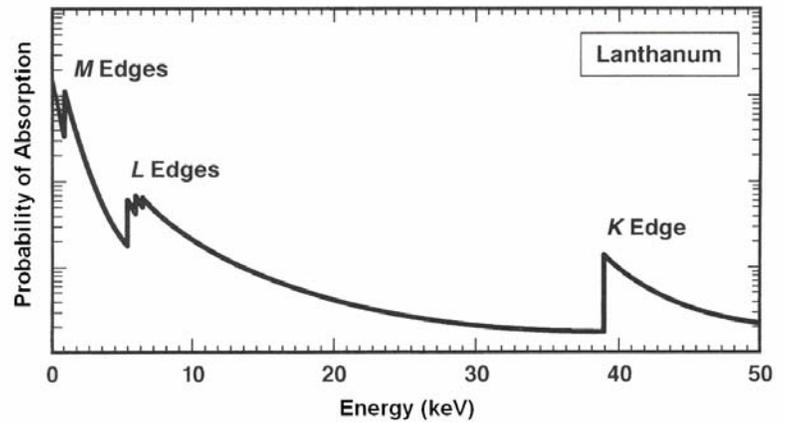
Measured intensities from the specimen need to be corrected for a host of **matrix effects (ZAF)**:

Z: Atomic Number Effect:

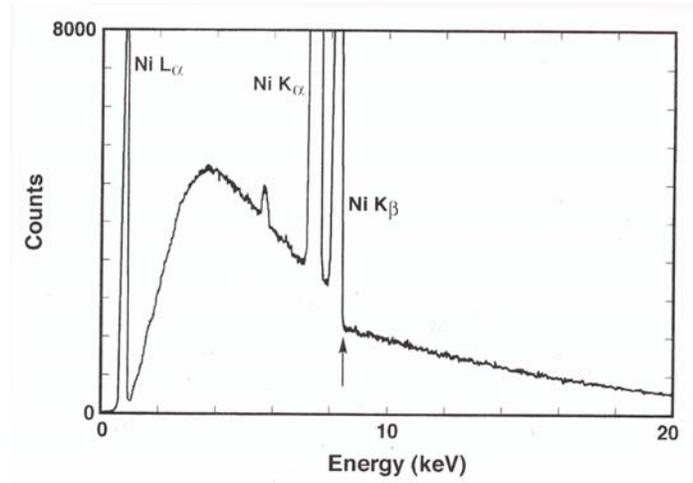
Two factors must be considered regarding atomic number: the backscatter coefficient and “stopping power”. The backscatter coefficient increases with atomic number—leading to the premature loss of beam electrons prior to ionization resulting in X-ray production. The rate of energy loss due to inelastic interaction increases with decreasing atomic number—leading to the same result. These two factors tend to cancel one another.

A: X-Ray Absorption Effect:

Absorption is usually the biggest factor that must be considered in the measurement of composition by x-ray microanalysis. As an X-ray travels through the sample, it may be absorbed, giving up its energy entirely to an electron and ejecting the electron from its orbital. The probability that an X-ray will be absorbed depends on its energy and the energy with which the electron is bound to its nucleus. The probability of absorption increases as the X-ray energy approaches this binding energy from above and reaches a maximum when the X-ray energy is just greater than the binding energy. At this point there is a discontinuity (**absorption edge**) in the probability curve. Lower energy X-rays no longer have sufficient energy to overcome the binding energy and the probability of absorption drops to a lower value. The probability of absorption then increases again as the X-ray energy approaches the binding energy of a more loosely bound electron. An absorption curve [1] for a given element includes an absorption edge for each electron shell.



Absorption edges can be directly observed when the X-ray spectrum energy range spans the critical excitation energy for the absorber element in the sample [1]. At the absorption edge, the continuum background abruptly decreases for X-ray energies slightly above the edge because the mass absorption coefficient increases abruptly at the absorption edge.



As X-rays are generated deeper in the specimen, progressively greater fractions are lost to absorption. The ratio of the measured X-ray intensity to the generated X-ray intensity at some position in the sample is dependent on the: mass absorption coefficient; specimen density; and path length. The probability of X-ray absorption as a function of path length through the sample is given by Beer's Law:

$$I/I_0 = \exp(-\mu_M \rho d) \quad \text{where:}$$

I/I_0 = fraction of X-rays transmitted;

d = thickness;

ρ = material density;

μ_m = mass absorption coefficient (available in published tables).

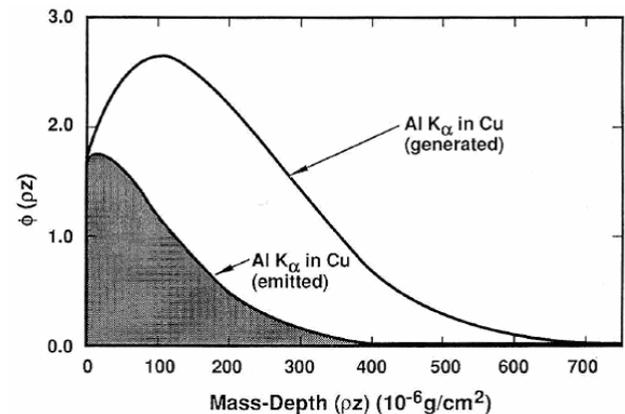
F: X-Ray Fluorescence Effect:

When an X-ray is absorbed by a sample atom, the absorbing atom is left in an excited state. It subsequently relaxes, emitting its own characteristic X-rays (secondary fluorescence). Since an X-ray can be absorbed only in an interaction with an electron having a binding energy less than the energy of the absorbed X-ray, the energy of the secondary fluorescence is necessarily less than the energy of the primary X-ray. For example, in a Cu-Fe sample, Cu $K\alpha$ radiation (8.04 keV) is of sufficient energy to excite Fe K radiation ($K_{ab} = 7.11$ keV). As a consequence, the measured iron intensity would be enhanced due to fluorescence by copper, while the copper intensity would be suppressed due to strong absorption by iron. In practice, secondary fluorescence is only significant if the characteristic energy is within approximately 3 keV of the critical ionization energy. The fluorescence effect can be calculated with sufficient accuracy and it is usually the least important of the three factors.

Matrix Effect Correction:

There are two basic approaches to correcting for matrix effects [1]:

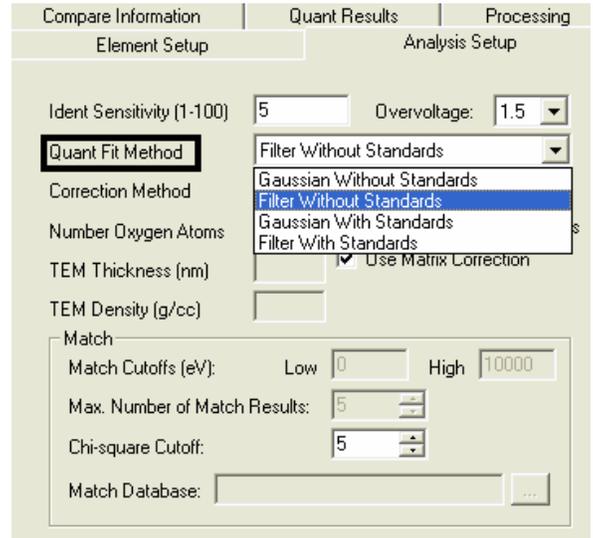
- One, the traditional approach, calculates Z, A and F from fundamental equations describing the physical phenomena.
- The other approach utilizes a “phi-rho-z curve”. A phi-rho-z curve is actually an ionization distribution in which ionizations, $\phi(\rho z)$, are plotted against mass-depth (ρz). While a phi-rho-z curve describes a physical process, the equations used to generate these curves are actually fit to experimental data. The intensity is the area under the phi-rho-z curve. The ratio of intensity between unknown and standard (see below) gives the atomic number factor. One can compare the intensity after absorption with the intensity generated and compute an absorption factor. The fluorescence factor is calculated with the traditional approach.



These two matrix correction approaches produce similar results. The phi-rho-z method is more accurate for the lighter elements and it is in light element analysis that most claims are made for phi-rho-z superiority. However, in many cases the differences between matrix corrections are less than the uncertainty associated with counting statistics. The phi-rho-z method is the default in the NSS software. (The Cliff-Lorimer option is used in TEM/STEM)

Compare Information	Quant Results	Processing
Element Setup		Analysis Setup
Ident Sensitivity (1-100)	5	Overtension: 1.5
Quant Fit Method	Filter Without Standards	
Correction Method	Proza (Phi-Rho-Z)	
Number Oxygen Atoms	ZAF	
TEM Thickness (nm)	Cliff-Lorimer (MBTS) w/o Absorbance	
TEM Density (g/cc)	Cliff-Lorimer (MBTS) w/ Absorbance	
Match		
Match Cutoffs (eV):	Low 0	High 10000
Max. Number of Match Results:	5	
Chi-square Cutoff:	5	
Match Database:	...	

Subtraction of the background spectrum is one component of quantitative analysis. There are two options in the NSS software: Gaussian which utilizes Kramer's law; and the use of a digital top hat filter. The latter is the default with our software.



General procedure for quantitative analysis in the SEM:

- Obtain standards for each of the elements identified in the qualitative analysis. Standards must be homogeneous at the microscopic level. Both specimen and standards must be flat polished with scratches less than 0.1 μm
- Obtain the x-ray spectrum of the specimen and standards containing the elements that have been identified in the specimen. All measurements for a given element, in both the specimen and the standards, should be made at the same: Deadtime; spectrometer take-off angle; calibration; resolution; beam energy; and beam current.
- Process the spectra of the specimen and standards to remove the continuum X-ray background signal so that the measured intensities consist only of the characteristic signal. The background could be a significant fraction of the characteristic peaks for minor and trace constituents
- Develop the x-ray intensity ratios (k value) using the specimen intensity I_i and the standard intensity $I_{(i)}$ for each element present in the sample. The measured intensity ratios should be equivalent to the ratios of mass or weight fractions:

$$I_i/I_{(i)} = C_i/C_{(i)} = k \text{ (k-value)}$$

In standardless quantitative analysis (what NSS terms “without standards”), the intensity that forms the denominator of the k ratio, $I_{(i)}$, is provided by calculation rather than direct measurement. Typically the standards are derived from a suite of experimental standards measurements (a standards data base) performed by the manufacturer and subsequently adjusted for the characteristics of the local instrument.

- Carry out matrix corrections to obtain quantitative concentration values.

$$C_i/C_{(i)} = I_i/I_{(i)} \cdot [ZAF]_i = [ZAF]_i \cdot k_i$$

This equation must be applied separately for each element present in the sample.

- [1] Joseph Goldstein et al. “Scanning Electron Microscopy and X-Ray Microanalysis”.
- [2] <http://www.microscopy.ethz.ch/aed.htm>
- [3] John J. Friel. “X-ray and Image Analysis in Electron Microscopy”, Princeton Gamma-Tech.
- [4] David Williams and Barry Carter. “Transmission Electron Microscopy: A Textbook for Materials Science”. Plenum
- [5] “Casino” Monte Carlo Simulation. <http://www.gel.usherbrooke.ca/casino/download2.html>
- [6] Images and much of text from: “Energy Dispersive X-ray Microanalysis Hardware Explained”, Oxford Instruments Analytical Technical Briefing.