SEM/EDS THEORETICAL STUFF

Philips 525 SEM Vacuum:

A rotary-vane mechanical pump continuously pumps the buffer tank and (on demand) the sample chamber.

An oil diffusion pump creates an ultra-high vacuum on the column and sample chamber.

The vacuum buffer tank “out-gasses” the diffusion pump.

How does a diffusion pump work?

Why does the column and specimen chamber need to be under ultra-high vacuum?

What problems will the vacuum present for specimen preparation?

Why do we desiccate air before it enters the column/specimen chamber?

Silicone based oil is heated in the boiler of the diffusion pump and the vaporized oil rises in the central tower and streams out of directional flutes directed downward in the pump throat. This allows air molecules to dissolve in the gaseous oil (gas dissolved in gas). As the oil-air mixture cools (due to water cooling coils wrapped around the pump throat) the oil condenses and returns to liquid, the air molecules come out of the gaseous oil solution and are pulled into the buffer tank vacuum. This removal of air from the top of the diffusion pump causes air from the sample chamber and column to diffuse towards the pump throat to replace the removed air molecules, thus the name “diffusion pump”. The beauty is that there are no moving parts to mechanically wear out. Modern silicone based oils withstand the repeated heating and thus diffusion pumps are very durable.

The electron beam:

The electron “gun” uses a tungsten filament that is heated by passing a current of electrons through it. As the current is increased, electrons are emitted from the filament and are directed toward an anode that is set to a positive bias of several kilovolts (1 – 30 kv, referred to as accelerating
voltage). The anode gives the electrons directionality and accelerates them, thus controlling their energy. As the filament current is increased, there reaches a point at which no more electrons will be given off. This setting is referred to as filament saturation. If the filament current is increased beyond this setting, the filament will overheat and the tungsten may then vaporize (i.e., burn out the filament). Even at the saturation current, some tungsten is vaporized from the filament surface thus causing the filament to become thinner with time. As this occurs, the filament will saturate at an increasingly lower current. Operators must recognize this change and be able to adjust the current accordingly. It is better to slightly under-saturate the filament as this will significantly extend filament life.

The number of electrons in the beam is determined by the “emissions” (filament) current at saturation. This is determined by the distance of the filament tip from the Wehnelt cap aperture. The closer the filament is to the positively biased Wehnelt cap, the more electrons are drawn off the filament thus allowing a higher saturation current, i.e., higher emissions.

As the electrons are accelerated by the anode, they then pass through a condenser lens that, as its name implies, condenses the electrons into a “beam”. The strength of this lens current determines the spot size, i.e., the diameter of the beam. Other lenses control the aiming of the beam so that it can be scanned over the surface of a specimen in a variety of patterns.

Electron microscope lenses are basically electromagnets. They create donut shaped electromagnetic fields such that the electrons are either repelled (e.g., to condense the electrons into a beam) or attracted. This is the same principle as an oscilloscope or any cathode ray tube (CRT) display.

What happens when high-speed electrons hit the specimen?

The electrons will interact with the specimen in a variety of ways but the penetration of the beam into the mass of the specimen is determined by basically four parameters:

- beam current (how many electrons in the beam)
- spot size
- accelerating voltage (i.e., speed or energy of the electrons)
- mean atomic number of the specimen
The latter 2 factors are the most influential in determining the penetration of the electron beam into the sample as illustrated in the following figure representing electron paths:

The following may result from the electron/specimen interaction:

Charging
Secondary Electrons
Elastically scattered Electrons
Inelastically Scattered Electrons
Backscattered Electrons
Bremsstrahlung
Characteristic X-Rays
Auger Electrons
Cathodoluminescence
Heating
Charging:
In order for the specimen to not accumulate electron charge, the specimen must be conductive and connected to a ground. Charging will cause the image to appear “washed out” and to move or change dimensions, lacking detail. The specimen stage and mounting stub are grounded. Non-conductive samples (such as most biological specimens) may be connected to the ground by conductive paint (e.g., silver or carbon paint) and/or coated with a conductive layer of metal (e.g., gold) using the “sputter” coater. The sputter coater uses an argon plasma to deposit a thin layer of gold on the specimen. Gold is a very good electrical conductor and does not degrade resolution appreciably due to its very fine grain size and the maximum resolution limits of our SEM.

Secondary electrons (SE):

When the electrons of the SEM beam (primary electrons) collide with electrons of the atoms of the specimen, some of the more weakly bound electrons may be ejected from these atoms and are referred to as “secondary electrons”. Any electron ejected from an atom due to collision with another high-energy electron is technically a secondary electron. These electrons are fairly low energy electrons and emanate near the surface of the specimen since secondary electrons emanating deeper in the specimen are easily absorbed by the mass of the specimen. Thus, secondary electrons are useful in imaging the surface topography of the specimen with good lateral resolution but yield little information as to the composition of the specimen.

Backscattered electrons (BSE):

When the electrons of the beam (primary electrons) collide with the nucleus of an atom (especially a large atom) it may be scattered in any direction without losing much of its energy. Those electrons scattered back towards the detector are referred to as “backscattered” electrons. They are often useful in imaging specimens with a high mean atomic number and are thus often informative for determining the sample composition. They also have greater energies and thus may be emitted from deeper within a sample. Higher accelerating voltages and higher mean atomic number specimen atoms will yield greater backscattered electron signals.

Both secondary and backscattered electrons may be detected by the SEM SE detector. There is a wire grid placed in front of this electron detector
that can be charged with a positive bias voltage (up to 300 volts) that will attract the weak secondary electrons towards the detector thus increasing the efficiency of detection. Since backscattered electrons are more energetic, we can selectively image these by reversing the grid to a negative bias (up to –300 volts) thus repelling the weak secondary electrons while the higher energy backscattered electrons still strike the detector because they are less affected by the grid bias. In either case, the electrons strike the detector in a pattern reminiscent of the topography of the specimen thus forming the image displayed on the SEM CRT monitor.

X-Rays:

There are three types of X-Rays generated when an electron beam collides with a specimen; Bremsstrahlung (continuum X-Rays), characteristic X-Rays, and secondary fluorescence X-Rays.

Bremsstrahlung (pronounced brem stra lung):

When a primary electron is scattered (deflected) inelastically by the interaction with an atomic nuclear coulomb field (and the inner-most electron shells) of an atom, it (the primary electron) is decelerated and some or all of its energy is given off as an X-radiation called a Bremsstrahlung (Ger.. = “breaking radiation”). This results in a wide spectrum of energies emitted, thus the name “continuum” X-Rays with the maximum energy being the energy of the primary electron (which is attributed to the accelerating voltage applied to the electron beam). With variable energies, these electrons do not yield useful data for elemental analysis of the specimen. Also, the lower energy Bremsstrahlung are readily absorbed by the specimen mass thus making any quantitative analysis problematic.
Characteristic X-Rays are another matter !!!

Characteristic X-Rays are generated in a quite different manner, yielding useful data for determining elemental composition of a specimen. When an electron from an inner (low-energy) shell of an atom is ejected by collision with a primary electron, it creates a “hole” where by another electron will be attracted to fill the hole. That is, the atom will be excited to a high energy level and will come back to relaxed or ground state when another electron falls from a higher energy orbit to fill the electron hole. The difference in energy between the lower energy “hole” orbit and the higher energy electron orbit will be given off as an X-Ray emission. The energy of this X-Ray is characteristic of the atom and orbit of origin thus yielding analytical data.

The number and energy levels of characteristic X-Rays will vary according to the atomic number of the atom impinged by the primary electron. Generally speaking, the higher the atomic number of the atom, the higher the energy of the characteristic X-Rays it will emit (per shell) and the higher number of low energy lines it will emit (e.g., K $\alpha,\beta,\gamma$).

The following figure illustrates the K series peaks according to atomic number of the atom of X-Ray origin.

![Atomic Number Order for the K Series Peaks](image)

A K$\alpha$ X-Ray will be emitted when an L shell electron fills the K electron hole, a K$\beta$ X-Ray will be emitted when an M shell electron fills the K shell hole, etc.

The number of characteristic X-Rays is determined by the mean atomic number of the sample, the probability of the X-Rays being absorbed by the specimen mass, and the number of secondary emission (fluorescence
X-Rays) due to the absorption of characteristic X-Rays. Thus, the counts on a qualitative elemental spectrum rarely mimics the quantitative analysis of a specimen.

Secondary fluorescence X-Rays:

When a characteristic X-Ray or (occasionally a strong) continuum X-Ray is absorbed within the mass of a specimen (e.g., when a high kV setting causes the electrons to penetrate deeply into the specimen), the energy of the X-Ray will excite an atom. The relaxation of the atom to ground state can then emit a characteristic X-Ray of energy equal or less than the exciting X-Ray. This might “expand” the elemental analysis but it will be at the expense of lateral resolution of analysis since X-Rays can travel through a sample considerable distances, depending on the mean atomic number of the specimen.

Occasionally, a characteristic X-ray is reabsorbed within the same atom that it was emitted from and causes another low energy electron to be ejected. The filling of this hole by a higher energy electron may cause the emission of a secondary X-Ray but the ejected electron, called an Auger electron (pronounced “Oh- shay”, after our very good and dear friend Pierre Auger who discovered these electrons in the early 1900s), is also characteristic of the emitting atom. Auger electrons, being of low energy (lower energy than the X-Rays that collided with them), are still characteristic of the emitting atom but they are only emitted from the first few angstroms of the specimen since they are easily absorbed within the mass of the specimen. Auger spectroscopy must be done in very ultra-high vacuum on the order of 10^{-8} or 10^{-9} torr since air molecules would easily “interfere” with these low energy electrons. Those who study “surface chemistry” often use Auger spectroscopy to detect picogram or less quantities of low atomic weight elements.

Heating:

The electron beam bombardment can generate considerable heat thus specimen characteristics are important to understand. If the specimen contains material having a low melting point, one may observe it vaporizing when struck with a high energy beam. This is not good since the vaporized material will be deposited on nearby surfaces (such as the detector(s)) thus contaminating them. It is paramount that the surfaces within the specimen chamber remain free of contamination. When in doubt about the composition of a specimen, use a lower beam energy (kv
setting) so as to minimize the possibility of contamination.

Detecting X-Rays:

The X-Ray detector is a silicon crystal (often doped with lithium, etc.) that changes its resistance to current flow with the absorption of X-Ray energy. This “pulse charge” (i.e., increase in conductivity) is registered as a count of X-Ray and the magnitude of this pulse charge is measured in keV by a multi-channel analyzer (MCA) and is characteristic to the shell and element of the X-Rays’ origin. The detector software uses a look up table (LUT) to determine the source of the X-Ray.

The X-Ray detector not only measures the qualitative signature of the X-Rays, but similar to the SE detector, can “image” the location of the X-Ray emission to create an X-Ray map. The geometry considerations are similar between the 2 detectors. By knowing the characteristics and geometry of the electron beam, detector and specimen relationship, the detector software can compensate for the factors described above (self-absorption, takeoff angle, acceleration voltage, etc.) and provide very good quantitative analysis of the specimen.

All current detectors have some thermal “leakage current” that is observed as “background” noise thus detectors are cooled with liquid nitrogen to minimize this effect.

The “Amp Time” setting determines the time interval that the detector circuitry “processes” X-Ray energy absorption. This in turn determines the % dead time in relation to the count rate (i.e., CPS). When the detector/MCA is processing X-Rays, it cannot accept additional X-Ray signals. Generally speaking, the higher the count rate, the higher the % dead time (i.e., the detector can become saturated).

When detecting high energy peaks (e.g., high mean atomic number), use a longer amp. time (time constant) and adjust CPS to give a 20 - 40% deadtime (e.g., adjust spot size and/or accelerating voltage).

When detecting low energy peaks, use the longest amp. time (time constant) at 400 - 800 counts/sec.

To have high throughput (maps, trace elements), use one of the faster amp. times and a count rate to give 30 - 60% deadtime.
Some artifacts to watch for:

When characteristic X-Rays are absorbed by the silicon atoms of the detector they often cause secondary fluorescence, thus emitting weak characteristic X-Rays of silicon. If this secondary X-Ray is absorbed by the detector it will still be registered as the count of the original element that emitted the first characteristic X-Ray. This is because the pulse charge of the secondary fluorescence X-Ray would be subtracted from the first X-Ray energy pulse charge but would be added back to it because it would be processed during the same “amp time” setting. However, if the secondary X-Ray is not absorbed by the detector (but instead is emitted from the detector surface), it will cause the occurrence of an “escape peak” of counts of the element that is 1.74 keV less than the original elemental peak (i.e., the energy of the silicon Kα X-Ray).

“Sum peaks” occur when 2 characteristic X-Rays are absorbed by the detector simultaneously and processed as a single pulse charge. This is more common with very high count rates.

Some generalizations for beam and image attributes:

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