**Qualitative and Quantitative analysis using the SEM**

*Reading Assignment: Chapters 4, 7, and 8 of Reed, S. J. B. (1996). Electron microprobe analysis and scanning electron microscopy in Geology. Cambridge University Press, 201 pp.*

1. **Detectors**

**1- Secondary Electron Imaging Detector: Scintillator - photomultiplier detector:**

* Everhart – Thornley type of detector is most commonly used (Fig. 1).
* Faraday Cage : biased at + 300 V
* Scintillator: CaF2 doped with Eu, and covered by a thin layer of Al (10 - 50 nm), biased at + 10 kV every electron produces a photon.
* Light guide
* Photomultiplier: photons hit electrodes, produce electrons with a gain of 105 - 106

**2- Back Scattered Electron Imaging Detector:**

* This detector, located between the objective lens and the sample, is either of the solid state type (Fig.2) or of the scintillator type (Fig. 3).
* The solid state detector consists of a semiconductor with 3 parts: P-type region, intrinsic region, and N-type region.
* The P-type portion consists of a Si wafer covered by a thin Au layer with negative bias.
* The instrinsic region consists of a Si slice ~ 3 mm thick, usually Li-drifted (to take care of any impurities in the Si crystal), where all the electron – hole pairs are generated.
* The N-type region is the portion that passes the signal on to the preamplifier. It is positively biased, and is again coated with Au (Fig. 4). The signal can then be used for creating the image.
* If the BSED is positively biased, it can collect some secondary electrons as well, giving additional topographic information.

**3- Cathodoluminescence Detector:**

* Cathodoluminescence is best observed by an optical microscope.
* A photomultiplier can also be used to detect these electrons, and in some cases is combined with an optical spectrometer to allow narrow band spectral measurements.

**4- Energy Dispersive Spectrometer:**

* The EDS consists of a Be window that receives the X-rays, leading them into a solid state detector (typically Si(Li) as above). The N-type portion is attached to a field effect transistor (FET) which amplifies the signal (Fig. 5). This is in turn mounted on a Cu rod immersed in LN2 to ensure proper cooling (Fig. 6). The signal is then routed to a multichannel analyzer (which sorts the pulses by voltage), and a PC for display (Fig. 7).
* energy gap in Si (difference between the conduction and valence bands)= 1.1 eV
* Mean energy used in generating one electron - hole pair = 3.8 eV
* # of electron hole pairs is proportional to the energy of the X-ray, and is converted to a voltage
* The ideal # of charges (electron – hole pairs) created per incident particle with energy E is given by: n = E/3.8
* Energy resolution: FWHM for Mn K. Typical resolution is ~ 128 - 150 eV for Si(Li), after taking into account noise and amplification distortions. Germanium detectors give a better resolution of 115 eV.
* Detector Efficiency: is low at very low KeV (absorption by window, by the Au coat in the P-type region, or by the dead layer of Si which lies between the Au layer and the active region), and drops off at KeV > 20 (only partial absorption by the detector; Fig. 8).
* Dead time: Signals arriving at the detector are averaged over a time interval known as “time constant” to minimize the effect of noise on pulse height analysis. This time constant is typically a few tens of microseconds. The “Dead time is the time taken for full pulse height analysis, and is related to the time constant. During this time, the system is unable to process any further pulses arriving at the detector. As signals arrive during the “dead time” at the detector, they accumulate, hence extending the dead time. The signal output therefore deviates from the signal input (Fig. 9). The percentage of the time during which the system is “dead” should be set at < 25 – 30%. Therefore, for 30% dead time in which the dead time is 30 seconds, the real time (livetime + deadtime) is 130 seconds. Dead time affects the total # of counts (peak height) if left uncorrected.
* Multiple Channel Pulse Height Analyzer (1024 channels at 10 eV each). This is what resolves your entire range of energies into specific “peaks”, in turn allowing for qualitative and quantitative analysis. The results are displayed in the form of counts vs. Energy (Fig.10).

**5- Wavelength Dispersive Spectrometer**

* The wavelength dispersive spectrometer consists of a monochromator (which is a special type of crystal designed to allow only specific wavelengths through), a gas proportional counter, and a pulse height analyzer. The monochromator and the counter are placed in a very strict geometrical arrangement.
* The *gas flow proportional counter* is used to detect X-rays on the microprobe, and constitutes an important part of this spectrometer; Figs. 11a & b). The counter is filled with P10 gas: 90% Ar, 10% CH4. X-rays then ionize the gas where 28 eV are absorbed per electron - ion pair created. These ions create a signal that is amplified and processed by either a *single channel analyzer* (SCA) or *multiple channel peak height analyzer* (MCPHA). The voltage applied to the gas flow proportional counter should be adjusted to ensure that ionization takes place in the proportional counter region (Fig. 11b).
* Xenon detectors can be used for shorter X-ray wavelengths. Non-flowing.
* Proper resolution is 15 - 20%
* The importance of the geometry, the working distance, and the takeoff angle (Fig. 12).
* Comparison between WDS and EDS (Table 1).

**II. Qualitative Analysis**

**Basic Principles:**

Qualitative analysis is carried out by the EDS. The multiple channel pulse height analyzer discriminates between the various peaks, each of which corresponds to a characteristic X-ray radiation by the different elements occurring in the sample. Because the most energetic characteristic peaks are the Kα peaks, these are most widely used for element identification.

**Problems and Artifacts:**

1. Peak broadening: results in a lower intensity, and an overall lower peak to background ratio (Fig. 13). This could lead to a problem of peak overlap.
2. Peak distortion: caused by collection of charges within the Si(Li) detector, and background shelf, or an area next to the peak in which the background is elevated.
3. Escape Peaks: Are small “satellite” peaks that appear at 1.74 keV below the main (parent) peak. They are produced when energy from an X-ray causes the emission of a Si K photon. These Si K photons are typically absorbed by the detector, but 1% of these do “escape”, lowering the # of counts for the parent peak (Fig. 14).
4. Sum peaks: Represent the sum of the energies of two major peaks in the spectrum, giving the impression of existence of some other element (Fig. 15). These sum peaks are produced when pairs of pulses arrive at the detector so close in time that the pulse processor sees them as one. Sum peaks are therefore a function of count rate, increasing as the count rate increases. A “pile up rejection unit” reduces the effects of sum peaks.
5. Si internal fluorescence: Is the appearance of a small Si Kα peak when there is no Si in the sample analyzed. It is caused by the X-rays producing such a peak in the detector as they pass through the Si(Li) detector.

**III. Quantitative Analysis**

***Basic Principles:***

Quantitative analysis is based on analyzing a standard and an unknown under identical conditions, and comparing the response of the detectors to both. The responses (represented by intensity of peaks obtained, Io for standard and I for sample) are then directly proportional to the concentrations of the elements contained (Co for standard and C for unknown). This is expressed as a k-ratio given by:

*k* = $\frac{I}{I\_{o}} ∝ \frac{C}{C\_{o}}$

***Using EDS:***

Beam current intensity variations do not affect the relative intensities of the characteristic peaks for the different elements. Nevertheless, beam current variations from the time of standardization will affect the overall intensities obtained, and will therefore affect the total wt%. It is therefore imperative to monitor the beam current intensity over time, and “recalibrate” it. In our lab, we do this by obtaining a spectrum on Co every ~ 2 hours; trying to always obtain the same number of total counts on it. Following beam calibration, the following steps become essential:

1. Peak identification: Identify the elements present in your sample, often correcting for escape and sum peaks, …. etc.
2. Background removal:
	1. Mathematical filtering
	2. Theoretical modeling: this is the method of choice.
	3. Linear interpolation
	4. Non-linear interpolation
3. Deconvolution: Also known as “peak stripping”. It is done by assuming a Gaussian distribution for all peaks, and removing those parts that are “extraneous” by one of the following methods:
	1. Overlap coefficients
	2. Reference deconvolution: using standards
	3. Filtered least squares fitting: yet another theoretical technique.
4. Corrections and Calculations:
	1. I and k ratio
	2. Corrections:
		1. Atomic number correction “Z”
		2. Absorption correction “A”
		3. Fluorescence correction “F”.

Resulting relation could be of the form:

$$\frac{C\_{sample}}{C\_{std}}= \left(\frac{I\_{sample}}{I\_{std}}\right).\left(\frac{Z\_{sample}}{Z\_{std}}\right).\left(\frac{A\_{sample}}{A\_{std}}\right).\left(\frac{F\_{sample}}{F\_{std}}\right).$$

***Using WDS:***

In this case, a stable beam current is an absolute necessity. The beam current is therefore routinely measured using a Faraday cup. The SCA ensures minimum overlap, and that all counts obtained are directly proportional to the concentration of the element analyzed. WDS analysis therefore involves the following steps:

1. Selection of the appropriate beam current (typically 15 nA is sufficient).
2. Pulse height analysis
3. Background corrections (as in EDS analysis, though backgrounds are not as problematic here owing to the much higher peak/background ratios obtained by the WDS.
4. Overlap corrections
5. Determination of K ratios through appropriate standardization.
6. Application of the matrix corrections (Z, A, and F) as above. Note that the “A” correction is the most important or critical. It is also largest for elements with Z = 11 – 14.

***Optimum conditions for quantitative analysis:***

* Eo has to be optimized; if too high, greater depth of field and hence fluorescence, if too low, greater absorption.
* Large takeoff angle (Fig. 16a & b)
* No tilting (Fig. 16c).
* Standards must be similar to the unknowns, especially in the case of WDS analysis.

***Limitations of Quantitative analysis with the SEM and microprobe***

1. EDS analysis can only work for major and minor elements (concentration = a fraction of a % by weight), not trace elements.
2. Can only detect elements with Z > 11 (for those SEM detectors with a Be window detector), and Z > 6 for windowless detectors. Microprobes can detect down to Z = 5 (B), but those require special crystals in their monochromators.
3. Cannot determine the oxidation state of the element analyzed. For example, Fe is reported as “total Fe”.
4. Analysis of relatively unstable samples under the beam requires particular care, and the use of special operating conditions. Clay minerals, serpentine minerals, and glasses are among the specimens that may become unstable under the beam, often undergoing some mobilization/ volatilization of the alkali elements. A defocused beam, and lower beam voltage may be necessary to obtain reasonable analyses.