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Energy Dispersive Spectroscopy

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Welcome

MyScope was developed by Microscopy Australia to provide an online learning environment for those who want to learn about microscopy. The platform provides insights into the fundamental science behind different microscopes, explores what can and cannot be measured by different systems and provides a realistic operating experience on high end microscopes.

We sincerely hope you find our website: www.myscope.training an enjoyable environment. In there you can explore the microscopy space and leave ready to undertake your own exciting experiments.

Module Contents

What is microanalysis?

Microanalysis is the identification of the chemical elements present either within or on the surface of an object, and additionally, how the atoms of the elements are arranged with respect to each other. Identification of the elements present may be qualitative or quantitative. Different isotopes of the elements, or their ratios, can also be measured. Microanalysis can also require working out the spatial relationships between the atoms in the object, i.e., its structure, particularly if it is crystalline. Some microanalytical techniques can provide information about crystal defects, chemical bonding or redox state.

In microanalysis, the analytical spot size ranges from about 100 µm to 100 nm, although many techniques are capable of generating maps of larger areas millimetres or centimetres across. The depth of the analysis is also important, and some techniques will analyse only the top few nanometers of the sample (surface techniques) while others will penetrate to depths of several microns. Smaller length-scales (<100 nm) that allow analysis at molecular or atomic resolution are part of nanotechnology or nanoanalysis.

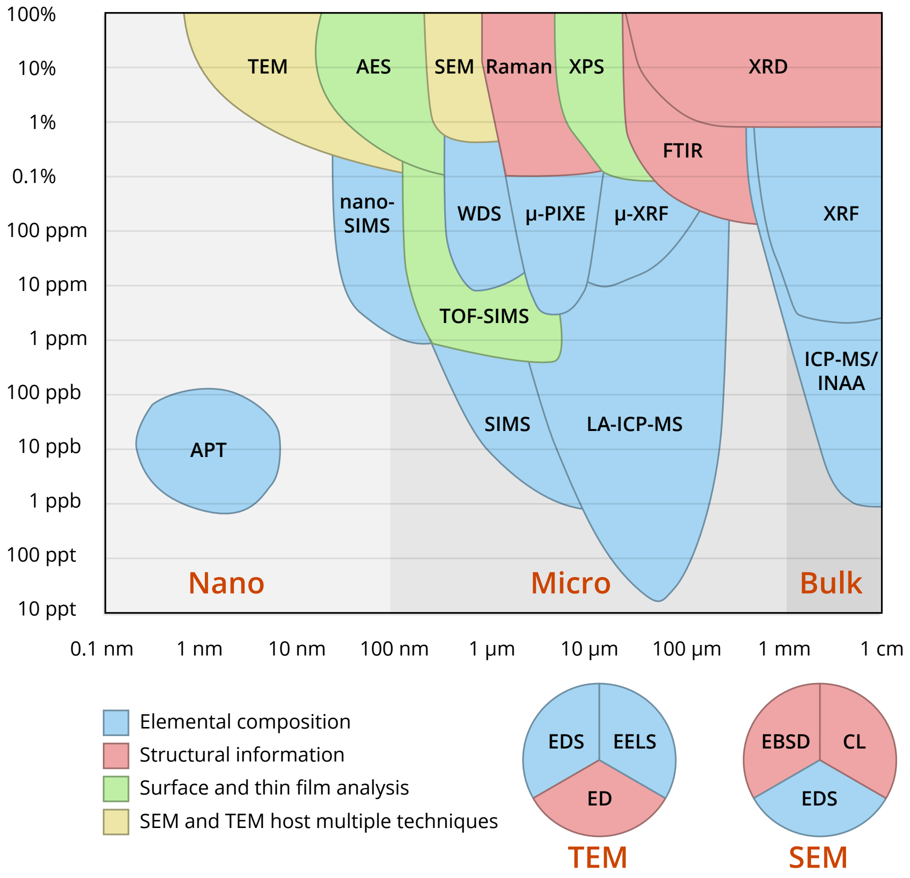
In most microanalysis techniques, the sample can be analysed in situ, whereas for nanoanalysis small portions of the sample may need to be cut out for analysis, and for many bulk techniques the sample needs to be pulverised or dissolved before it can be analysed.

Most microanalysis techniques involve focussing a microbeam on the object to be analysed and measuring an output beam that results from the interaction of the input beam with the atoms and molecules making up the sample. The input beam may comprise light (including laser beams), X-rays and other electro-magnetic waves, electrons, protons or ions. The outputs that are measured also include light, X-rays, electrons and ions.

There are many techniques available for microanalysis. For example, see http://www.ammrf.org.au/techniquefinder/ or http://en.wikipedia.org/wiki/List_of_materials_analysis_methods.

Two of the most important considerations in microanalysis are spatial resolution, or the size of the object or particle to be analysed, and the detection limit of the technique.

The diagram below shows some of the most commonly used microanalytical techniques arranged according to their spatial resolutions and sensitivities.



Scanning electron microscopes (SEMs) and transmission electron microscopes (TEMS) can be fitted with a range of detectors that can give information about chemical composition and structure, as shown in the diagram. The best technique to use will depend on the required spatial resolution and depth resolution, whether qualitative or quantitative chemical analysis, or structural analysis, is needed, and the minimum detection limit.

In this module, some of the most common techniques used in combination with electron microscopy will be presented.

What is energy dispersive X-ray spectroscopy?

Energy Dispersive X-ray Spectroscopy (EDS, EDX or XEDS) is a qualitative and quantitative X-ray microanalytical technique that can provide information on the chemical composition of a sample for elements with atomic number (Z) >3, although for specific sample and equipment configurations (Z) >2 is now achievable

An electron beam is focussed on the sample in either a scanning electron microscope (SEM) or a transmission electron microscope (TEM). The electrons from the primary beam penetrate the sample and interact with the atoms from which it is made. Two types of X-rays result from these interactions: Bremsstrahlung X-rays, which means ‘braking radiation’ and are also referred to as Continuum or background X-rays, and Characteristic X-rays.

The X-rays are detected by an Energy Dispersive detector which displays the signal as a spectrum, or histogram, of intensity (number of X-rays or X-ray count rate) versus Energy. The energies of the Characteristic X-rays allow the elements making up the sample to be identified, while the intensities of the Characteristic X-ray peaks allow the concentrations of the elements to be quantified.

The underlying principles for generation of X-rays and detection by EDS are the same for SEM and TEM. However, due to the differences in construction of the two types of microscope, and the different accelerating voltages used in their operation, there are some differences in how EDS detectors perform on the two platforms. The spatial resolution of EDS analysis in the SEM depends on the size of the interaction volume, which in turn is controlled by the accelerating voltage and the mean atomic number of the sample, Z. For EDS in the SEM, spatial resolution and depth resolution is on the order of a few microns. In the TEM, the sample is a thin foil and there is less spreading of the electron beam at higher accelerating voltages, so the spatial resolution is better at higher kV. The spatial resolution of EDS analysis in the TEM is on the order of nanometers while the depth resolution is governed by the thickness of the sample.

The detection limit of EDS analysis in the SEM depends on the composition of the sample being analysed, but is in the range 0.1-0.5 wt%. It is an effective technique for major and minor element analysis, but lacks the sensitivity for trace-element analysis. In the TEM detection limits of ~0.01-0.1 wt% can be achieved.

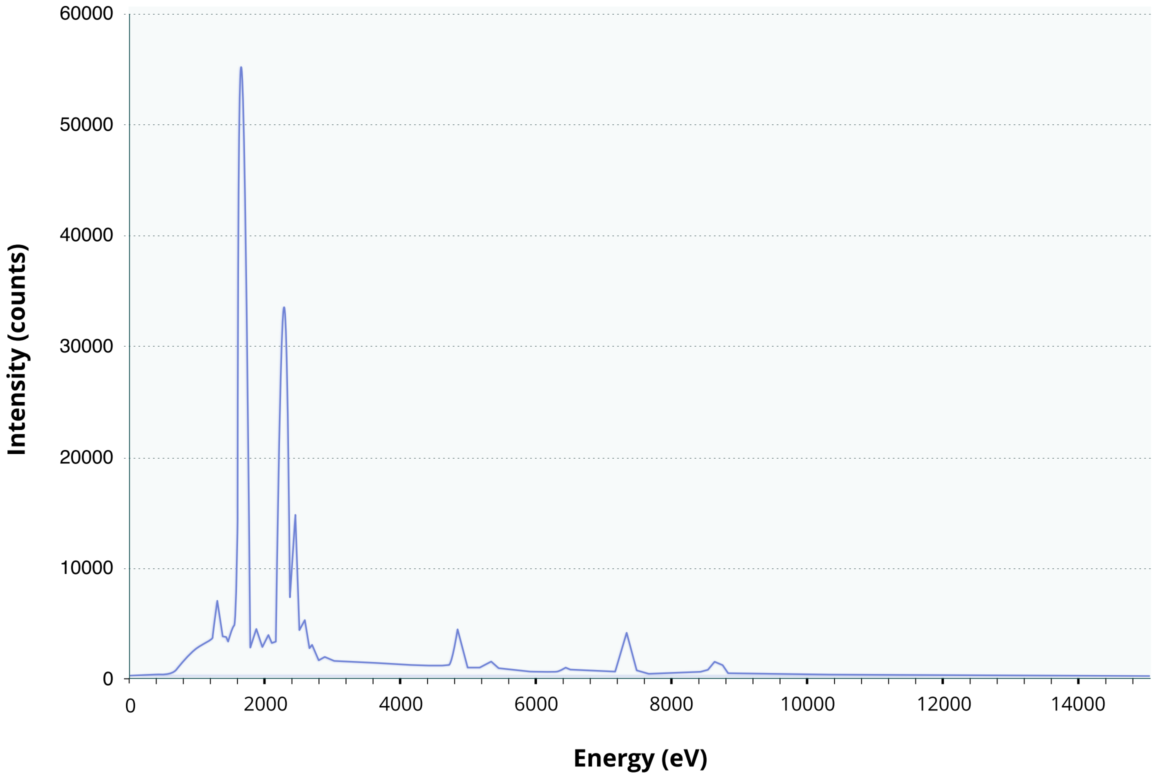
EDS is considered a non-destructive analytical technique, that is, the sample can be re-analysed many times. In reality, most materials will experience some damage under an electron beam, and some samples are particularly susceptible, e.g., clay minerals and glasses. No special sample preparation, other than that required to image the sample in the SEM or TEM, is required for qualitative analysis, but for quantitative analysis in the SEM the sample must be bulk, flat and polished.

As in SEM and STEM imaging, the electron beam can be rastered over an area of the sample to produce X-ray element distribution maps.

Outputs from EDS analysis

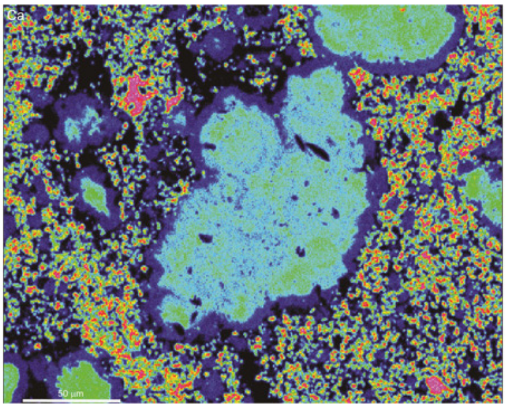
Spectrum

Spectrum: a plot of the number of X-rays detected versus their energies. Characteristic X-rays form peaks superimposed on Bremsstrahlung X-rays. The Characteristic X-rays allow the elements present in the sample to be identified.



Map

Map: an image showing how the concentration of one element varies over an area of a sample. In this example, red colours indicate higher concentrations and blue colours reflect lower concentrations.



Quantitative analysis

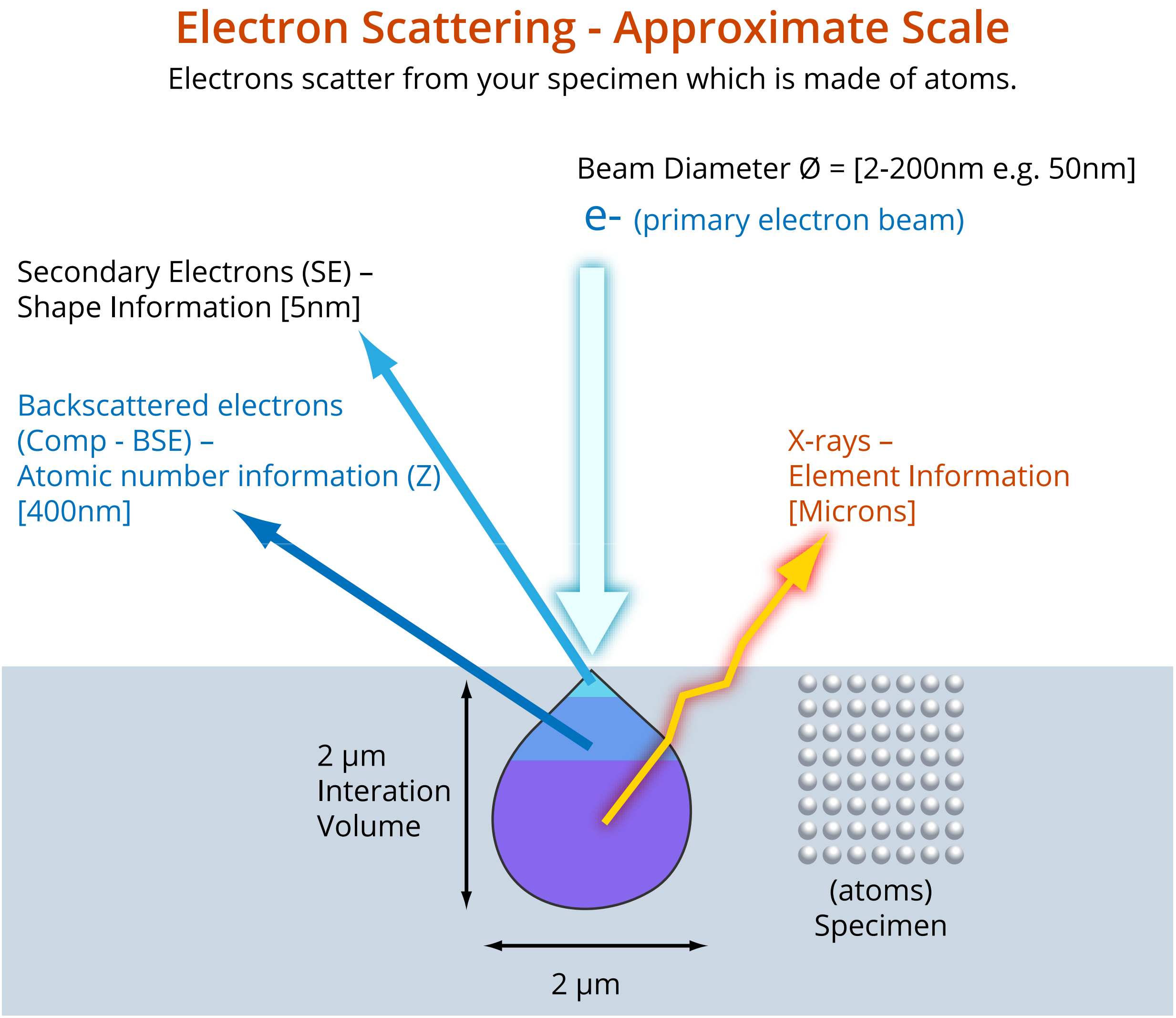
Quantitative analysis: concentrations of major and minor elements (weight percentages) in different phases in the sample can be calculated by comparison with standard reference materials.

DESCRIPTION	r171 (2)	r172 (2)	r173 (5)	r175 (7)
MINERAL	ACANTHITE	CHALCOPYRITE	ELECTRUM	PYRITE
S	9.7	34.5	0.4	53.4
Fe2+	1.0	29.8	0.8	48.3
Cu	0.8	33.9	b.d.	b.d.
Zn	3.3	1.2	b.d.	b.d.
Se	4.7	b.d.	b.d.	b.d.
Ag	81.9	b.d.	45.5	b.d.
Au	b.d.	b.d.	51.8	b.d.
Total	101.4	99.4	98.5	101.7

Generation of X-rays in the electron microscope

The specimens examined in an electron microscope are made up of atoms. When electrons from the primary beam of the electron microscope are focussed on a specimen, they penetrate it and interact with the atoms that make up the sample material. In the scanning electron microscope (SEM) the electrons from the primary beam spread out in the sample to form the interaction volume. The size of the interaction volume depends on the accelerating voltage of the primary electron beam and the mean atomic number (or density) of the sample. The interaction volume will be larger for a larger accelerating voltage, but smaller for samples with a higher mean atomic number.

In the SEM secondary electrons are produced from the surface of the sample or topmost part of the interaction volume; backscattered electrons come from the top half of the interaction volume; and X-rays are generated within the whole of the interaction volume. Therefore, the typical spatial resolution for X-ray microanalysis in the SEM is of the order of a few microns.

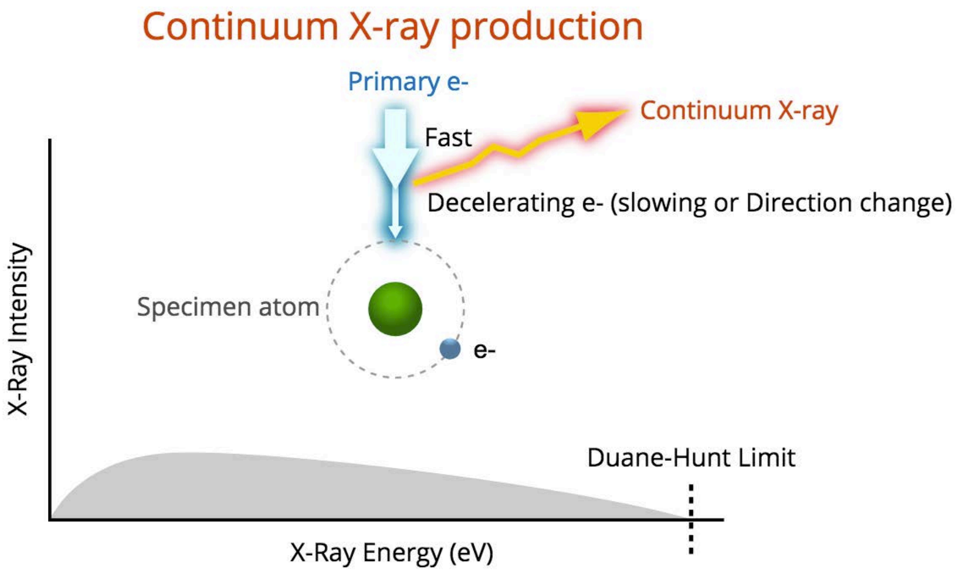


The typical spatial resolution of different signals, Secondary electrons, Backscattered electrons and X-rays, in the scanning electron microscope.

In the TEM, the sample is very thin (~10-200 nm) and there is minimal spreading of the electron beam as it passes through the sample. Therefore, the spatial resolution for X-ray microanalysis in the TEM is approximately of the same order as the sample thickness.

Bremsstrahlung X-ray generation

Two types of X-rays are produced by interaction of the electron beam with the sample in both the SEM and TEM: Bremsstrahlung (which means 'braking radiation') and Characteristic X-rays. Bremsstrahlung X-rays are produced by slowing down of the primary beam electrons by the electric field surrounding the nuclei of the atoms in the sample (see Bremsstrahlung animation). Note: Bremsstrahlung X-rays are also referred to as continuum or background X-rays. The primary-beam electrons lose energy and change direction due to inelastic scattering in the sample. Some of the lost energy is converted to X-rays which have a range of energies, from ~0 up to Eo – the energy of the electrons in the primary beam. Bremsstrahlung X-rays cannot have energies greater than the energy of the electrons in the primary beam so this energy forms the upper energy limit of the X-ray spectrum and is known as the Duane-Hunt limit.

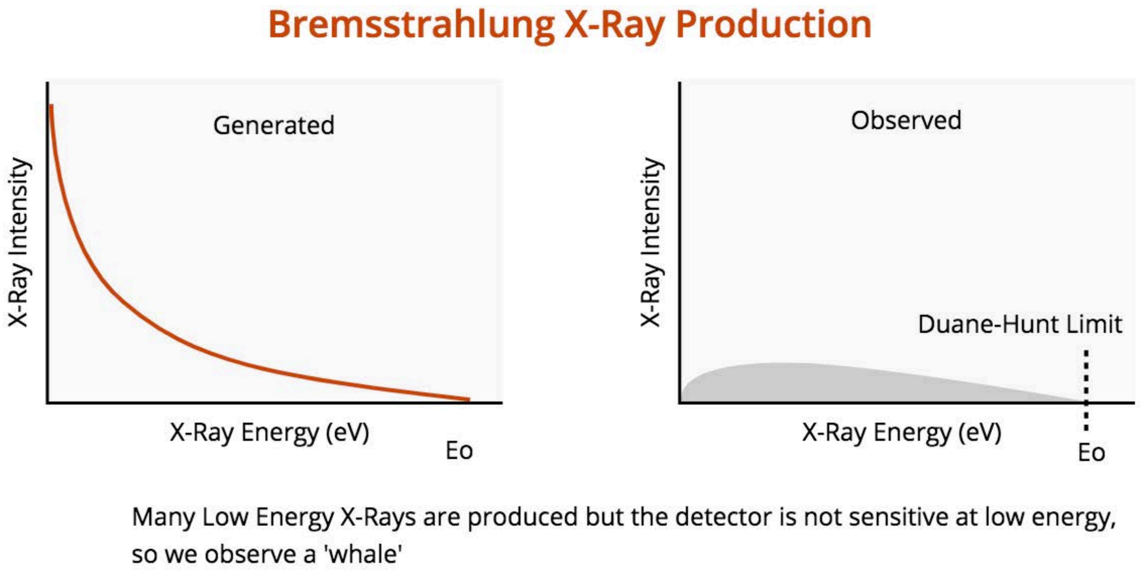


The primary beam electrons are slowed down or deflected by the electric field around the atoms in the specimen. Part of the energy that they lose is converted to Bremsstrahlung X-rays with energies between ~0 and the Duane-Hunt limit.

A primary beam electron may lose all of its energy in a single interaction event in which case it will produce one X-ray with energy Eo, but it is much more likely that the energy will be lost in a number of interactions in which small proportions of the initial energy are lost and an equivalent number of low-energy X-rays is produced.

The X-ray intensity, or number of X-rays produced, is zero where E = Eo (the Duane-Hunt limit) but increases rapidly at very low energies. This means that the X-rays produced by the primary beam electrons comprise mostly a large (almost infinite) number of low-energy X-rays.

Although a large number of low-energy Bremsstrahlung X-rays is generated, most are absorbed within the sample or the detector and the X-ray intensity observed in the spectrum decreases at low energy so that the Bremsstrahlung X-ray spectrum resembles a 'whale'.



The difference between generated and observed Bremsstrahlung X-ray spectra. Although many low-energy X-rays are generated most of them are absorbed so the observed spectrum records a decrease in X-ray intensity at low energy.

Kramer's law

The intensity, I, of the Bremsstrahlung X-rays at any energy E in the spectrum is given by Kramers' Law

$$I \approx i_p.Z(E_o - E)/E$$

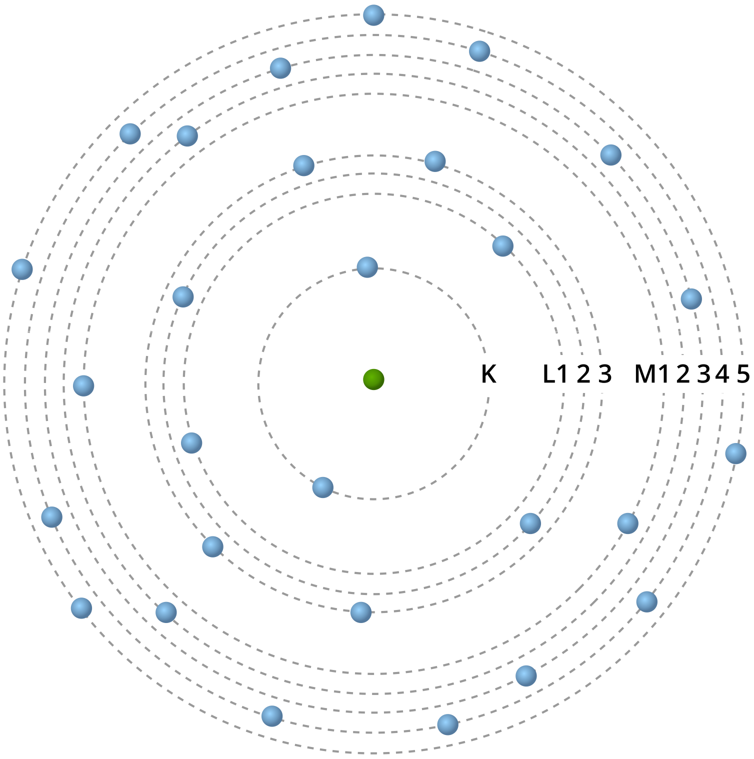
where i_p is the electron probe current, and Z is the mean atomic number.
The intensity is zero where $E = E_o$ (the Duane-Hunt limit) but approaches infinity (∞) as E approaches zero.
Note that according to Kramers' Law, the intensity of the Bremsstrahlung X-rays is proportional to Z, the mean atomic number of the specimen. This means that heavier materials like Pb or Au will produce more Bremsstrahlung X-rays than samples made from lighter elements such as C or Al.

Characteristic X-rays

The atoms of each element in the sample consist of a nucleus made up of neutrons and positively charged protons, and a cloud of negatively charged electrons that surrounds the nucleus. The number of protons in the nucleus of the atom defines its atomic number, Z, while in a neutrally charged atom the number of protons is matched by the number of electrons.

The electrons in the electron cloud have a stable set of energy levels, also known as electron shells. The shell closest to the nucleus is known as the K shell, followed outwards by the L, M, N, O, P and Q shells. EDS microanalysis is mostly concerned with electrons in the inner shells, i.e., the K, L and M shells. The maximum number of electrons in each shell is governed by quantum mechanics, with a maximum of two electrons in the K shell; eight electrons in the L shell; 18 electrons in the M shell, and so on. Each shell, apart from the K shell, is split into subshells, with the electrons in related subshells having slightly different energies. The L shell has three subshells; the M shell has five subshells, and so on.

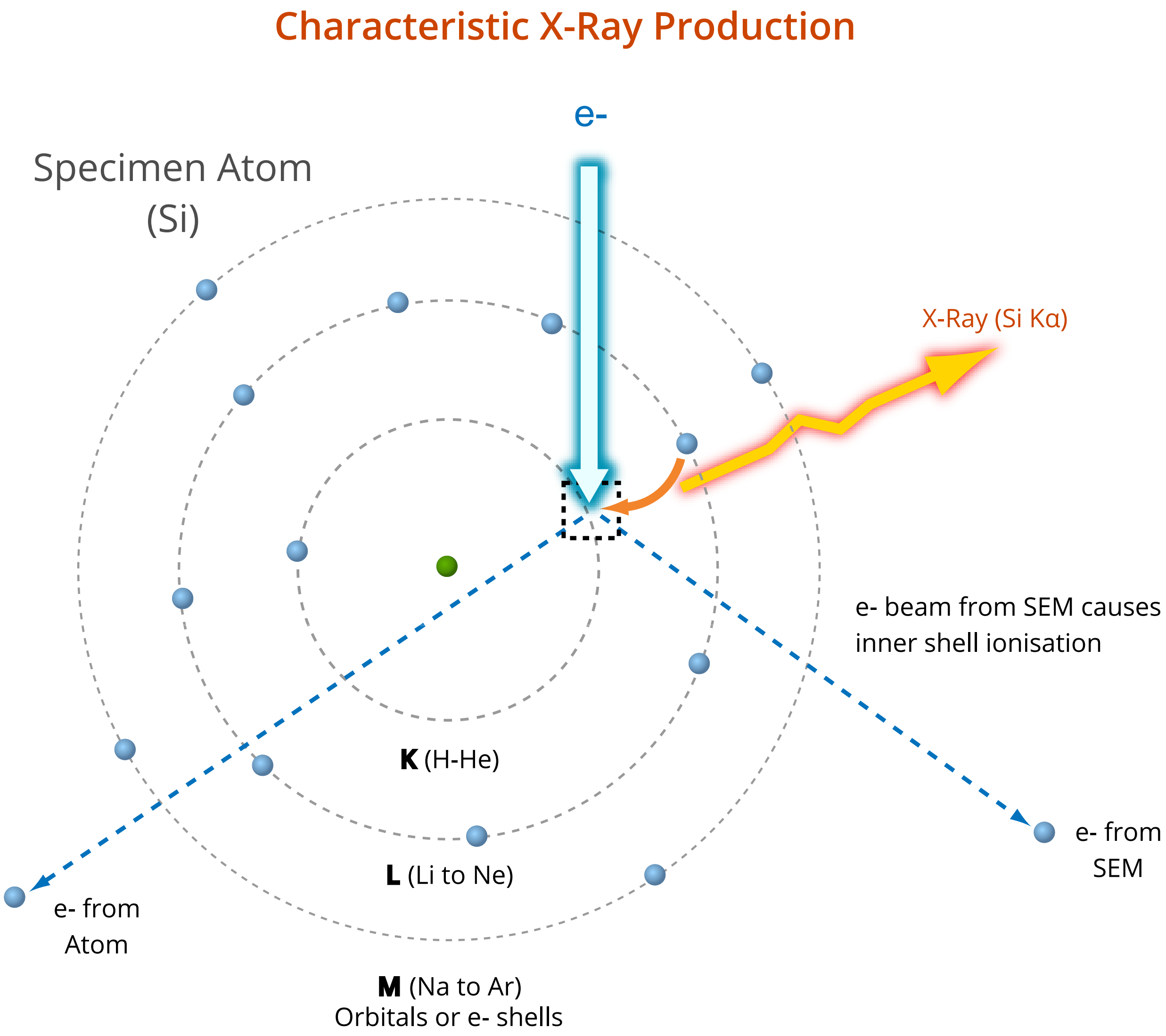
The K shell has the highest ionisation energy or critical ionisation energy in the atom. That is, more energy is needed to remove an electron from this shell than from subshells further from the nucleus. The further from the nucleus the electron is, the lower its ionisation energy. Characteristic X-rays are produced by electron transitions between the inner electron shells. The electrons in each shell and subshell have specific ionisation energies, and these are different for every element, that is, the ionisation energy for the K shell in Si (1.84 keV) is different from the ionisation energy of the K shell in Pt (78.4 keV).



A schematic drawing of an atom showing the nucleus surrounded by the K, L and M electron shells. The K shell can have a maximum of two electrons; the L shell has three subshells and can have a maximum of eight electrons; the M shell has five subshells and can have a maximum of 18 electrons.

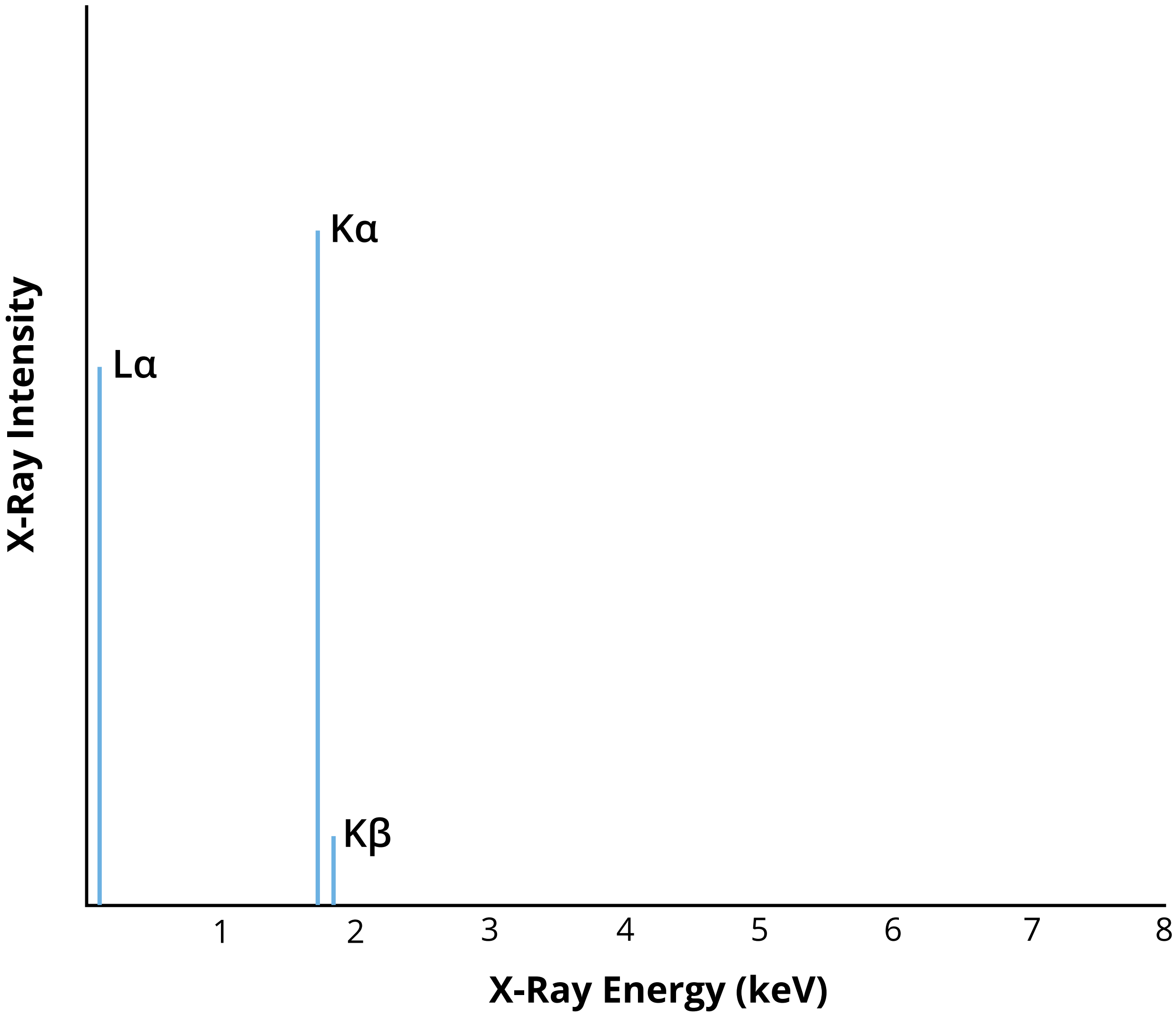
Characteristic X-ray generation

The production of Characteristic X-rays is a two-stage process: ionisation followed by relaxation (see Characteristic animation). Firstly, an electron is removed from one of the inner shells of the atom by an electron from the primary beam so that the atom is ionized and in an unstable state. Secondly, the atom regains stability when an electron from an outer shell fills the inner shell vacancy and an X-ray photon is emitted. The energy of the emitted X-ray is equal to the difference between the ionisation energies of the electrons involved in the transition.
Note that inner shell ionisation and Characteristic X-ray emission can result from irradiation by a primary beam of protons (PIXE) or X-rays (XRF) as well as electrons (EDS/WDS).



An electron from the primary beam dislodges an electron from the K shell of a Si atom in the sample. An electron from the L shell fills the vacancy and a Si Kα X-ray is generated. The energy of the X-ray is equal to the ionisation energy of the K shell minus the ionisation energy of the L shell.

As each element has specific ionisation energies for each subshell, so the difference between the energies is characteristic of the element involved in producing the X-ray photon. For Si, the ionisation energy of the K shell is 1.84 keV, the ionisation energy of the L shell is ~0.10 keV and the ionisation energy of the M shell is ~0.01 keV.

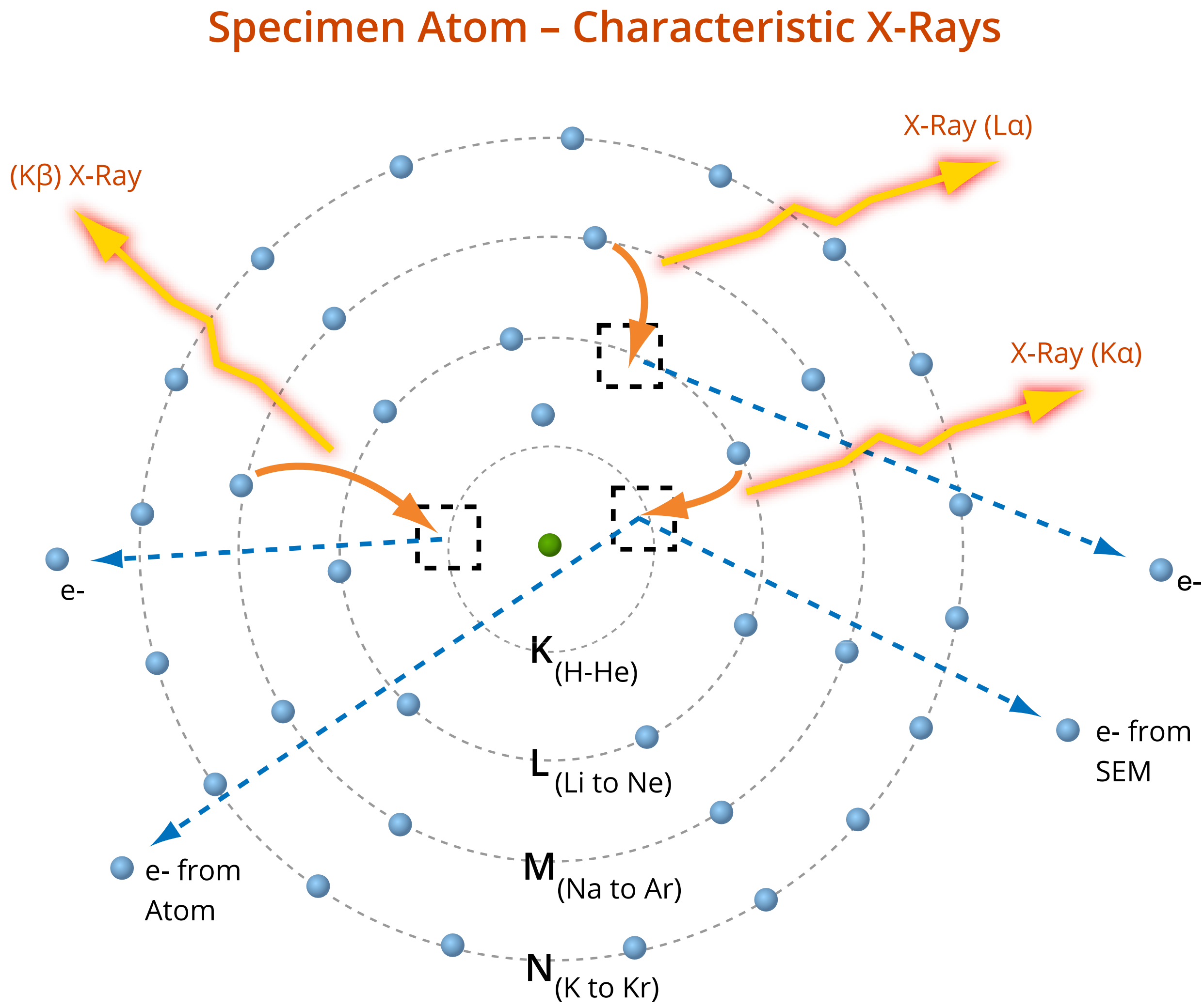


The ideal Characteristic X-ray spectrum for Si. The Characteristic X-ray lines, Kα, Kβ and Lα, have discrete energies.

The Characteristic X-ray spectrum for Si shows three spectral lines. The line at low energy (~0.09 keV) results from ionisation of the L shell with an electron from the M shell filling the vacancy: E = 0.10 – 0.01 keV. (This line would be at or below the limit of detection for most EDS detectors.) The line at ~1.74 keV results from ionisation of the K shell with an electron from the L shell filling the vacancy (E = 1.84 – 0.10 keV), whereas the smaller peak at higher energy (~1.83 keV) results from ionisation of the K shell and an electron from the M shell filling the vacancy (E = 1.84 – 0.01 keV).

Nomenclature

In spectroscopy, the most commonly used naming convention for Characteristic X-ray lines is the Siegbahn notation. The first component of the name is the element involved, e.g. Si. The second component is the electron shell that was ionized to produce the X-ray, e.g. K, L or M. The third component reflects the relative intensity of the line within each shell, e.g. α is the most intense line, followed by β and γ. The lines within each shell make up a family, or series, of lines for that shell, e.g., the K family comprises the Kα and Kβ X-ray lines.
In the Si spectrum, the lowest energy X-ray line is the Si Lα line; the line at 1.74 keV is the Si Kα line and the line at ~1.83 keV is the Si Kβ line.

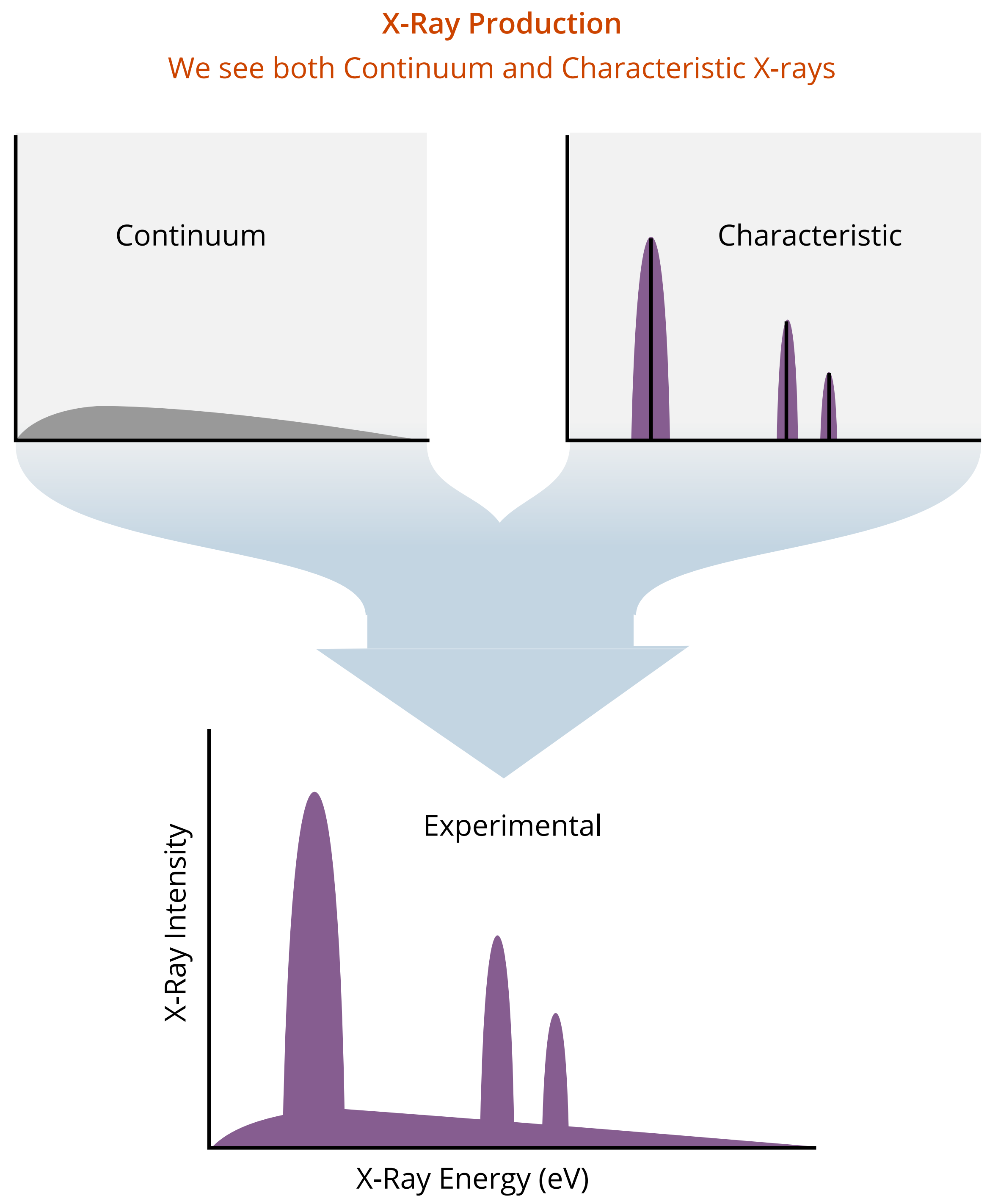


The electron transitions involved in generating the Kα Kβ and Lα X-ray photons.

For each element, the electrons in the K shell have the highest ionisation energies while the ionisation energies of electrons in outer shells are lower. More energy is required to ionize the K shell, and it follows that the energies of the K family X-ray lines for each element are greater than those of the L family, which are greater than those of the M family. That is, for every element: EK > EL > EM

The X-ray spectrum

The spectrum seen in the output from the Energy Dispersive Spectrometer (EDS) shows the Characteristic X-ray lines superimposed on the Bremsstrahlung X-rays. Although the Characteristic X-rays have discrete energies, in measuring them the signal is averaged and the lines become peaks which are superimposed on the continuum.

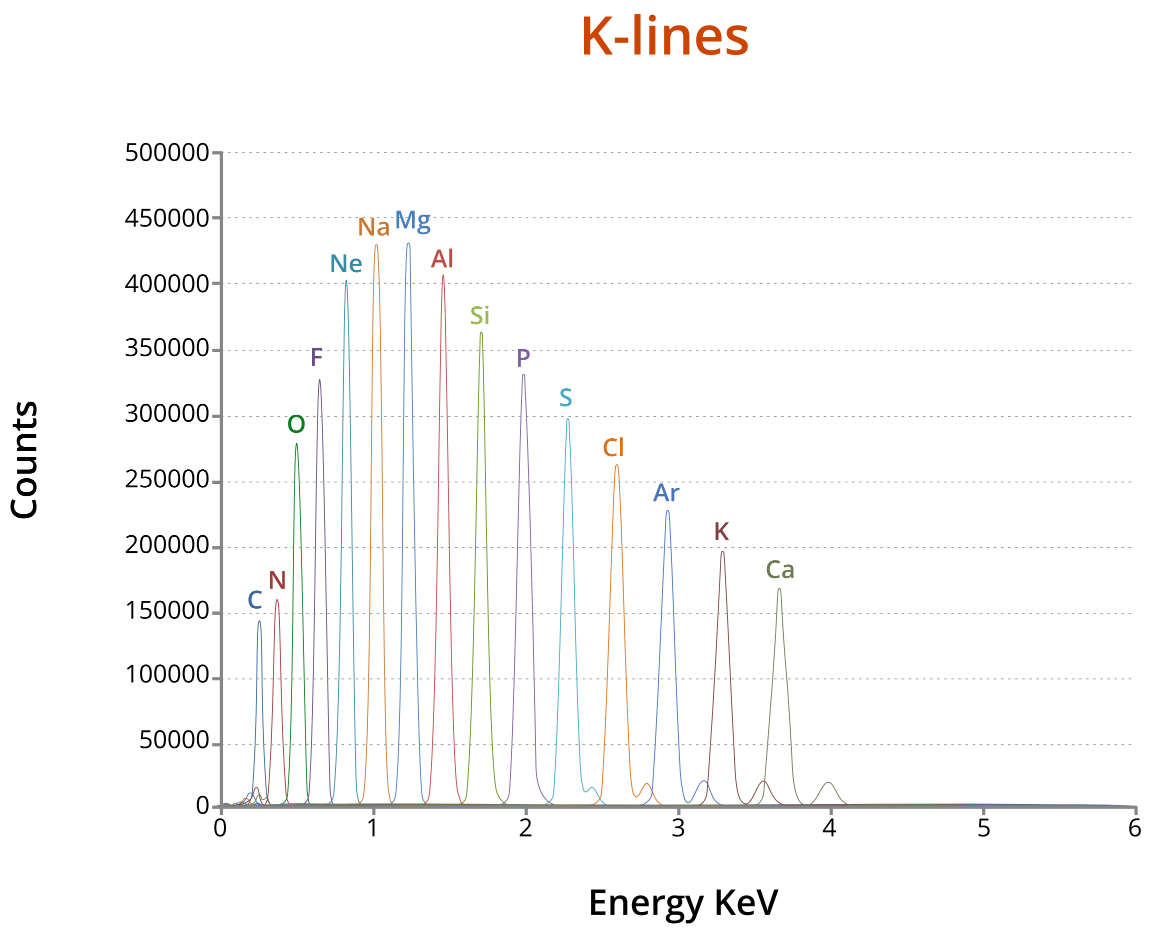


The X-ray spectrum displayed by the Energy Dispersive system comprises Characteristic X-ray peaks superimposed on the continuum (Bremsstrahlung X-rays).

Moseley's law

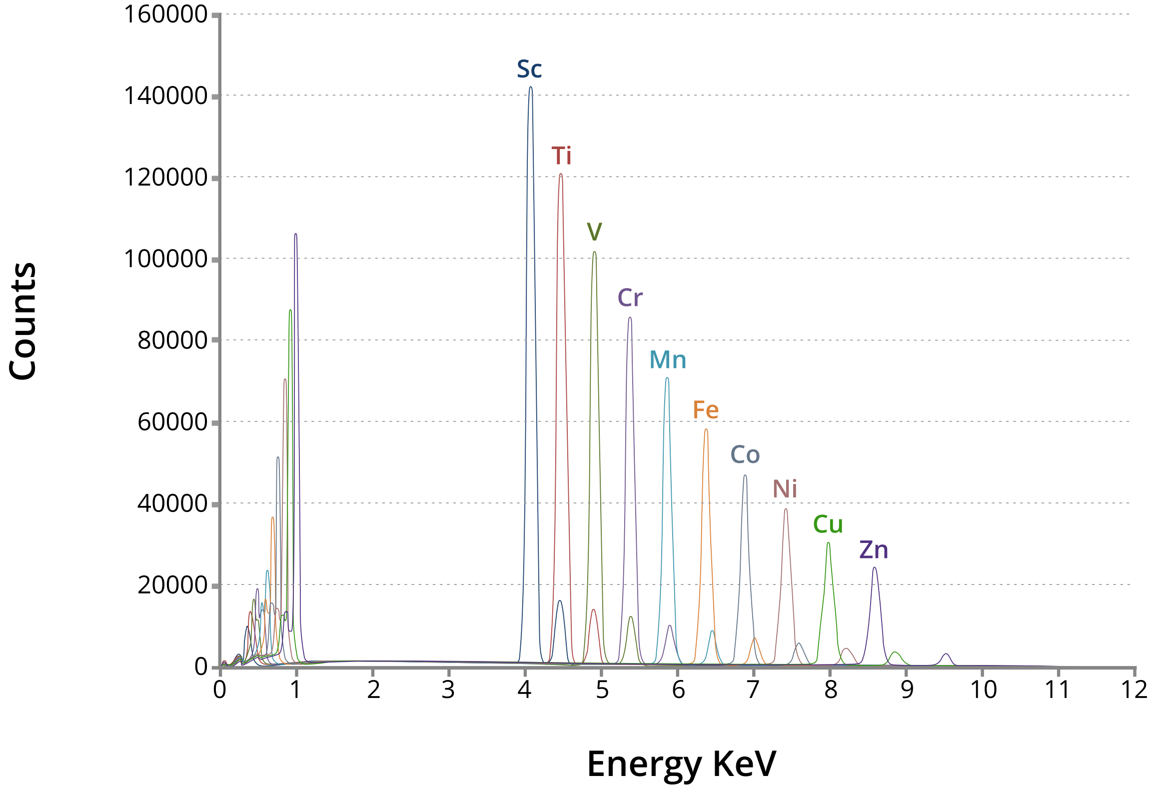
There is a relationship between the energy of the Characteristic X-ray lines for each element and its atomic number: the energy is proportional to the square of the atomic number, Z. This means that as the atomic number increases, the Kα X-ray line, for example, will plot at a higher energy in the ED spectrum. This relationship, known as Moseley’s Law, was discovered by Henry Moseley in 1913.

An alternative system for naming Characteristic X-ray lines follows the recommendations of IUPAC, where each line is designated by the to-shell or subshell and the from-shell or subshell. In this system, the Si Lα line would be the Si L3-M5 line; the Si Kα line would be the Si K-L3 line and the Si Kβ line would be the Si K-M3 line.



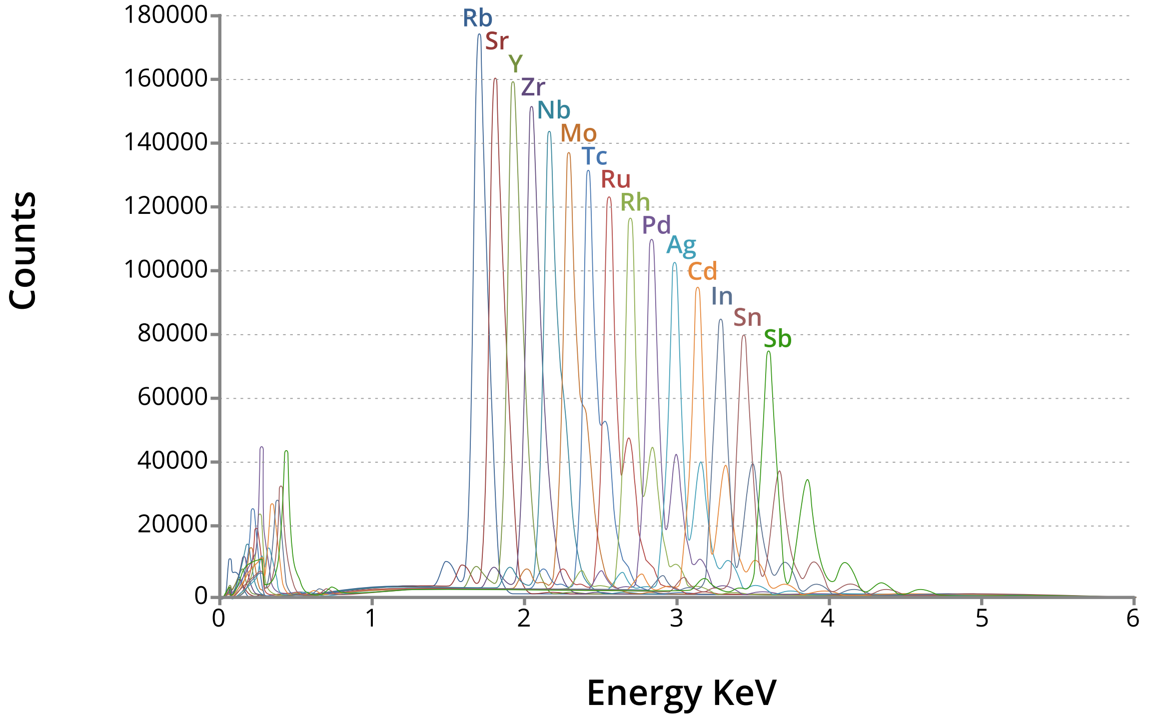
- *The Kα X-ray peak for carbon (Z=6).*
- *For sulphur (Z=16) the Kα and Kβ peaks can just be resolved.*
- *For calcium (Z=20) the Kα and Kβ peaks are clearly resolved.*

KL-lines



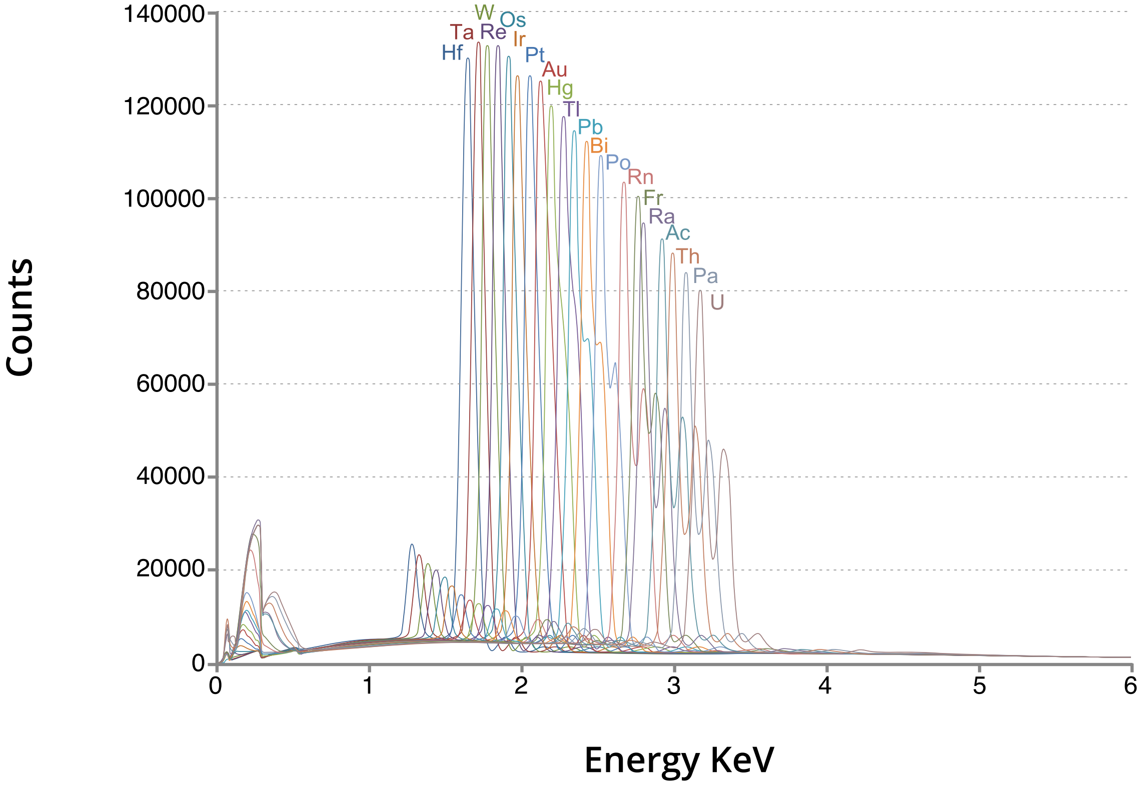
- *For scandium (Z=21) the Kα and Kβ peaks are resolved and L-family peaks are visible at low energy.*
- *For zinc (Z=30) the K-family peaks are resolved but the L-family peaks at low energy are not.*

L-lines



- *For rubidium (Z=37) the Ll peak can be seen on the low-energy side of the main L-family peak.*
- *For technetium (Z=43) the Lα and Lβ peaks can just be resolved. M-family lines are present at low energy.*
- *For antimony (Z=51) the L-family peaks are resolved.*

M-lines



- *For hafnium (Z=72) the Mζ peak (low energy) and Mγ peak (high energy) can be seen on either side of the main M family peak.*
- *For lead (Z=82) the Mα and Mβ peaks can just be resolved.*
- *For uranium (Z=92) the Mα and Mβ peaks are distinct, but not completely separate.*

X-ray intensity

The height of the Characteristic X-ray peaks in an ED spectrum, or the X-ray intensity, may be given in X-ray counts or count rate (counts per second or cps). It is tempting to assume that the height of the X-ray peak in the spectrum will be proportional to the concentration of the element in the sample. For spectra generated from a TEM this is largely true but for spectra generated from an SEM it is not the case. Factors related to the sample, the system used to generate the X-rays and the detector used to measure the X-ray spectrum can all influence the height of the X-ray peaks.

Concentration

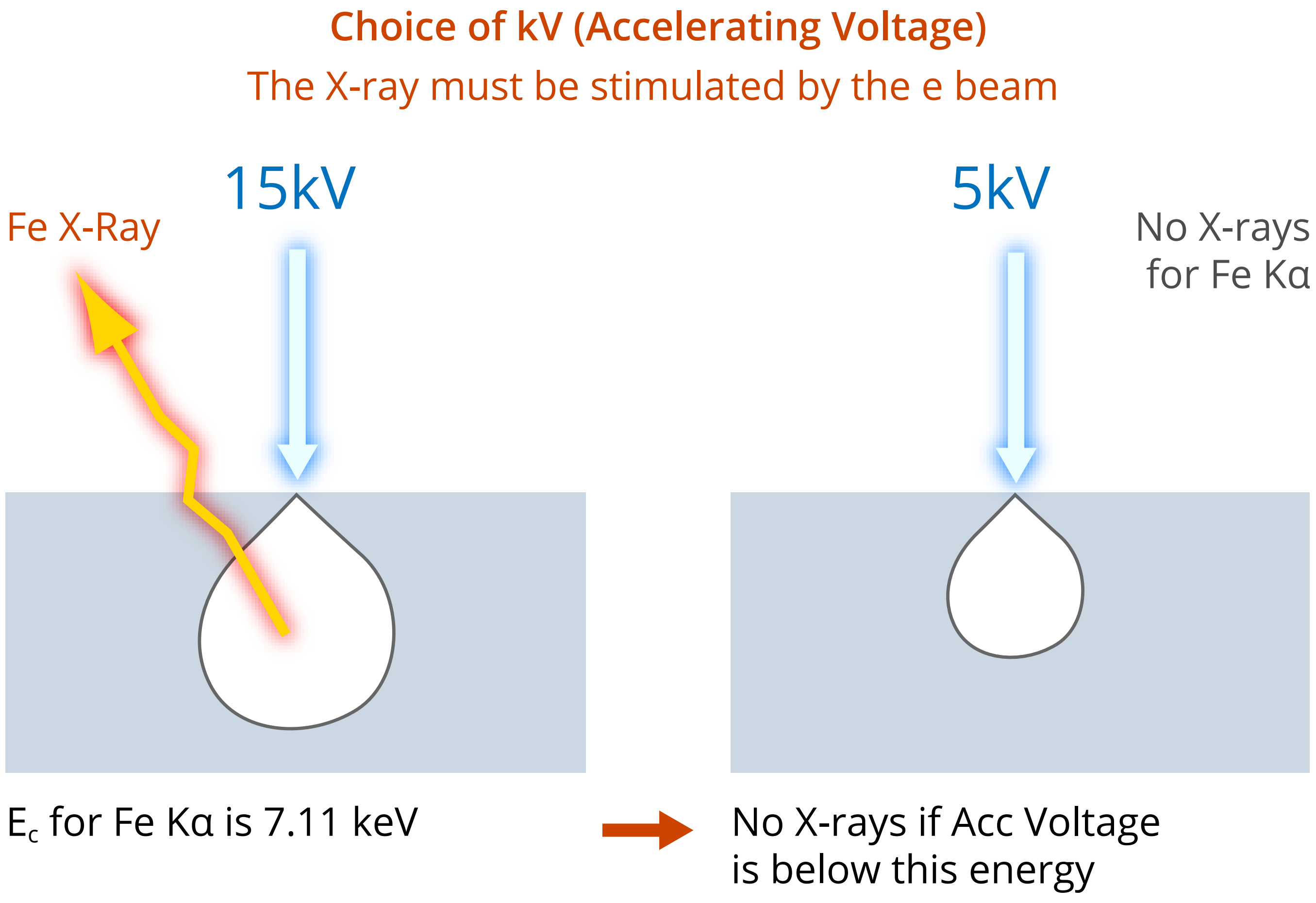
While the intensities of the peaks in an X-ray energy spectrum are not directly proportional to element concentration, it is true that the concentration of the element in the sample will influence the height of the X-ray peak. Elements present in major amounts (> 10 wt%) will have major peaks in the spectrum while elements present in minor (1-10 wt%) or trace amounts (<1 wt%) will have small or undetectable peaks in the spectrum.

Beam current, probe current or spot size

The beam current or probe current reflects the number of electrons in the primary beam of the electron microscope. It is controlled by the condenser lens or spot size control. The number of electrons in the primary electron beam is directly proportional to the number of X-rays generated from the sample and the number of X-ray counts recorded in the X-ray spectrum. Increasing the beam current will increase the number of X-rays generated from the sample but will not change the relative heights (intensities) of the Characteristic X-ray peaks in the spectrum.

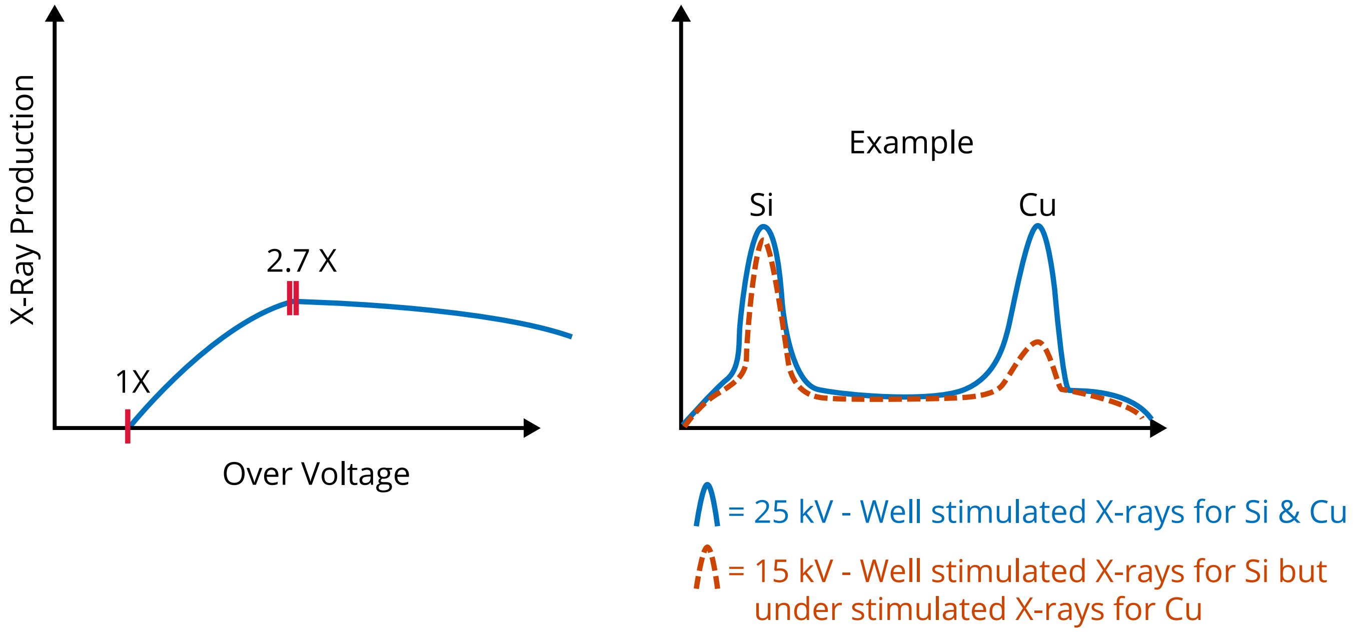
Accelerating voltage or overvoltage ratio

The accelerating voltage used in the electron microscope controls the energy of the electrons in the primary beam. In the SEM, accelerating voltages are typically 5-30 keV but in TEMs much higher accelerating voltages, 100-400 keV or more, are used. In order to generate Characteristic X-rays the electrons in the primary beam must have enough energy to overcome the ionisation energy, also called the critical ionisation energy, of the inner-shell electrons in the atoms of the sample. With the high accelerating voltages used in TEMs this is not a problem, but in SEMs care must be taken to use a sufficiently high accelerating voltage to stimulate X-rays from all elements in the sample.



If the energy of the electrons in the primary beam is less than the critical ionisation energy then no X-rays will be generated. If the accelerating voltage is 15 kV, both K and L family X-rays will be generated from Fe. If the accelerating voltage is 5 kV, no K family X-rays will be produced

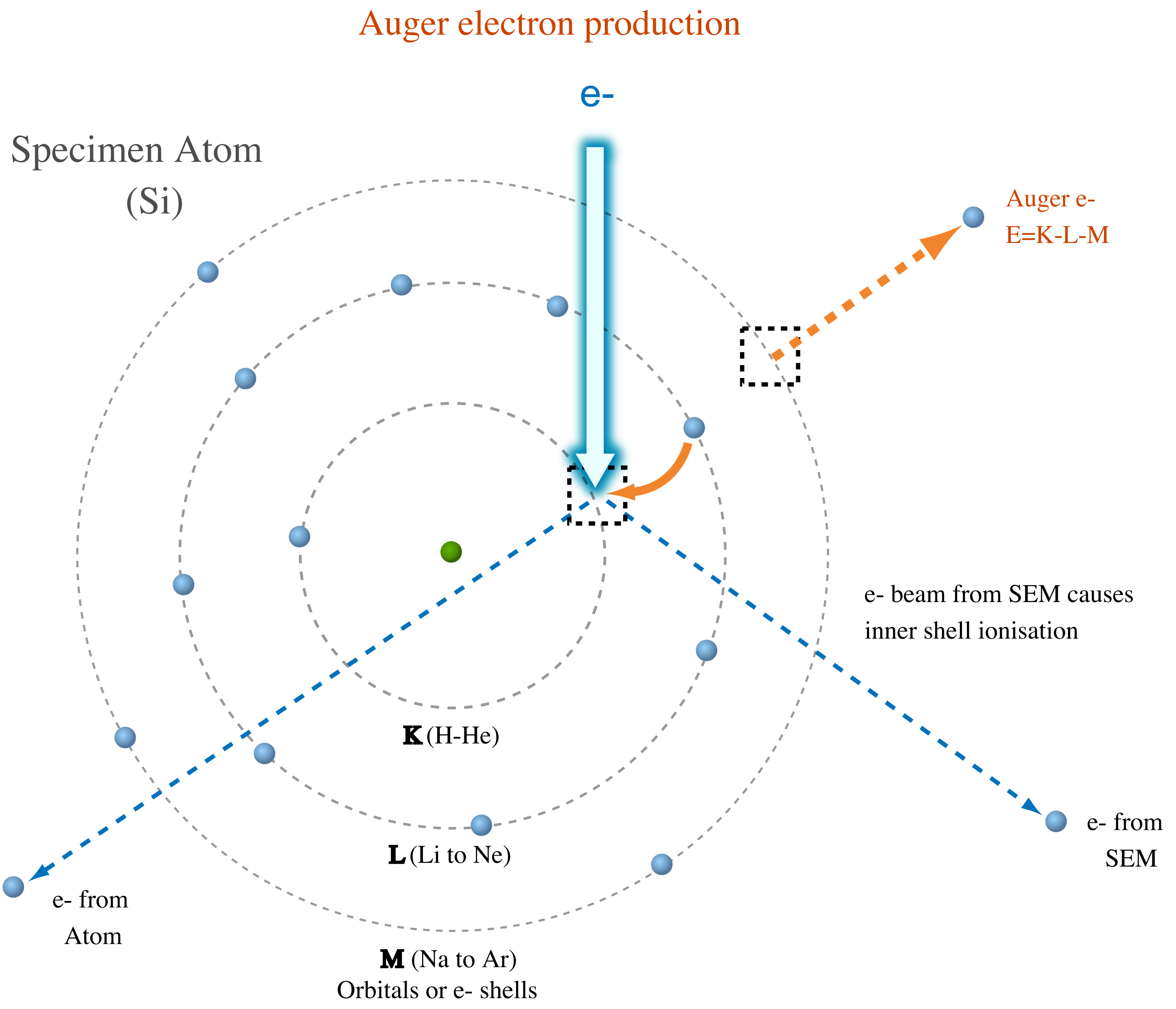
The overvoltage ratio is the ratio of the energy of the electrons in the primary beam, Eo, to the critical ionisation energy, Ec, needed to ionize an inner shell of an atom in the sample. For example, if the accelerating voltage is 15 kV, the energy of the electrons in the primary beam is 15 keV. The critical excitation energy of the Fe Kα X-ray is 7.11 keV, and therefore the overvoltage ratio, U = Eo/Ec, is 2.11. For efficient generation of X-rays, the overvoltage ratio should be at least 2 (the optimum value is ~2.7).



An overvoltage ratio of at least 2 is needed for efficient generation of X-rays. If low accelerating voltages are used, higher energy X-rays will not be efficiently generated.

Fluorescence yield

Remember that the production of Characteristic X-rays is a two-stage process: ionisation followed by relaxation with the production of an X-ray photon. However, this is not the whole story, and there is a competing process, the generation of Auger electrons, that can also lead to stabilization of the ionized atom. In this case, when an electron from an outer shell fills the vacancy in the ionized inner shell an electron is ejected from the same or another outer shell and no X-ray photon is produced. The ejected electron is known as an Auger electron and it has an energy equal to the difference between the ionisation energies of the two shells involved in the initial transition minus the ionisation energy of the shell from which the Auger electron is ejected. So the energy of the Auger electron is also related to the electronic configuration of the atom from which it came and is characteristic of the element concerned.



The fluorescence yield is the relative yield of X-rays to Auger electrons. Elements with low ionisation energies, i.e. the lighter elements (Z<11), have low fluorescence yields. That is, when an inner-shell ionisation occurs it is more likely that an Auger electron will be produced rather than an X-ray photon. The intensities of X-ray peaks for elements of low atomic number are smaller compared to those with a higher fluorescence yield.

X-ray absorption

Not all of the X-rays that are generated in the sample by the primary electron beam are emitted from the sample. This is particularly true in the SEM where X-rays are generated within the interaction volume at a depth of many microns. X-rays may be absorbed by other elements in the sample due to the photo-electric effect (see Photo-electric animation). If the energy of an X-ray photon is equal to the critical ionisation energy of an electron in another element in the sample, then there is a high probability that the X-ray will be absorbed and a photo-electron produced.

While the absorption of X-rays depends on the other elements present in the sample, it is true that low-energy X-rays are more likely to be absorbed than those with higher energies, while elements with higher atomic numbers tend to be strong absorbers of lower energy X-rays.

The length of the path that the X-ray travels through the sample will also influence absorption. The longer the path length, the more likely it is that the X-ray will be absorbed. Again, low-energy X-rays are more likely to be affected by longer path lengths than higher energy X-rays.

X-ray detection by EDS

The most commonly used system in both SEMs and TEMs for detecting the X-rays that are generated and emitted from the sample is the energy dispersive X-ray analysis system (EDS, EDX or XEDS). Other detection systems, e.g. wavelength dispersive spectrometers (WDS) or microcalorimeters, may be used for more specialized applications. Although EDS analysis systems show many variations, depending on their age and manufacturer, all are composed of three basic parts: a detector, a pulse processor and a multi-channel analyser or display.

The detector

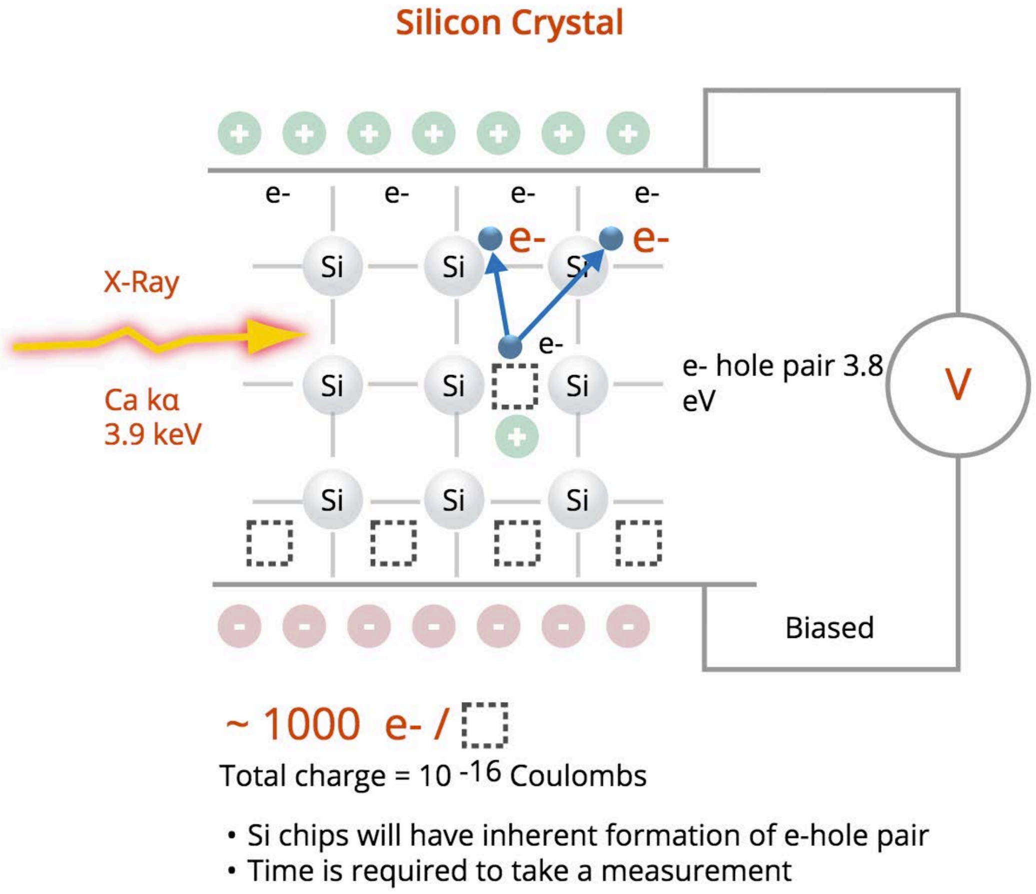
The detector is based on a semiconductor device, usually a crystal of silicon although intrinsic germanium detectors have been used on TEMs. The first detector developed for commercial systems in the late 1960s was the lithium-drifted silicon or Si(Li) detector, but it is now giving way to the silicon-drift detector or SDD.

The detector consists of:

- A collimator to ensure that only X-rays generated from where the primary electron beam interacts with the sample will be collected.
- An electron trap to ensure that X-rays, but no electrons, enter the detector.
- A window to isolate the detector crystal, under high vacuum, from the chamber of the microscope. Older windows were composed of Be which did not allow low-energy X-rays (< ~0.9 keV) to pass through it, but more modern windows are composed of polymers that will allow low-energy X-rays (down to ~0.1 keV) to pass. There is also a windowless configuration that removes the absorption issue.
- A semiconductor crystal detector.
- Electronics to detect the charge recorded by the detector, convert it to a voltage pulse and pass it to the pulse processor.

The operating principle is the same for all types of detector; the energy of the incoming X-ray is dissipated by the creation of a series of electron-hole pairs in the semiconductor crystal. A high bias voltage is applied across the crystal and this causes electrons and holes to move to electrodes on opposite sides of the crystal, producing a charge signal which is passed to the pulse processor. The size of the signal is proportional to the energy of the incoming X-ray. For a silicon detector, ~3.8 eV is used to generate each electron-hole pair (~2.9 eV for Ge). So for an incoming Ni Kα X-ray of energy 7.477 keV, 1968 electron-hole pairs will be produced, and for an Al Kα X-ray of 1.487 keV, 391 electron-hole pairs will be generated.

To minimize electronic noise, the detector must be cooled. Si(Li) detectors are cooled to liquid nitrogen temperatures and are attached to dewars that require regular filling. SDD can operate at higher temperatures (~ -70°C) and employ thermoelectric (Peltier) cooling which is a significant saving in time and money.



The energy of the incoming X-ray, in this case Ca Kα, generates electron-hole pairs in a silicon crystal detector. A bias voltage across the detector causes movement of electrons and holes to opposite sides of the crystal, generating a charge signal.

Si(Li) detector crystals are about 3 mm thick. X-rays produced in SEMs may have energies up to ~30 keV, and these will be efficiently processed by the Si(Li) crystal. Higher energy X-rays, e.g., 100-400 keV as produced in TEMs, will pass through the Si(Li) crystal and its efficiency declines at energies above ~25 keV. Intrinsic Ge detectors maintain their efficiency to process X-rays with energies in excess of 100 keV which is why they were preferred for some TEM detectors.

The pulse processor

The charge generated in the detector crystal is converted to a voltage pulse and passed to a pulse processor that removes noise from the signal, discriminates the energies of the incoming X-rays and discriminates between X-rays that arrive in the detector almost simultaneously.

The pulse processor removes noise by averaging the incoming signal. The time spent averaging the signal can be varied by adjusting the time constant or process time of the detector system. A longer process time means the signal is averaged for longer and the resolution of the spectral peaks is improved. A longer process time is needed for quantitative analysis where spectral resolution is important, whereas if maximizing the number of X-rays in a spectrum or map is most important a shorter process time can be used, e.g. in X-ray mapping or in TEMs. A longer process time also increases the dead time of the system which means that it takes longer to acquire a spectrum or map.

When the system is not counting incoming X-rays but processing the previously collected signal, it is said to be ‘dead’. As described above, using a longer time constant or processing time will increase the dead time of the system. The system dead time also depends on the X-ray count rate. At high count rates, the pulse processor may not be able to differentiate between two incoming X-rays so both are rejected. As the count rate increases, more X-rays are rejected and the dead time increases. If the dead time increases to 100% then no X-rays are processed by the pulse processor and no data are collected, in which case the detector is said to be ‘flooded’. Si(Li) detectors operate at count rates of about 5,000 to 20,000 cps with optimal dead times of 20-30%. The reason why SDD are now preferred to Si(Li) detectors is that they can handle much higher count rates of >100,000 cps and dead times of ~50%. The count rate can be optimized by adjusting the beam current (probe current or spot size) and/or the process time. It is important to select a process time and beam current that will give an acceptable X-ray count rate and detector dead time for analysis, as well as the desired spectral resolution.

X-ray count rate and dead time

- If a second X-ray arrives before the preceding one is processed, it will be rejected
- X-rays too close together → data rejected → increase in dead time
- 20-50% dead time is acceptable
- Reduce dead time (and high count rates) by reducing the beam current or spot size
- There are more spectral artifacts at higher count rates

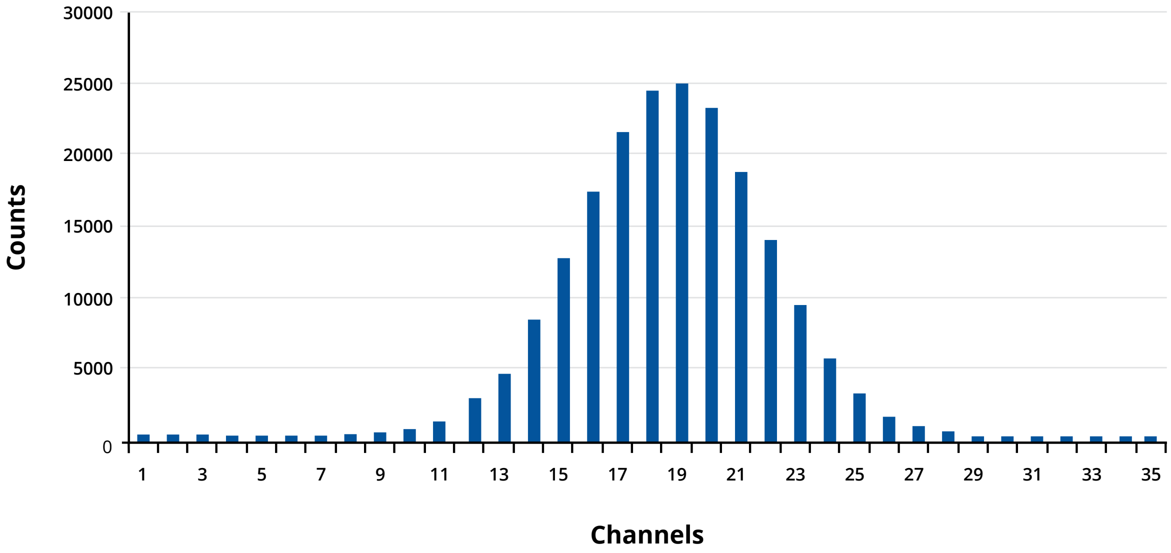
If the X-ray count rate is too high the dead time increases and fewer X-rays are counted to generate the X-ray spectrum.

The multi-channel analyser or display

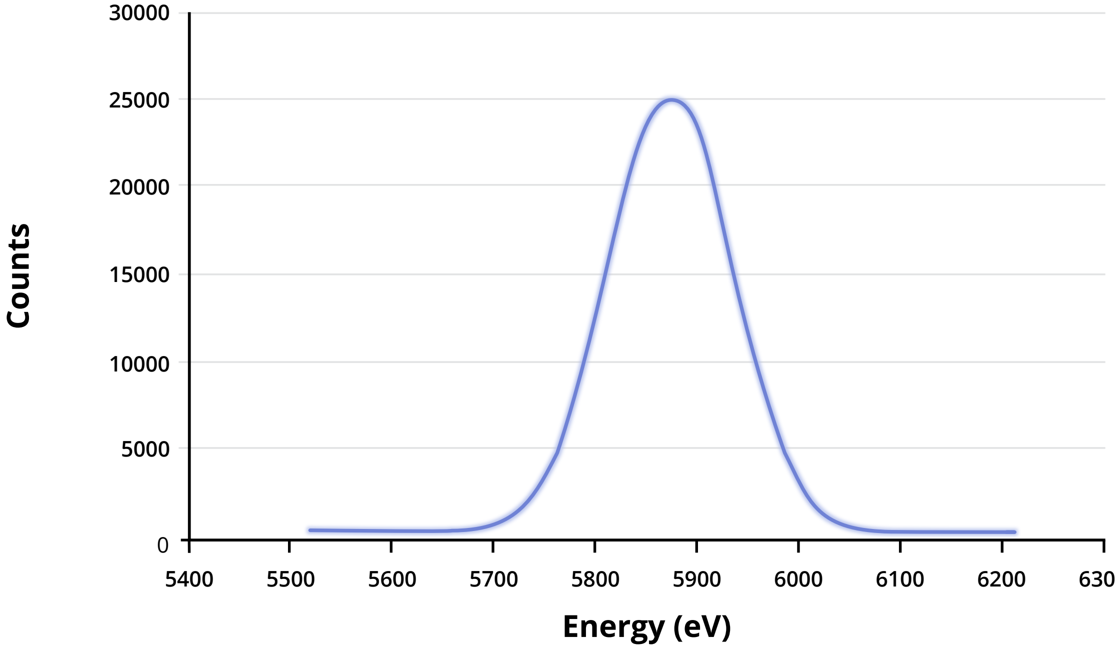
The output from the pulse processor is passed to a multi-channel analyser or computer display. The energy range of the spectrum, e.g., 0-20 keV for SEMs or 0-40 or 80 keV for TEMs, is divided into a number of channels, e.g., 1024, 2048 or 4096 channels, with energy widths of 5, 10 or 20 eV per channel. The number of X-rays with the relevant energy is assigned to each channel, and the result displayed as a histogram of intensity (number of X-ray counts) versus Energy. In the example below, channel 1 has an energy range from 5500-5520 eV and 498 X-ray counts; channel 2 has an energy range from 5520-5540 eV and has 477 counts, and so on.

ENERGY	COUNTS	ENERGY	COUNTS	ENERGY	COUNTS	ENERGY	COUNTS	ENERGY	COUNTS
5520	498	5660	614	5800	12957	5940	14131	6080	476
5540	477	5680	733	5820	17424	5960	9530	6100	419
5560	460	5700	1047	5840	21671	5980	5951	6120	410
5580	494	5720	1703	5860	24564	6000	3382	6140	370
5600	490	5740	2973	5880	24937	6020	1904	6160	348
5620	522	5760	4867	5900	23267	6040	1138	6180	373
5640	554	5780	8475	5920	19001	6060	697	6200	405

The data can then be plotted as a histogram of the number of X-rays assigned to each channel



or a spectrum of the number of X-rays versus the energy of the X-rays.

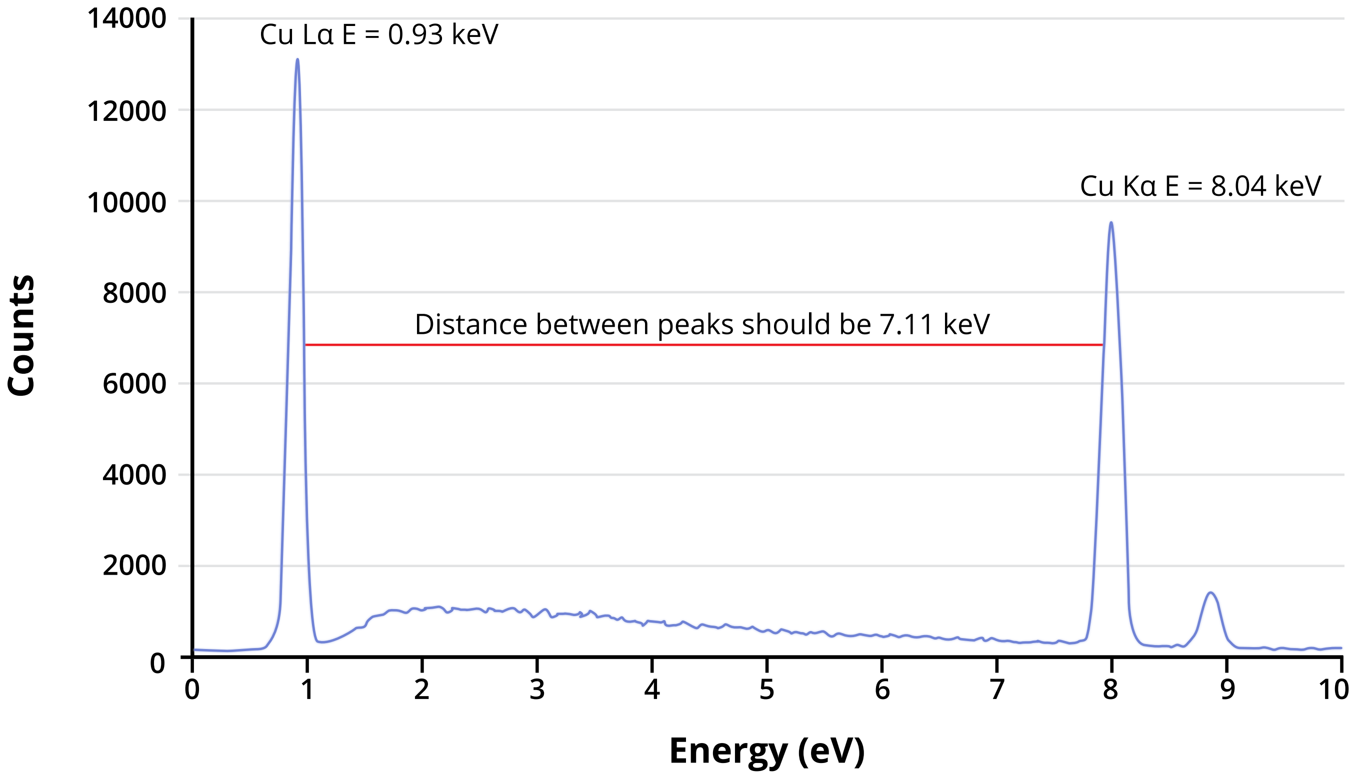


Care and calibration

EDS systems are generally very stable in normal laboratory environments. Si(Li) detectors on SEMs have lasted for many years but it is too early to tell if SDD will be as durable. Detectors on TEMs are subject to a more hostile environment dominated by high-energy electrons and X-rays. Detectors on TEMs are provided with shutters which should be closed, except when a spectrum is being collected, so that the crystal is protected.

The performance of EDS detectors may be degraded by buildup of hydrocarbon contamination or ice on the detector window or by loss of the high vacuum within the detector. Low-energy X-rays are more affected than higher energy X-rays, so the performance of the detector can be monitored by recording the change in the L/K ratio, i.e., the number of X-ray counts in the Lα peak compared to that in the Kα peak for a standard reference material, e.g., Co, Ni or Cu.

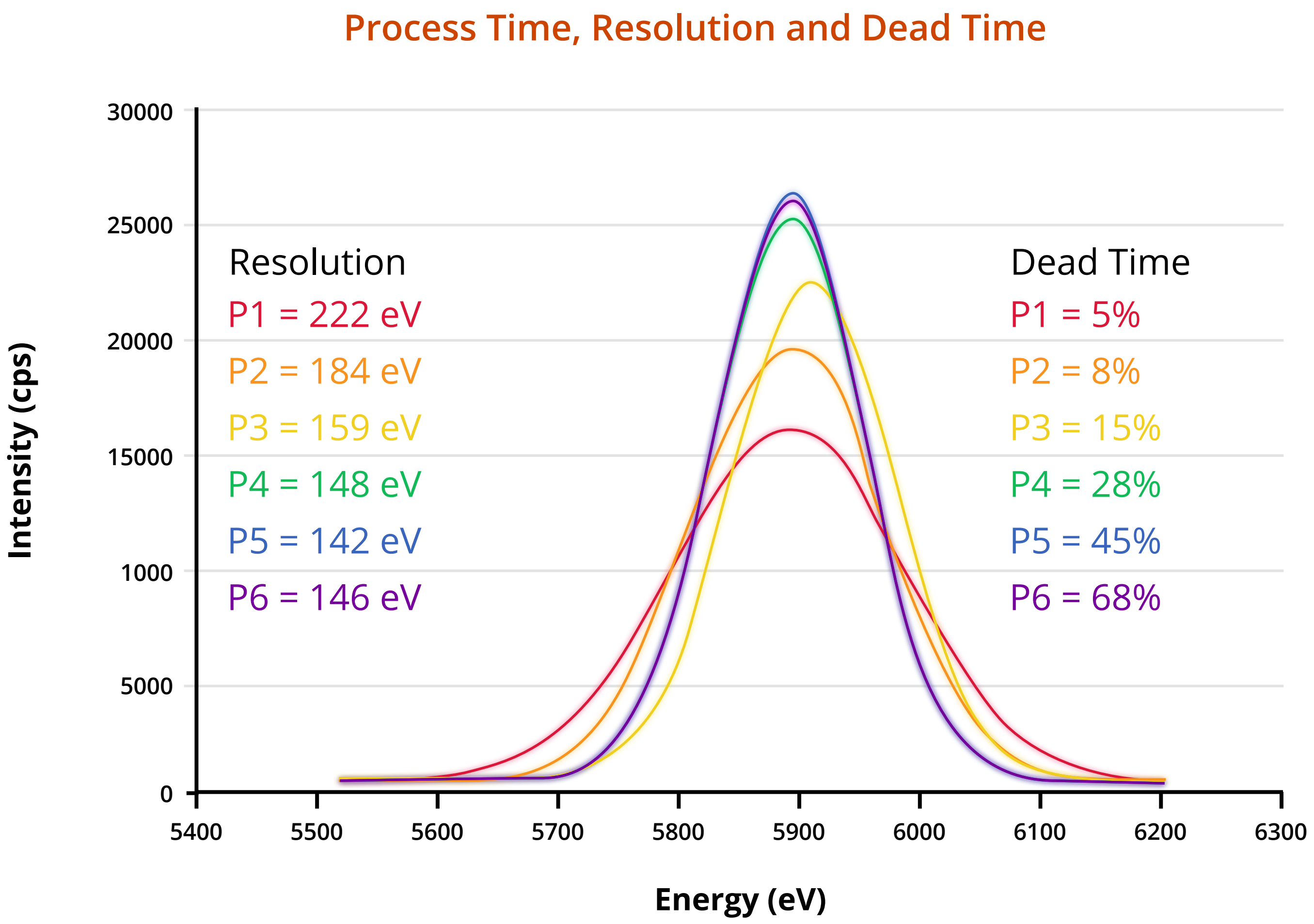
EDS can be calibrated for electronic drift by fixing the zero channel and gain by reference to a spectrum of the same material. Metals such as Co, Ni or Cu are commonly used as they have a peak (the Lα peak) at low energy that can be used to fix the zero position of the spectrum, and a peak at higher energy (the Kα peak) that can be used in combination with the Lα peak to rectify gain errors. This will ensure that X-ray counts are plotted in the correct energy channels.



The EDS can be calibrated by reference to a sample that has a peak at low energy so that the zero position of the spectrum can be fixed, and a peak at higher energy so that gain errors can be corrected. The performance of the detector can be monitored by recording the ratio of the number of X-ray counts in the Lα and Kα peaks.

EDS spectral resolution

Characteristic X-rays have discrete energies but in the process of detecting and measuring them the discrete lines spread into Gaussian peaks. A Characteristic X-ray peak in an ED spectrum has a spectral resolution that is related to the width of the Gaussian peak and is a function of the detector that was used to collect the spectrum, and its electronics. The spectral resolution of a peak is defined as the width of the peak, in eV, measured at half of the peak height. This is known as the FWHM (full width half maximum) resolution.

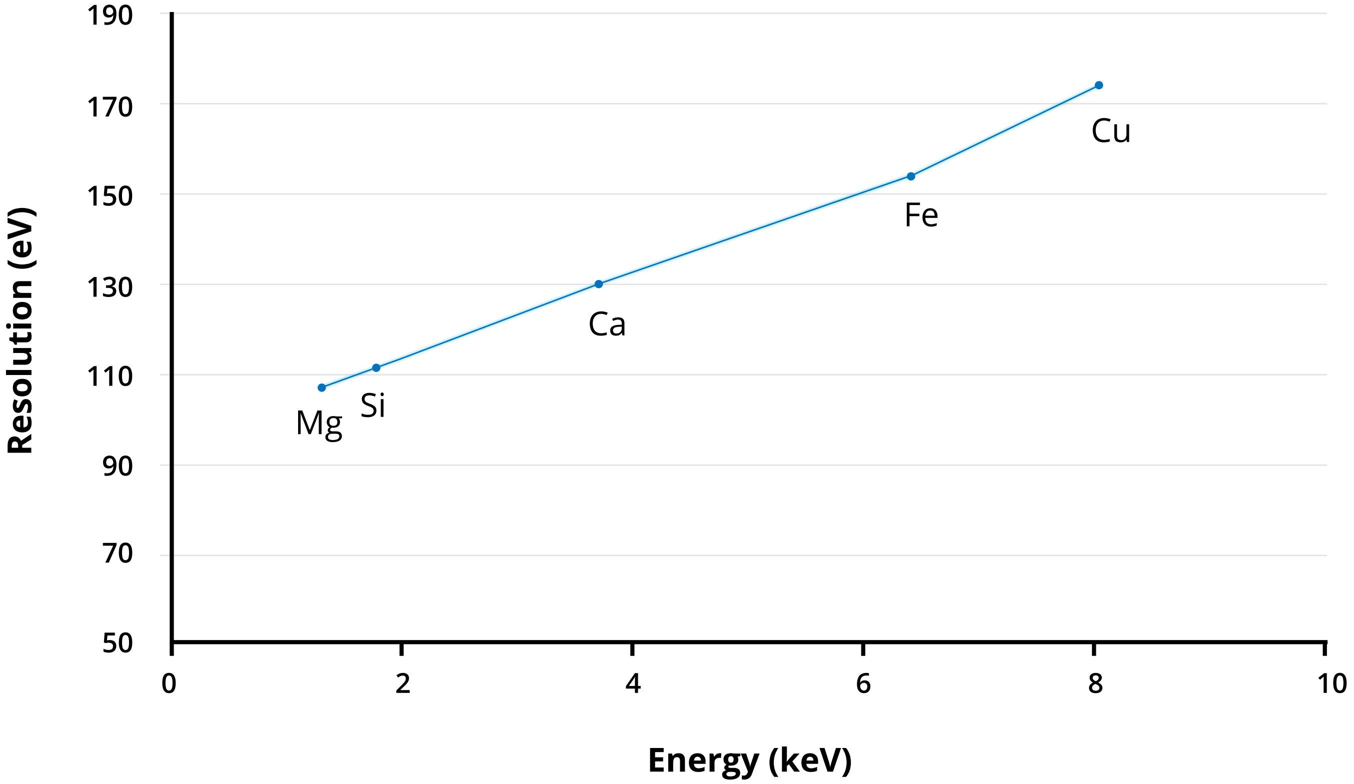


The Mn Kα X-ray peak at six different process times. The shorter the process time, the shorter the dead time and the worse the resolution. For longer process times, the resolution is better, but the dead time is also greater.

Spectral resolution is related to the time constant or process time used when collecting the spectrum. The process time is the time spent by the pulse processor in averaging the incoming X-ray signal. The longer the process time, the better the resolution will be. In the diagram above, P1 is the shortest process time while P6 is the longest. However, longer processing times mean longer dead times in which the system is not counting incoming X-rays and so the actual time required to acquire the spectrum increases.

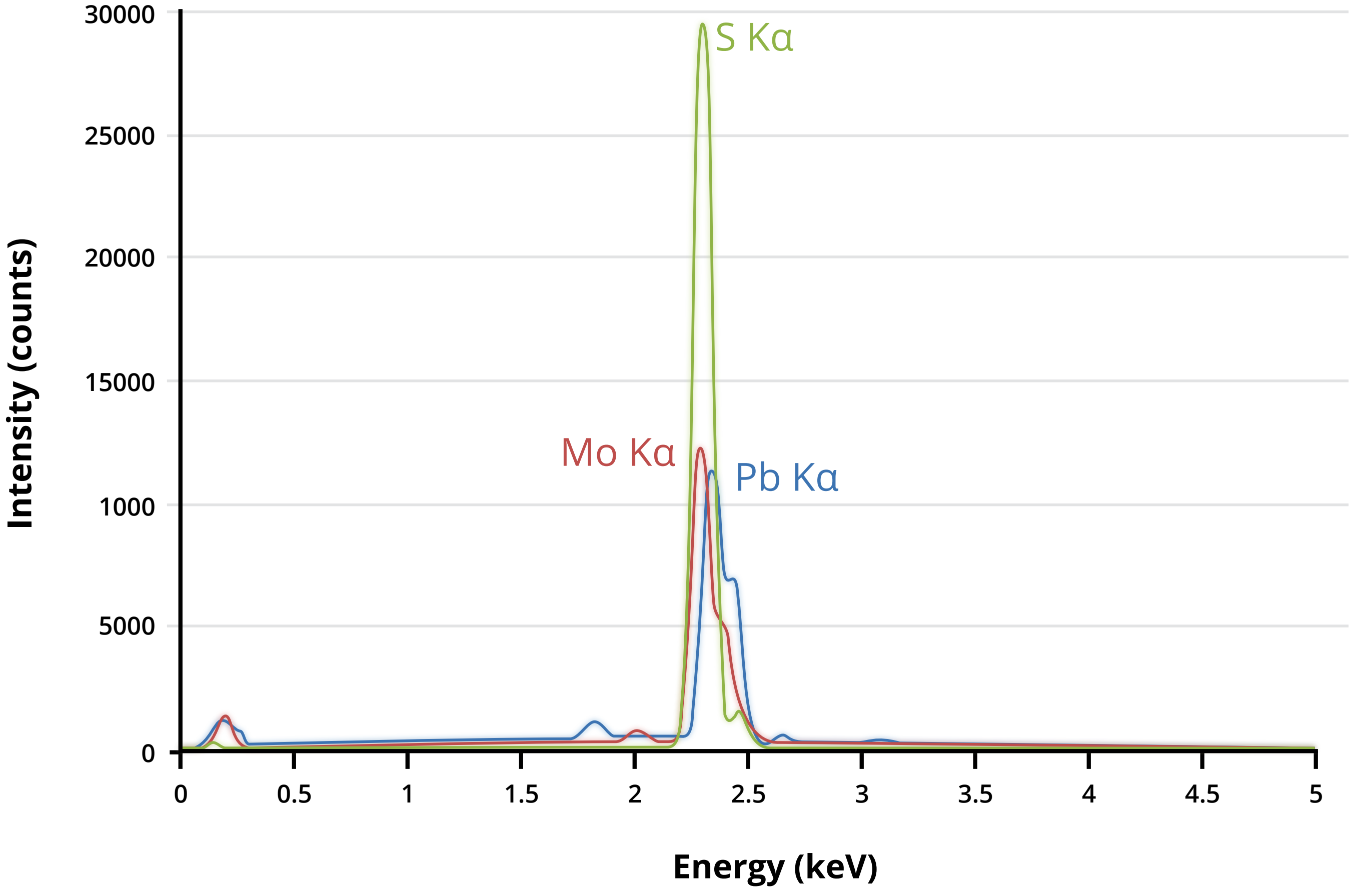
The resolution of ED spectrometers is traditionally measured by the FWHM resolution of the Mn Kα X-ray peak at 5.9 keV. Resolutions vary from about 125 to 150 eV for different spectrometers. The lower number (eV) is a narrower peak and therefore a higher resolution peak.A narrower peak is higher resolution because the peaks can get closer together before they overlap.

Spectral resolution is also a function of X-ray energy, with lower energy x rays having higher spectral resolution. For modern SDD the resolution of the C Kα peak is in the range 56-72 eV and the F Kα peak is in the range 60-75 eV.



A plot of resolution versus energy for Kα X-ray peaks.

Good spectral resolution is needed to separate overlapping peaks and recognize or quantify the elements present in a sample. Characteristic X-ray peaks from different families related to different elements may plot in the same part of the ED spectrum and give rise to overlapping peaks, e.g., S K family, Mo L family and Pb M family all have energies of ~2.3 keV.



Overlapping peaks of S Kα, Mo Lα and Pb Mα. Good spectral resolution is needed to deconvolute such overlapping peaks.

For both qualitative and quantitative analysis good spectral resolution is needed to be able to identify and quantify the elements present in the sample.

EDS spectral artifacts

Several artifacts can be produced in ED X-ray spectra because of the way the X-rays are detected and processed. Three common artifacts are the internal fluorescence peak, escape peaks and sum peaks.

Internal fluorescence peak

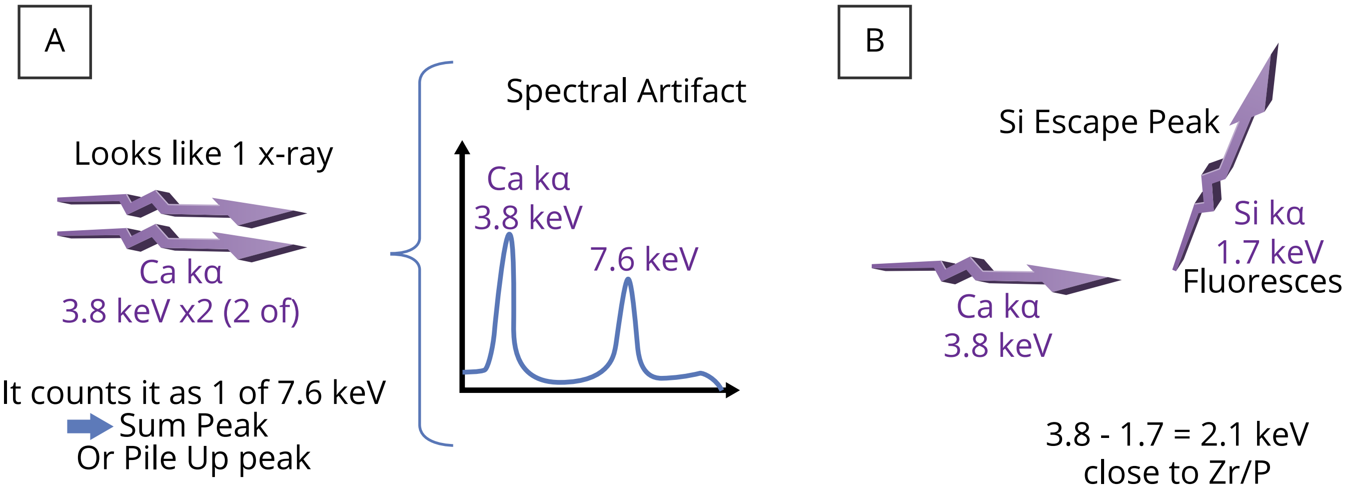
X-rays coming into the detector can generate Characteristic X-rays from the Si crystal. These X-rays are processed in the usual way and result in a small Si Kα peak in the ED spectrum, even when there is no Si in the sample being analysed. Improvements in design and construction of semiconductor detectors has minimized these artifacts, but they may be present in older detectors.

Sum peaks

Sum peaks are produced when the pulse processor cannot distinguish between two X-rays that arrive almost simultaneously. Instead of recording two X-rays with either the same or different energies, one X-ray with energy equal to the sum of the energies of the two incoming X-rays is recorded and plotted in the spectrum.

Escape peaks

Escape peaks are produced when instead of all of the energy of an incoming X-ray being converted to electron-hole pairs, a Si Kα X-ray is generated from the silicon detector crystal. The energy measured for the incoming X-ray is reduced by the magnitude of the Si Kα X-ray, i.e. 1.74 keV, and an escape peak is detected in the ED spectrum. Less than 2% of incoming X-rays will fluoresce Si Kα X-rays, so escape peaks form minor peaks located at an energy 1.74 keV less than the energy of related major peaks in the spectrum.



A. *The energies of two incoming X-rays are added together and a sum peak is recorded in the spectrum.* ***B***. *The energy of the incoming X-ray is reduced by 1.7 keV, the energy of the Si Kα X-ray, and an escape peak is recorded in the spectrum.*

Sum peaks and escape peaks become more significant at high X-ray count rates or if the dead time is >60%. Commercial EDS software packages generally mark the positions of escape peaks and sum peaks related to the major Characteristic X-ray lines so that they can be readily identified in ED spectra.

In quantitative ED microanalysis corrections must be made for spectral artifacts. The X-rays attributed to escape peaks and sum peaks must be subtracted from the spectrum, and the counts returned to the peaks where they should have been recorded. This correction procedure is known as pulse pile-up correction.

Qualitative EDS X-ray microanalysis using SEM and TEM

What elements are present in the sample?

Qualitative microanalysis means that the elements present in the sample are identified from their Characteristic X-ray peaks, but their abundances are not determined. While commercial peak-identification software is improving all the time, it is not yet 100% accurate. Elements that are present in the sample may be missed, and elements that are not present may be falsely identified.

For qualitative microanalysis of an unknown sample, consideration must be given to the operating parameters of the microscope and also the properties of the sample to be analysed.

Microscope operating parameters

In the SEM, if the sample is stable under high-vacuum in the electron microscope and is not susceptible to damage by the electron beam, then an accelerating voltage of 15-20 kV is recommended for SEM analysis. This is sufficient to efficiently generate at least one family of X-ray lines for all elements. In the TEM, the chief requirement is to collect enough X-ray counts in the spectrum from a thin specimen for good analysis. This is generally achieved at the highest accelerating voltage.

If the sample is likely to be damaged by a high-energy primary electron beam in either the SEM or TEM, then it may be necessary to use a lower accelerating voltage. If this is the case in the SEM, the higher energy X-ray lines may not be efficiently generated and low-energy X-rays will have to be used for element identification, e.g., the L or M lines for elements with $Z > 20$. An alternative approach to reducing sample damage is to lower the electron dose by using a broader (defocused) beam.

The electron beam current (probe current or spot size) will control the X-ray count rate or intensity of the generated X-rays. The beam current should be adjusted to minimize damage to the sample but generate sufficient X-rays to allow reliable identification of peaks. At the same time, the beam current needs to be adjusted to minimize spectral artifacts and achieve system dead times of 20-50%.

The electron beam – sample – detector geometry should be optimized. Set the sample stage to the microscope's manufacturer's recommended working distance. The X-ray EDS detector will have been installed with an optimal working distance also, and this will vary from microscope to microscope.The X-ray detector should be as close as possible to the sample to maximize collection of the generated X-rays, but this may be limited by the presence of other detectors and safe operation of the microscope. There should be a clear path between the sample and the X-ray detector.

Sample preparation

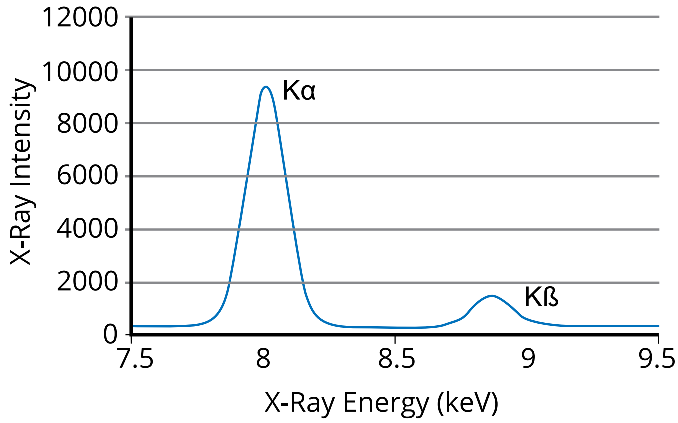
No special sample preparation beyond that required for electron imaging is required for qualitative analysis in either the SEM or TEM. In the SEM the elements present in rough or unpolished samples can be determined by qualitative EDS microanalysis but some care needs to be exercised when collecting X-rays from these samples. If the electron beam is focussed in a hole in the sample then X-rays may not be able to escape from the hole and will not be detected. Similarly, if the X-rays have to travel through the sample to get to the detector they will be absorbed and not detected in the ED spectrum.

Conductive samples do not need to be coated, but insulating samples may need to be coated to make them conductive prior to qualitative X-ray microanalysis. Carbon, Au, Pt or any other conductive coating material may be used, but X-rays will be produced from the coating material and will be present in the ED spectrum. Characteristic X-rays from the coating material may overlap with X-rays produced from the elements in the sample, so carbon is the preferred coating material as it minimizes spectral interferences.

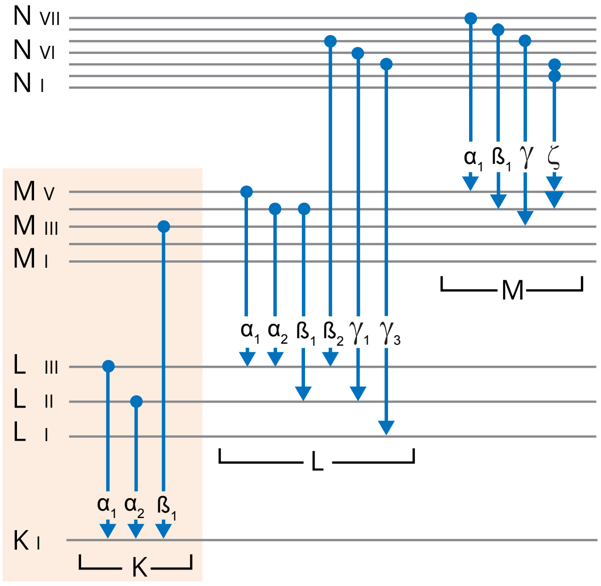
X-ray peak identification

The energies of the Characteristic X-rays emitted by the elements in a sample allow them to be identified. However, the presence of overlapping peaks from different elements means that correct identification depends on being able to recognize the peaks in the different X-ray families. The relative weights of the Characteristic X-ray lines in each family are consistent and this, along with their energies, allows related peaks in the X-ray spectrum to be recognized. By measuring the energies of the major X-ray peaks in each family, the corresponding element can be identified. Commercial peak-identification software can do this, but the results need to be verified.
At energies above 4 keV, the peaks of the K and L families are resolved

K family

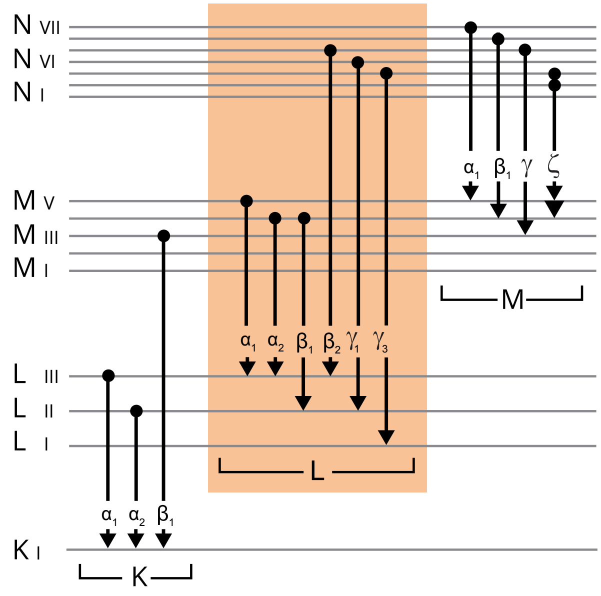


Electron transitions of major X-Ray lines

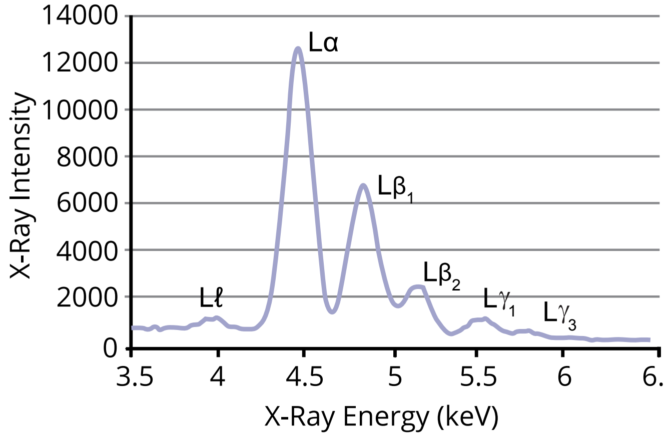


The K family of X-rays has two peaks, Kα and Kβ, with intensity ratios of approximately 10:1. Note: There are actually two X-ray lines in the Kα X-ray peak: Kα1 and Kα2, but they cannot be resolved by ED spectrometers so the combined peak is referred to as Kα.

Electron transitions of major X-Ray lines

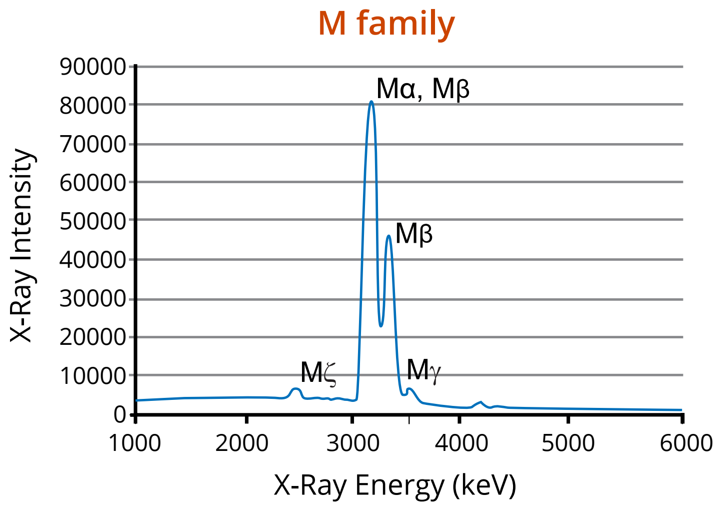


L family

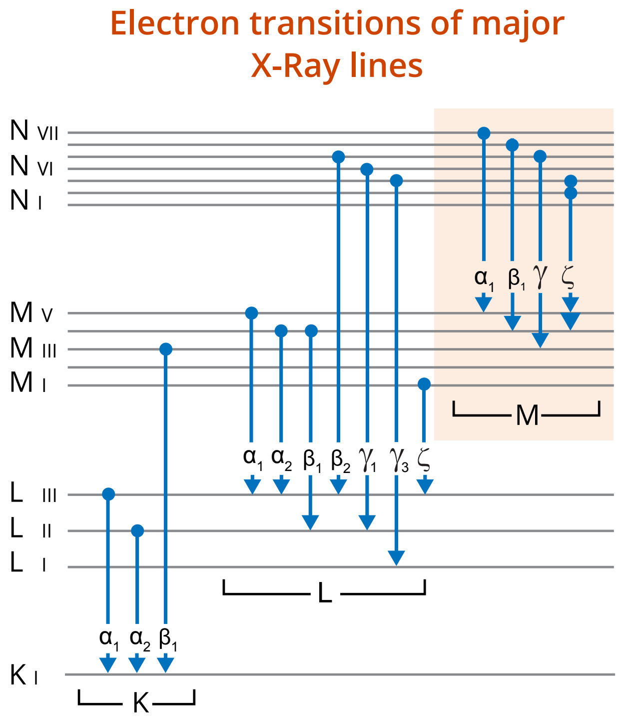


The L family of X-rays is more complicated with six lines commonly visible in the spectrum. The Ll (ell-ell) line results from electron transitions between the M I and L III subshells, and forms a small peak on the low-energy side of the family. The Lα, Lβ1 and Lβ2 lines form a series of three peaks with descending magnitudes and relative intensities of ~10:7:2. The Lγ1 and Lγ3 lines form small peaks on the high-energy side of the family.

M family peaks are not present at energies above 4 keV



M family

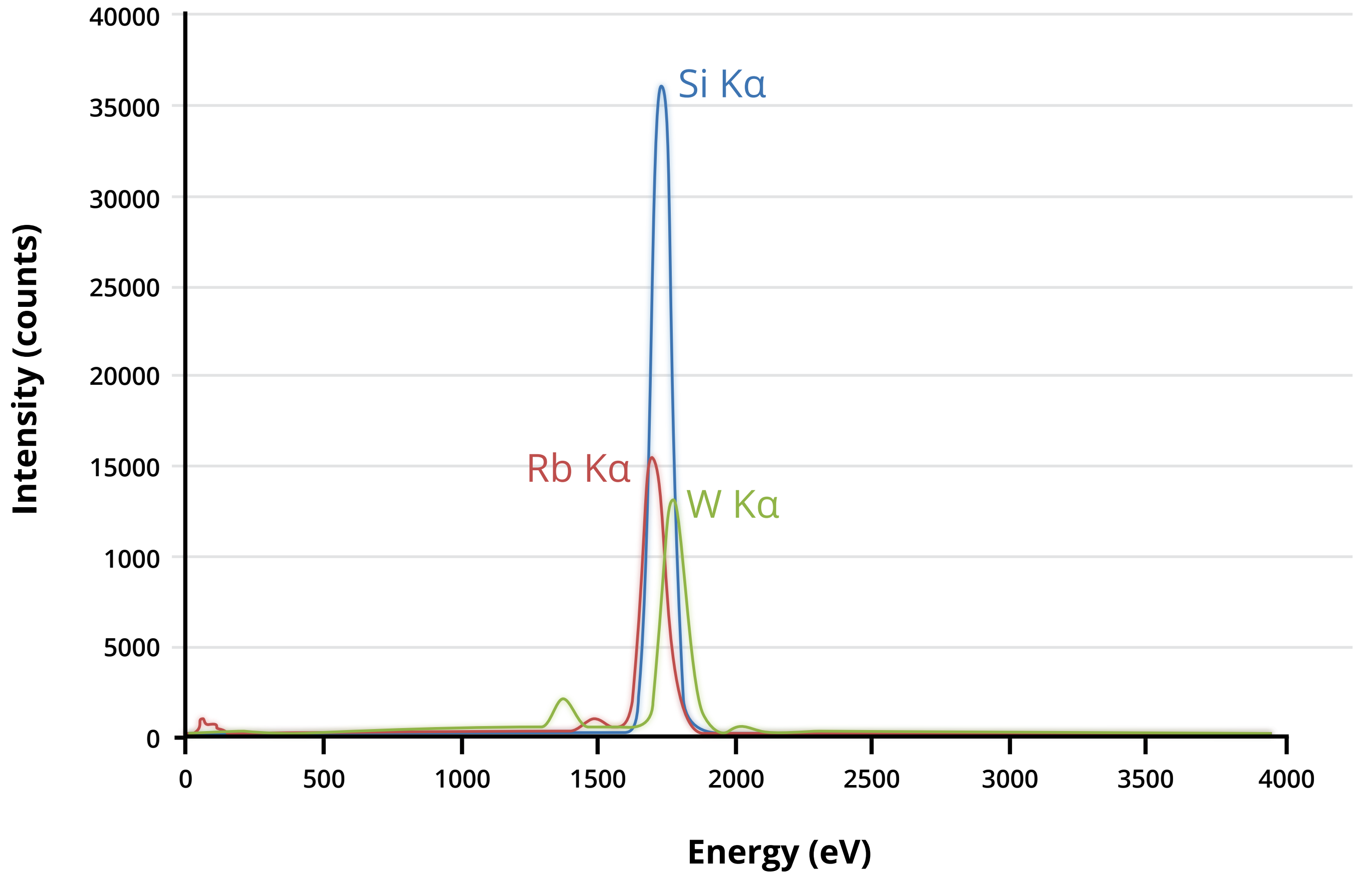


Electron transitions of major X-Ray lines

The Mα and Mβ peaks may not be fully resolved, but the Mζ (M zeta) peak on the low-energy side of the family and the Mγ peak on the high-energy side are usually present and allow M family peaks to be identified.

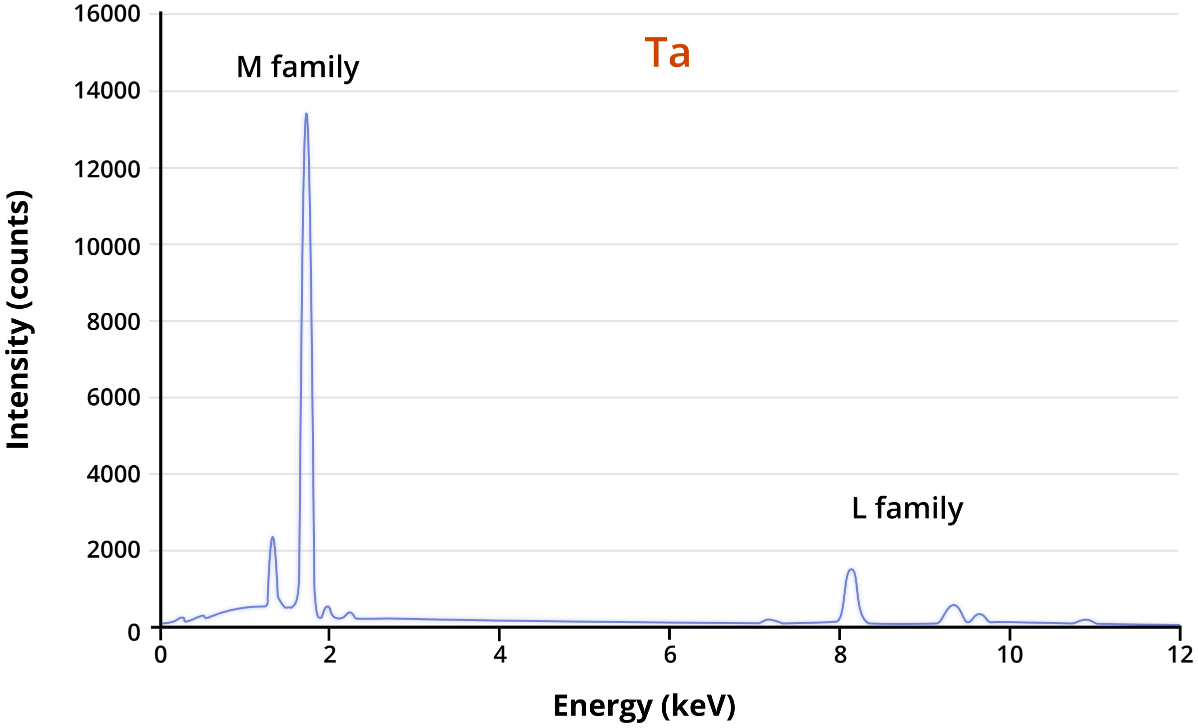
At low energy

At energies below ~2.5 keV, the main peaks of the K, L and M families are not resolved and only one main peak is present. The minor peaks, Ll, Mζ and Mγ, can be used to help identify the family.

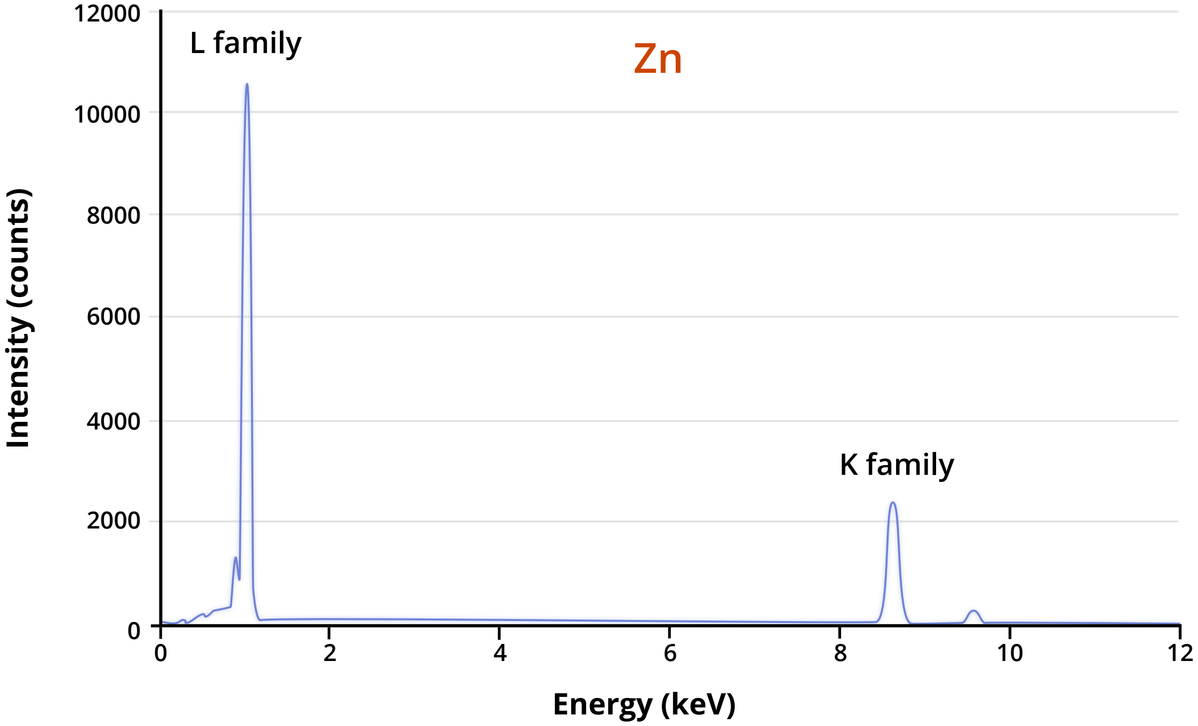


Strategy

- For SEM analysis, use an accelerating voltage of 30 kV to ensure efficient X-ray generation. The higher accelerating voltages used in TEM analysis means that higher energy K and L lines can be used for identification.
- Run the automatic peak-identification software that comes with your system. Verify the results as follows.
- Identify and label major peaks at 4 keV and above:
    - There are no M family peaks
    - There are at least two resolved peaks for both K and L families (see above) so these can be identified along with related minor peaks
    - If there are L family peaks there should be M family peaks at low energy, and these can be identified, e.g. Ta L and M families



    - If there are K family peaks there should be L family peaks at low energy, and these can be identified, e.g. Zn K and L families



- Any unidentified peaks below 4 keV should be K family peaks, and can be identified.
- Consider unidentified minor peaks in the spectrum: are they Characteristic peaks of elements present in minor/trace amounts (only the most intense peak of the family may be visible above the continuum), or are they spectral artifacts?
- Consider the possibility of overlapping peaks, particularly at low energies (below ~2.5 keV) where each family has only one main peak, e.g. Si, Rb and W or S, Mo and Pb.

Clearly, the more you know about your sample and how it was prepared before undertaking chemical analysis the fewer surprises you will have. But be suspicious: don't just look for the elements that you think will be in the sample. Make sure you identify all the elements that are present.

Quantitative EDS X-ray microanalysis using SEM

How much of each element is present in the sample?

In quantitative EDS microanalysis in SEM, the mass fractions or weight percents of the elements present in the sample are calculated. The spectra are processed to remove Bremsstrahlung X-rays and spectral artifacts, and then the Characteristic X-rays are compared with data measured from standard reference materials. In so called Standardless Quantitative analysis, or semi-quantitative analysis, the spectra are compared with data collected from standards in the factory of the manufacturer of the EDS system and stored with the system software. In fully Standardized Quantitative analysis the spectra from the standards are collected on the same instrument as the spectra from the sample being analysed, which allows for more accurate analyses.

Qualitative analysis to identify the elements present in the sample is a good prelude to quantitative analysis as it will allow the best operating parameters for the microscope to be selected.

Microscope operating parameters

If the sample is stable under high-vacuum in an electron microscope and is not susceptible to damage by the electron beam, then an accelerating voltage of 15-20 kV is recommended for quantitative analysis. This is sufficient to efficiently generate at least one family of X-ray lines for all elements.

If the sample is likely to be damaged by a high-energy primary electron beam, then it may be necessary to use a lower accelerating voltage. In this case, the higher energy X-ray lines may not be efficiently generated and low-energy X-rays will need to be used for element quantification, e.g., the L or M lines for elements with $Z > 20$. An alternative approach to reducing sample damage is to lower the electron dose by using a broader (defocused) beam.

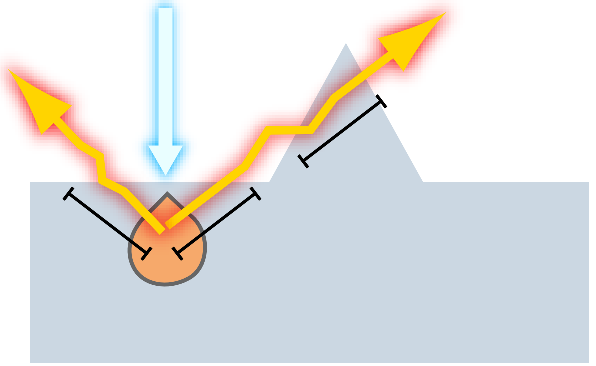
The electron beam current (probe current or spot size) will control the X-ray count rate or intensity of the generated X-rays. The beam current should be adjusted to minimize damage to the sample but generate sufficient X-rays to allow reliable quantification (see Precision and Accuracy and Detection Limits). At the same time, the beam current needs to be adjusted to minimize spectral artifacts and achieve system dead times of ~20-50%. The beam current needs to be established at the beginning of an analysis session and monitored throughout the session as any drift will affect the number of X-rays generated from the sample which in turn will affect the quantification. Thermionic emitters or hot (Schottky) field emitters are required for quantitative microanalysis. Cold field emitters lack the required beam stability.

The electron beam – sample – detector geometry should be optimized. Set the sample to the recommended working distance. The X-ray detector should be as close as possible to the sample to maximize collection of the generated X-rays but this may be limited by the presence of other detectors and safe operation of the microscope. There must be a clear path between the sample and the X-ray detector.

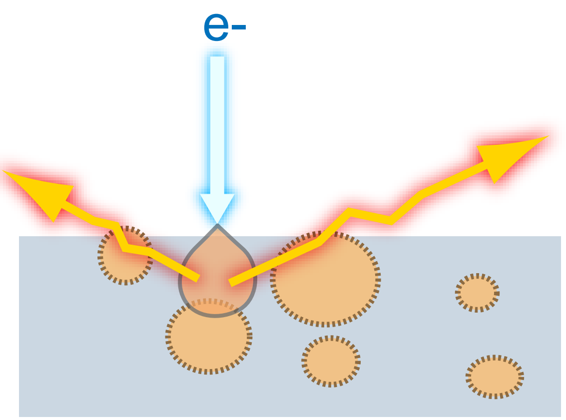
Sample preparation

For standardized quantitative analysis the samples must be flat and polished. Samples should also be homogeneous, 'bulk' not porous or thin films on a substrate, otherwise the matrix correction procedures will not work correctly

Specimen must be - stable, flat, homogenous, void free

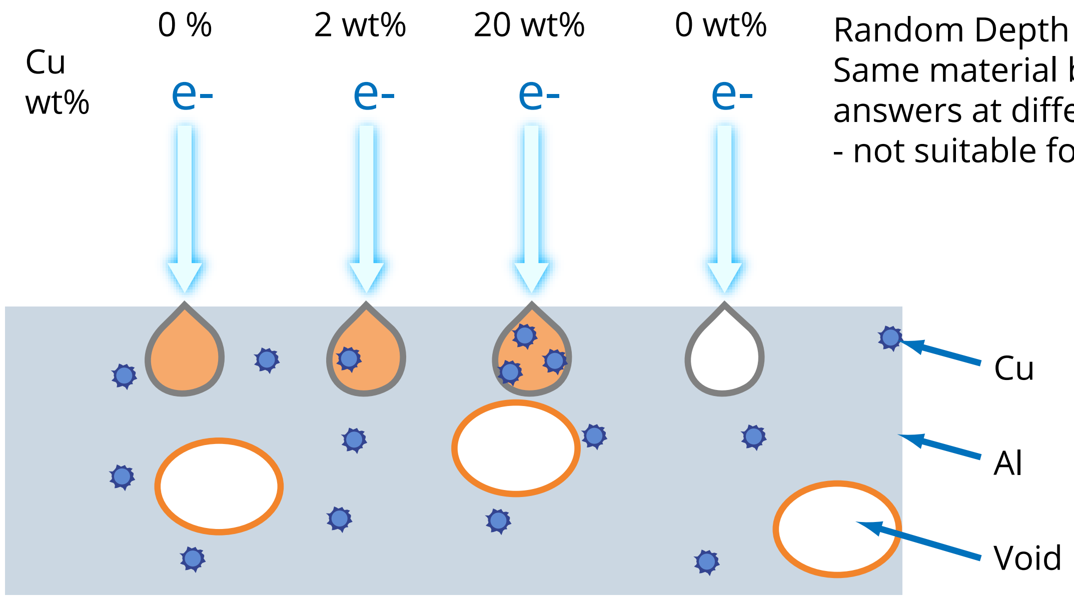


X-ray on right is under corrected for absorption



X-rays above are over corrected for absorption

Specimen must be Homogenous over x-ray generation volume for correct answer



Random Depth Profile
Same material but different answers at different places
- not suitable for analysis

Proper sample preparation is critical for quantitative analysis. If the samples are not (A): polished and void free and (B): homogeneous on the scale of the interaction volume, special analytical techniques must be used.

The size of the particles that can be analysed will depend on their mean atomic number, and the accelerating voltage. (Remember that X-rays will be generated throughout the interaction volume and that the size of the interaction volume depends on kV and Z). Generally, particles to be analysed must be greater than ~2 microns across to be analysed by point analysis.

Ideally, if a conductive coating is required for the sample, the standards should be coated with the same material. Carbon is the recommended coating material as it doesn’t interfere with Characteristic X-ray peaks from elements in the sample.

Limitations of quantitative analysis

Some of the limitations of quantitative EDS analysis are listed below:

- Light elements (Z < 11) cannot be routinely analysed by EDS.

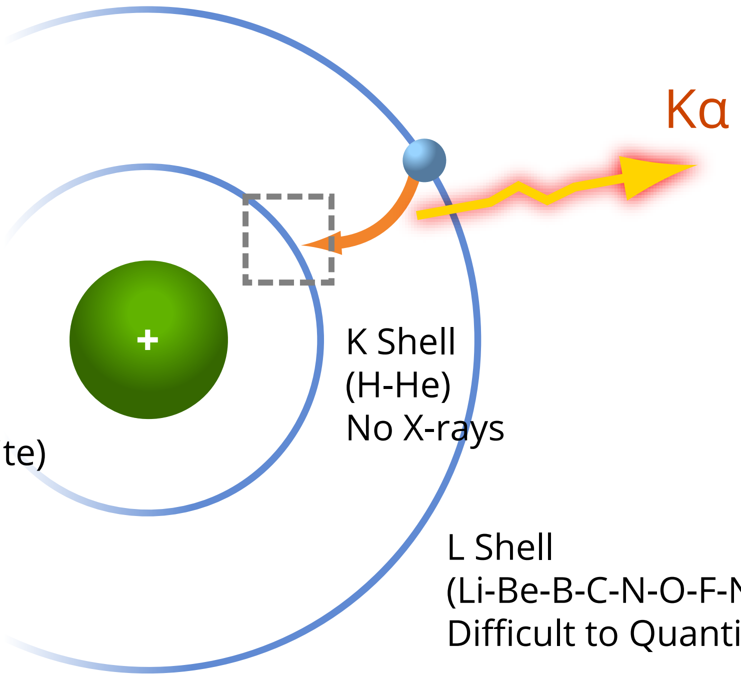
  Hydrogen (Z = 1) and He (Z = 2) do not have Characteristic X-rays, and the Li (Z = 3) K X-rays are of too low energy to be detected by EDS.

  Beryllium (Z = 4) to Ne (Z = 10) X-rays can be detected by EDS, but there are two problems. Firstly, they are low energy X rays subject to strong absorption by the specimen. Secondly, the electrons involved in generating the Characteristic X-rays are also the valence electrons involved in the chemical bonding of the element, therefore the shapes and positions of the peaks may change in different compounds. The samples and the standards must be closely matched for best results.

Light Elements

Light Elements are difficult to measure as valence electrons are involved in characteristic x-ray production and chemistry.

For heavy elements (>= Na) the Kα x-ray is not associated with chemical bonds.



Heavy Elements e.g.
Fe Kα (metal) = Fe Kα (oxide)
- No bond shift

Light Elements e.g.
C Kα (diamond) ≠ C Kα (Graphite)
- there is a bond shift

K Shell
(H-He)
No X-rays

L Shell
(Li-Be-B-C-N-O-F-Ne)
Difficult to Quantify

- Carbon is the most commonly used coating material for non-conductive samples and cannot be analysed if the sample is carbon coated. A different coating material must be used if analysing for carbon.
- Many minerals contain oxygen bonded with a range of cations. It is common practice to calculate the amount of oxygen in the sample by measuring the percentages of the cations and calculating oxygen by stoichiometry. This generally is more accurate than analysing for oxygen.
- Calculating oxygen by stoichiometry requires knowledge of the valence state of the cations to which it is bonded. This information is not available from EDS analysis
- Some samples may contain structurally bound water or carbonate. Complete analyses of these samples cannot be derived by EDS analysis.

Standardized quantitative analysis

Different combinations of electron microscope and ED X-ray detector will involve different protocols for quantitative microanalysis, but there are six basic steps required for Standardized Quantitative analysis that should be common to all systems:

1. Define the list of elements that you want to analyse for. Use qualitative analysis to identify all of the elements present in the samples that you want to analyse. Older software packages may only derive quantitative data for a specified element list but newer systems will derive quantitative data for all of the elements detected in the spectrum to be processed.
2. Perform any calibration of the EDS system that is necessary for quantitative analysis. At a minimum, it will be necessary to measure the beam current or the X-ray count rate on a pure element standard.
3. Measure spectra from standards for the elements that you want to analyse for. Ideally, the spectra will be collected under the same conditions, and on the same instrument, that will be used for collecting spectra from the samples to be analysed. If no standards are available, it may be necessary to use default spectra, and this will affect the accuracy of the analysis.
4. Collect spectra from the samples to be analysed. Be sure to monitor the beam current for drift between analyses.
5. Process the spectra to calculate the mass fraction or weight percent of the elements present or the percentages of the elements defined in an element list.
6. Assess the quality of the analysis. Is it a ‘good’ analysis? If not, why not?

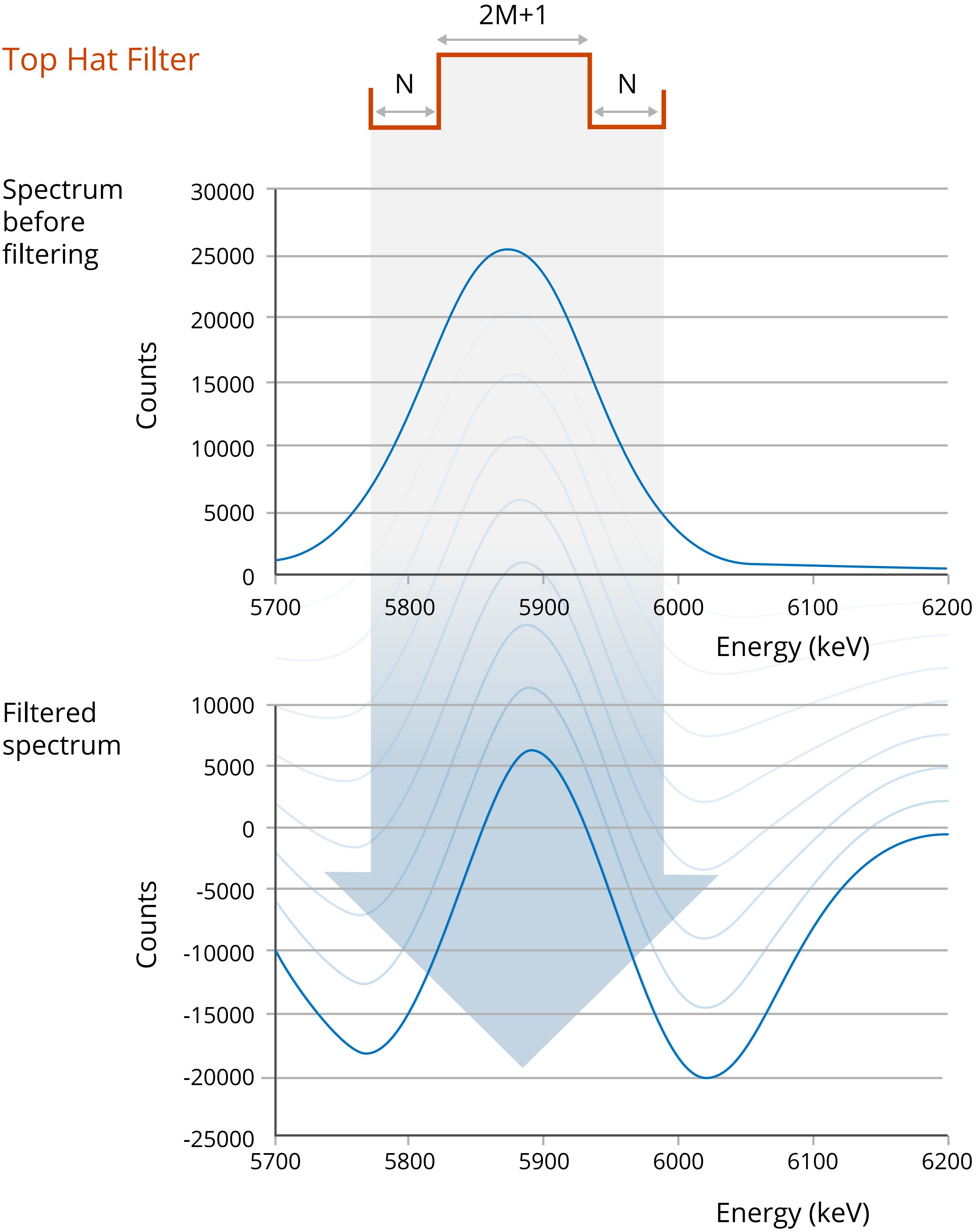
Standardless or semi-quantitative analysis

Most commercial EDS X-ray analysis systems will be installed with default spectra for all elements and the most commonly used X-ray analysis lines. This data allows an estimation of composition to be made for spectra collected on different instruments, and this information can be helpful in identifying different phases in a sample, for example. However, differences between the instrument and conditions for collection of the default spectra and those being used to undertake analysis elsewhere will limit the accuracy and precision of the results, so that they cannot be published as quantitative analyses.

Spectral processing

At the heart of quantitative microanalysis is spectral processing or data reduction. The objective is to calculate the number of X-ray counts in the peak of interest and compare that to the number of X-ray counts in a standard with a known concentration of the element of interest, and from this derive the mass fraction of the element in the sample. There are two steps involved: firstly, the Bremsstrahlung (background or continuum) X-ray counts have to be subtracted from the spectrum, and secondly the Characteristic X-ray peaks have to be processed to derive the concentration of the element concerned.

Different materials have different mean atomic numbers, and because the number of Bremsstrahlung X-rays varies with mean atomic number (Kramer’s Law) the background counts, i.e., the contribution of Bremsstrahlung to the total counts in the X-ray peak, need to be subtracted before the counts in the Characteristic peaks can be calculated. Background subtraction in EDS analysis is most commonly achieved by using a mathematical filter known as a Top-Hat Filter as the first step. The filter is applied to each channel in the spectrum, and a value for the corresponding channel in the filtered spectrum is calculated. The value for any channel in the filtered spectrum can be approximated by finding the average value of the central channel and the three channels on either side of it ($2M + 1$), and subtracting from that value the average of the four channels on the low-energy side of the ‘hat’ (N), and the average of the four channels on the high-energy sides of the ‘hat’ (N), where $M = 3$ and $N = 4$. The result is to remove the slope and noise from the background continuum, and to subtract the background continuum from the Characteristic X ray peaks.



The application of a top-hat filter to part of an ED spectrum. Optimum values for M and N in the filter are 3 and 4 channels respectively, so the total filter is 15 channels wide.

Concentration calculation

The K ratio is the ratio of the intensity (number of X-ray counts) in the filtered peak for an element of interest in the sample to the intensity in the filtered peak for the standard assigned to that element:

K = Ismpl/Istd

We would expect the concentrations of the element in the sample and the standard to be related to the measured X-ray intensities, so the concentration of the element of interest in the sample can be approximated by the K ratio multiplied by the concentration of the element in the standard, which is known:

Csmpl = K.Cstd

If we apply this relationship to calculate the concentrations of the elements in a sample, we find that some of the calculated concentrations are too low, some are too high and some are about right. It turns out that every element in the sample has an effect on the measured X-ray intensity of every peak in the X-ray spectrum. That is, the measured intensity depends on the composition of the whole sample. Therefore, to calculate the concentrations of the elements in the sample we must apply matrix corrections to the raw intensities to allow for differences in composition between the sample and the standard.

There are three parts to the matrix corrections based on:

- Z - differences in mean atomic number,
- A - differences in absorption of X-rays, and
- F - differences in the production of secondary X-rays, or X-ray fluorescence.

The matrix corrections are therefore commonly known as ZAF corrections.

Atomic number correction, Z

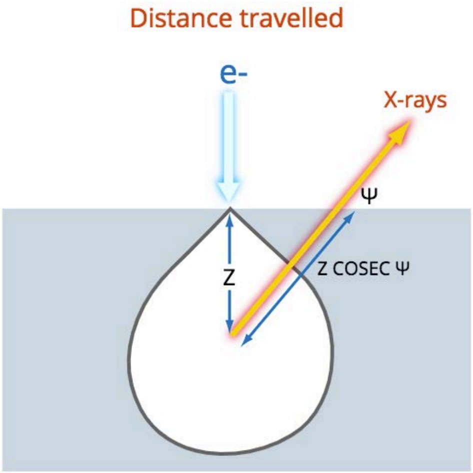
There are two parts to the atomic number correction: a backscattering component and a stopping power component. Remember that as the mean atomic number of the sample increases the number of electrons that are backscattered also increases, and this is what gives rise to contrast in backscattered electron images. The electrons that are backscattered are ejected from the sample and cannot generate X-rays from it, so if the sample has a different mean atomic number than the standard a correction to the measured X-ray intensity must be made.

The stopping power is the rate of energy loss by the incident electrons per unit of mass penetrated in the sample, and it decreases with increasing mean atomic number, Z. The mass penetrated increases with increasing Z, and more X-rays are generated from samples with higher Z. The stopping power correction has the opposite sense to the backscatter correction, and the sum of the two corrections makes up the mean atomic number correction, Z.

Absorption correction, A

X-rays generated within the sample travel in all directions through it, and may be absorbed within it. X-rays are either absorbed within the sample or they pass through it – they do not gradually lose energy as electrons do. In the energy range for X-rays generated in the SEM, X-ray absorption is most commonly due to the photo-electric effect. This means that if the energy of the Characteristic X-ray is equal to the ionisation energy of an electron shell of an atom in the sample, there is a strong probability that the X-ray photon will be absorbed and a photo-electron will be generated (see the Photo-electric animation). Clearly, the probability of the X-ray being absorbed is dependent on the other elements in the sample and their ionisation energies.

The probability of the X-ray being absorbed also depends on the distance that it travels through the sample before it escapes and enters the X-ray detector. The path length of the X-ray through the sample is given by z cosec ψ where z is the depth in the sample from which the X-ray is generated and ψ is the takeoff angle of the detector. The absorption correction factor is given by μ cosec ψ where μ is the Mass Absorption Coefficient (MAC).



The distance travelled through the sample by an X-ray photon generated at depth z is z cosec Ψ, where Ψ is the takeoff angle of the X-ray detector.

In general, MACs increase as the energy of the absorbed X-ray decreases so corrections for low Z elements are large while those for high Z elements are smaller. Also, high Z elements tend to be strong absorbers so large corrections are required for low Z elements in a matrix containing high Z elements.

Mass absorption coefficients

Mass absorption coefficients are stored as a matrix of numbers of absorption of a particular X-ray line (the emitter) by an absorber: For example, a portion of the MAC matrix for Kα X-rays for Z = 23 to 29 is shown below.

EMITTER	V 4952 EV	CR 5415 EV	MN 5899 EV	FE 6403 EV	CO 6930 EV	NI 7478 EV	CU 8048 EV
V	94.6	73.8	498.4	403.4	328.2	268.5	220.8
Cr	111.1	86.7	68.4	454.8	370.8	303.9	250.4
Mn	125	97.6	76.9	61.3	401.9	330.1	272.4
Fe	145	113.2	89.3	71.1	57.1	370.2	306
Co	160.9	125.7	99.1	79	63.5	51.4	329.4
Ni	187.9	146.8	115.8	92.3	74.1	60	49
Cu	200.7	156.8	123.8	98.7	79.3	64.2	52.4

Note that the MAC for absorption of Fe Kα by Co (79.0) is different from the MAC for absorption of Co Kα by Fe (57.1).
Note also that the MAC for absorption of the Fe Kα X-ray by Cr is high (454.8) while that for absorption of the Fe Kα X-ray by Mn is low (61.3). This means that the Fe Kα X-ray is strongly absorbed by Cr, if it is present in the sample, but not by Mn. In an Fe-Cr alloy the measured intensity of the Fe Kα X-ray will be too low. However, in an Fe-Mn alloy there will be little effect on the measured intensity of the Fe Kα X-ray.

Fluorescence correction, F

The X-rays produced in the sample by the electrons of the primary beam have the potential to produce a second generation of X-rays. This process is known as secondary fluorescence, or just fluorescence. Fluorescence occurs when Characteristic X-rays produced by the primary-beam electrons from one element in the sample have an energy greater than the critical ionisation energy of an electron shell in another element present in the sample. For example, Fe Kα X-rays (E = 6.40 keV) are able to fluoresce Cr Kα X-rays (Ec = 5.99 keV), but Cr Kα X-rays (E = 5.41 keV) cannot fluoresce Fe Kα X-rays (Ec = 7.11 keV). In this case, in an Fe-Cr alloy, the measured intensity of the Cr Kα X-ray will be too high although there will be little effect on the measured intensity of the Fe Kα X-ray.

Corrected concentration calculation

The calculation of the concentration of an element in a sample must therefore take account of the differences in composition between the sample and the standard. A ZAF factor can be calculated that takes account of the stopping power, backscattering coefficient, absorption and fluorescence effects.
Csmpl = K.Cstd.ZAFsmpl/ZAFstd
The ZAF factor for the standard can be calculated from its composition, which is known, but the composition of the sample needs to be known before the ZAF factor can be calculated. As the composition of the sample is not known, an iterative technique is used, with an initial composition calculated from the measured K ratio. The ZAF factor for this composition is calculated and the composition of the sample is recalculated, and the process repeated until there is no change in the calculated composition.

Accuracy, precision and detection limits

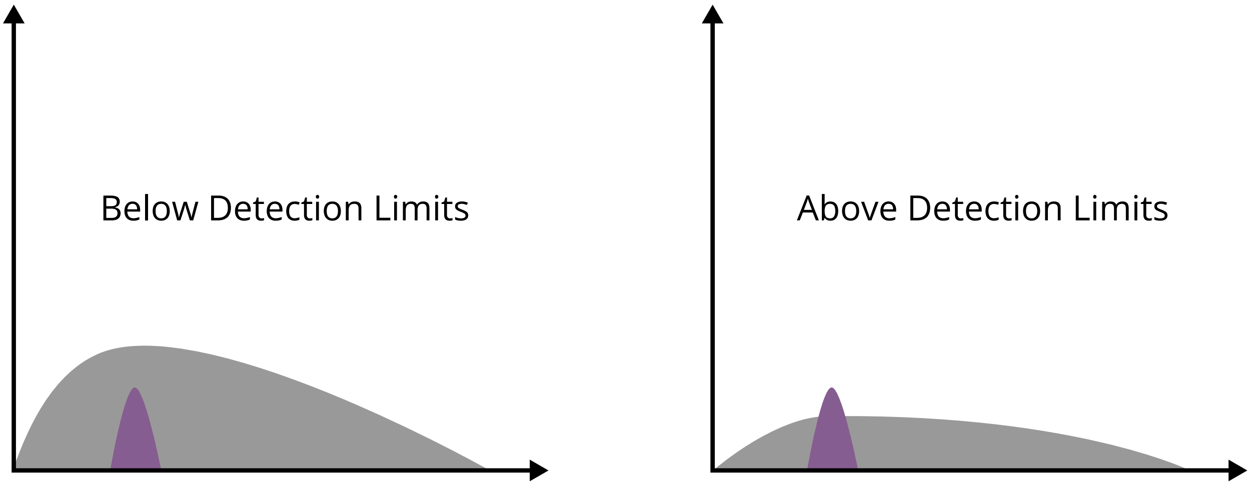
Accuracy refers to the “truth” of the analysis. It depends on the standards used and the spectral processing and corrections applied to the raw data. It is an absolute description.
Precision refers to the reproducibility of the measurement of the X-ray counts in the EDS spectrum. It depends on the number of X-rays in the spectrum and the statistics related to that number. Measurement of precision allows comparison of analyses from different grains, different analysis sessions or different studies. It is a relative description.
The minimum detection limit is the concentration corresponding to a peak that can just be distinguished statistically from background fluctuations. This is generally taken to be a peak height equal to three times the standard deviation of the background count. This will vary between different elements and analytical lines, and for the same element in different matrixes. For routine EDS analysis, the detection limits are about 1000 ppm or 0.1 wt%.

Detection limits

Detection limit = $3 / m \sqrt{Rb/Tb}$ Analytical Standards are required

m = cps/% Rb = background count rate Tb = time on background

Typical Detection Limit EDS = 0.1 wt%
WDS = 0.02 wt%
} The minimum amount you can measure



Specimen 1 Specimen 2

The denser the material, the bigger the background

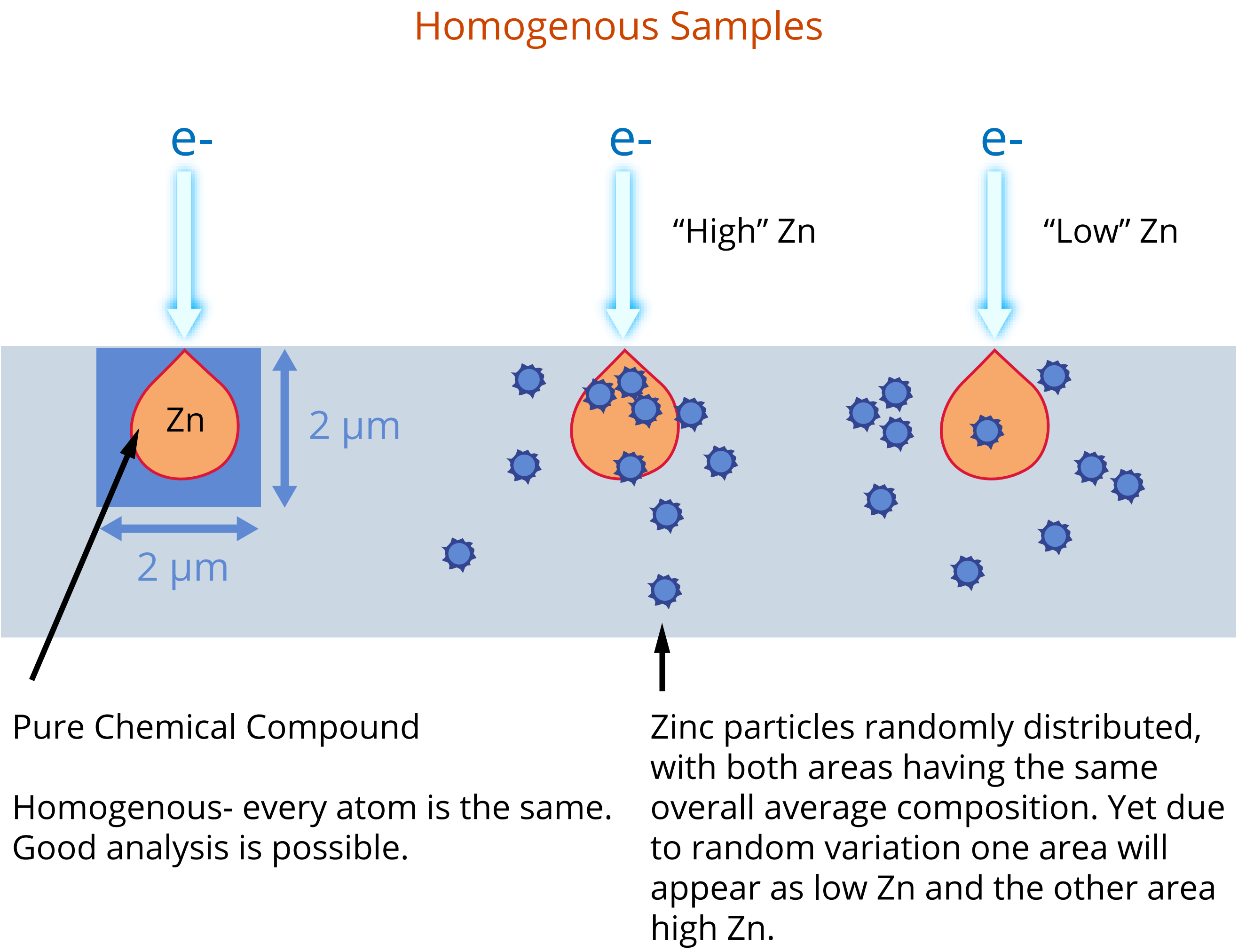
Detection limits for EDS and WDS microanalysis.

Random and systematic errors

Experimental uncertainty is due random and systematic errors.
Random errors are statistical fluctuations, in either direction, in the measured data due to the limitations of the measurement device.
Systematic errors are reproducible inaccuracies that are consistently in the same direction and are likely to be caused by an error in the experimental setup, e.g., incorrect reading of accelerating voltage or beam current.
In EDS analysis, sources of error may be related to the sample, the microscope, the EDS detector and the data reduction software.

Errors related to the sample include

1. The sample is not homogeneous – only one phase should be intersected in the interaction volume



Pure Chemical Compound

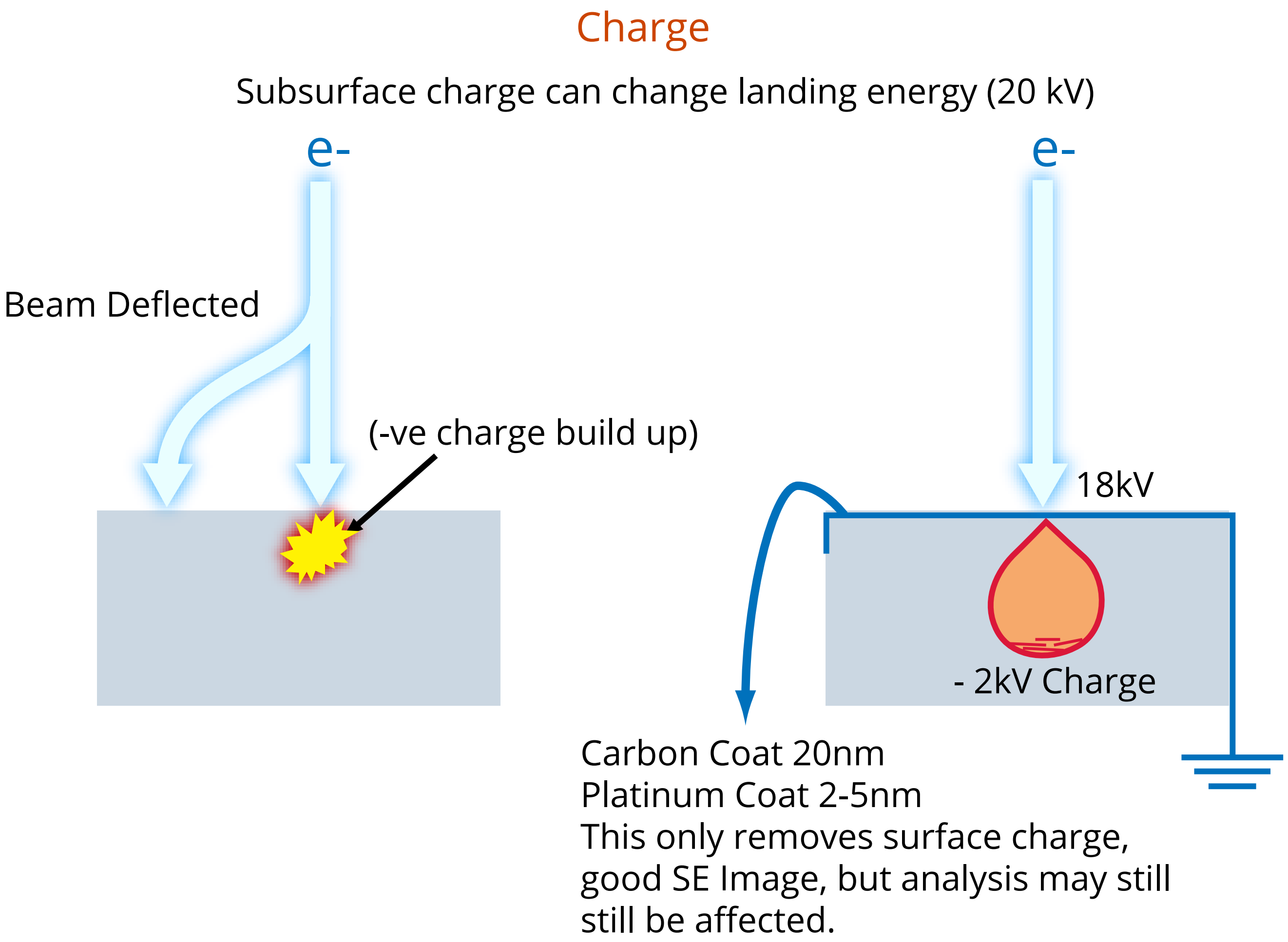
Homogenous- every atom is the same. Good analysis is possible.

Zinc particles randomly distributed, with both areas having the same overall average composition. Yet due to random variation one area will appear as low Zn and the other area high Zn.

How a non-homogeneous sample can affect quantitative analysis.

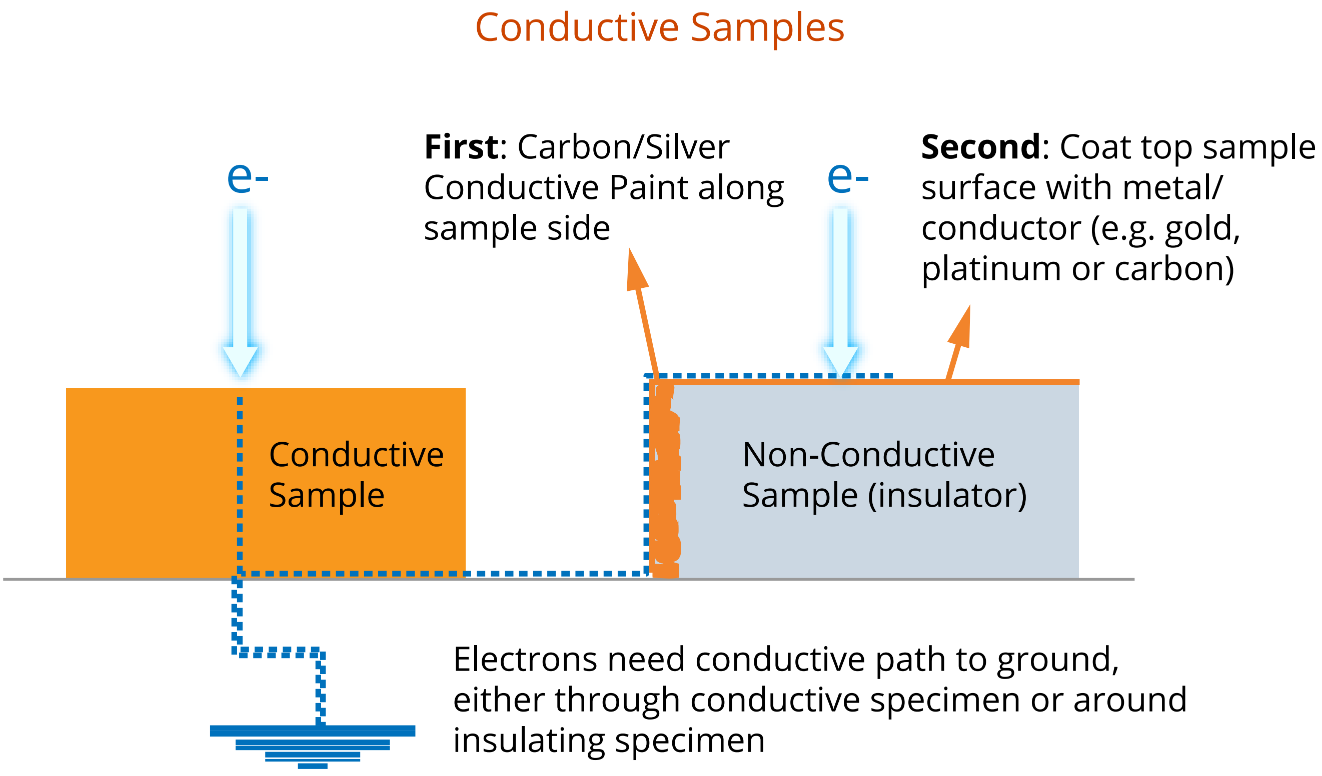
2. The sample is not stable in the microscope – sample outgassing, melting or volatility of some elements, e.g. clay minerals, Na in glass.
3. The sample is not well polished or is porous.

4. The sample is not conductive – charging can affect the effective energy of the primary-beam electrons.



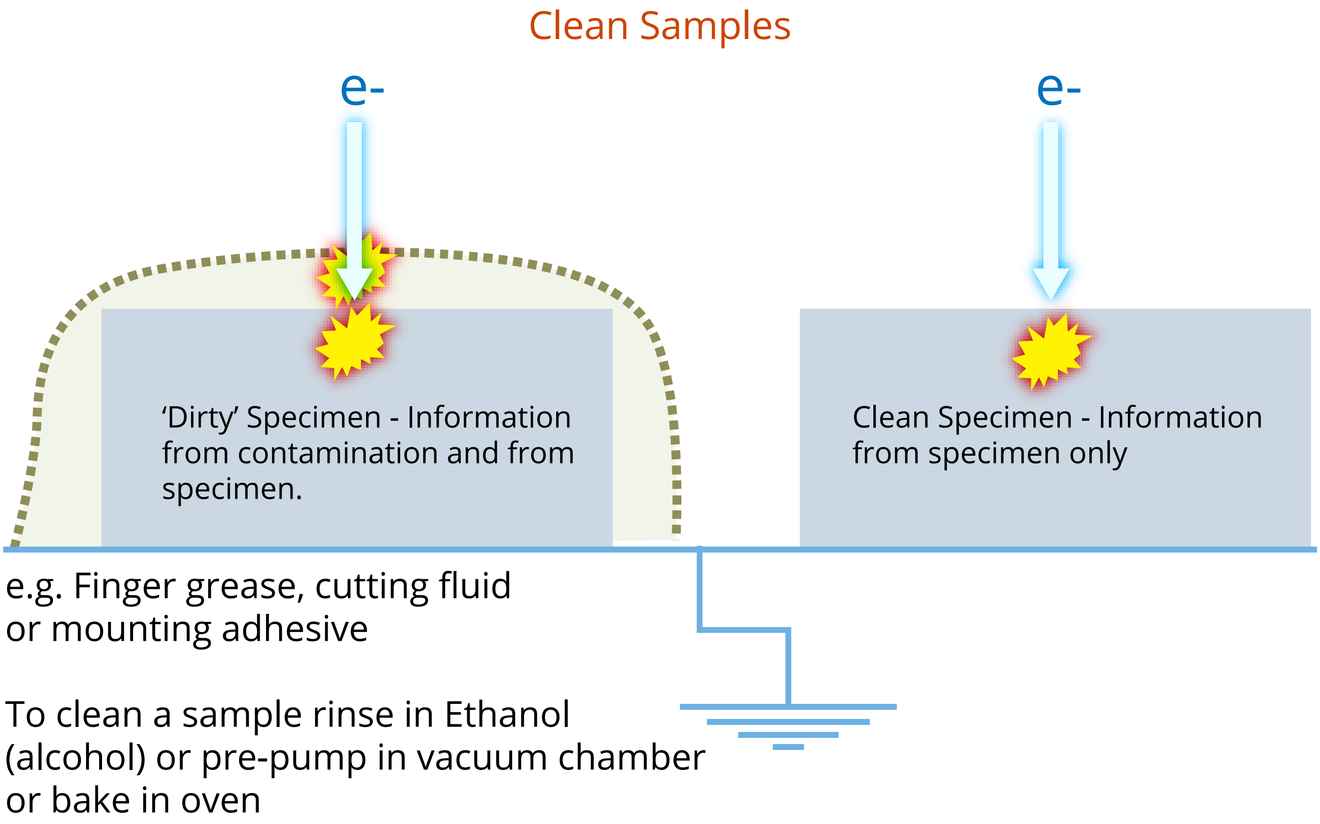
The build-up of electrons on the surface of a non-conducting sample can deflect the primary electron beam and change the effective kV of the analysis system.

5. For insulating samples, a conductive path must be made from the surface of the sample to electrical ground.



An insulating sample can be made conductive by coating the surface with a conductive material and by creating a conductive path from the surface of the sample to ground with either conductive paint or conductive tape.

6. The sample is not clean – there may be fingerprints, dust or lint on the surface.



Contamination of the surface of the sample can result in inaccurate analyses as X-rays are generated from both the sample and surface contaminants.

7. For light-element analysis, inappropriate standards or inappropriate correction procedures.

Errors related to the microscope include

1. Incorrect reading of accelerating voltage.
2. Instability of the beam – the beam current must be stable while the X-ray spectrum is being collected.
3. Incorrect setting of working distance.

Errors related to the EDS detector system include

1. Incorrect setting of takeoff angle.
2. Incorrect setting of detector-sample geometry.
3. Instability of detector electronics.
4. Build up of ice or contamination on the detector window.

Errors related to data processing

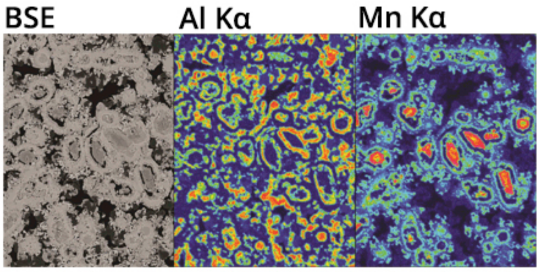
1. Insufficient counts in the X-ray spectrum to overcome statistical fluctuations.
2. Background subtraction routines.
3. Matrix correction models.
4. Correction of spectral artifacts.
5. Correction for overlapping peaks, i.e. spectral deconvolution.

Accuracy and precision

Care must be taken to minimize the potential errors in the analysis system. The accuracy of the analysis depends on the sum of all the errors. It can only be defined by reference to standards. A well-characterized standard should be analysed in every analysis session to verify the analysis conditions.
It is difficult to quantify all sources of errors for EDS analysis. The combined errors limit the precision of EDS analysis to ±2% relative for major components.

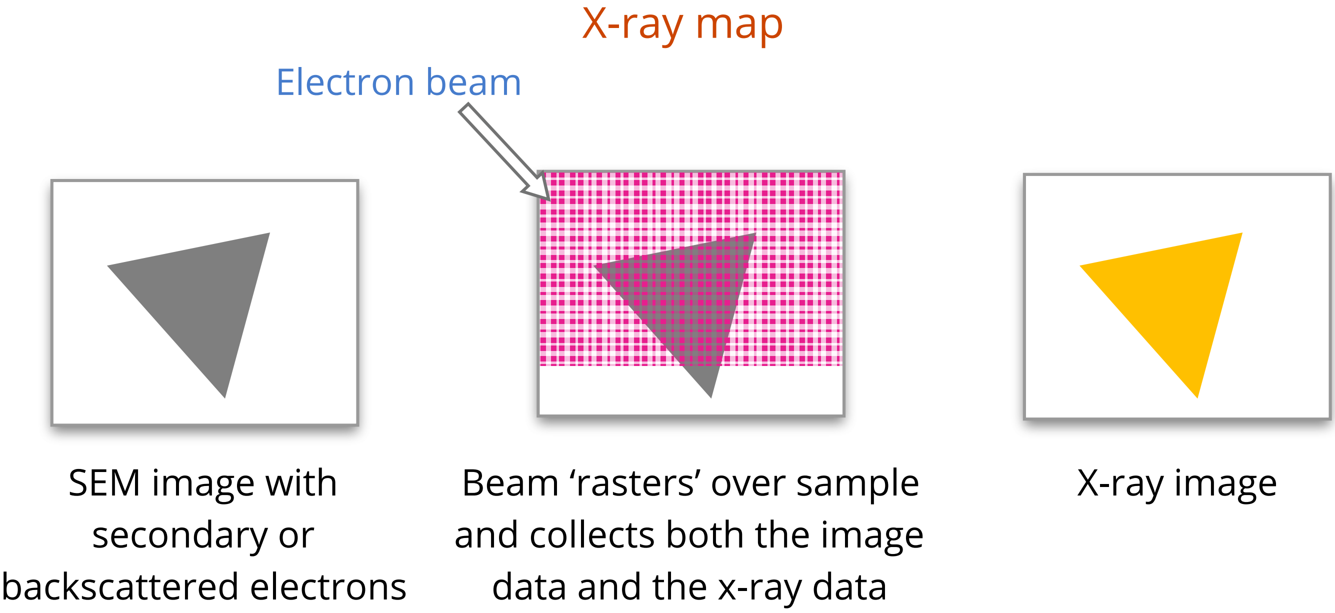
X-Ray mapping

X-ray mapping provides images of elemental distributions in a sample. The information that X-ray maps provide can be readily assimilated and, in many cases, a problem can be solved by knowing the distribution of a particular element without requiring quantitative point analysis. While BSE images can show variations in composition in a sample, X-ray maps can show which elements are responsible for the variation.



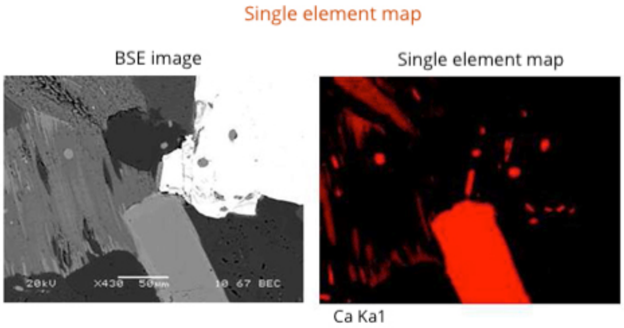
Comparison of BSE image and X-ray element distribution maps.

Elemental X-ray maps are produced by recording the number of X-ray photons of a specified energy generated from each point over a fixed counting time, while the electron beam is rastered over a rectangular area.



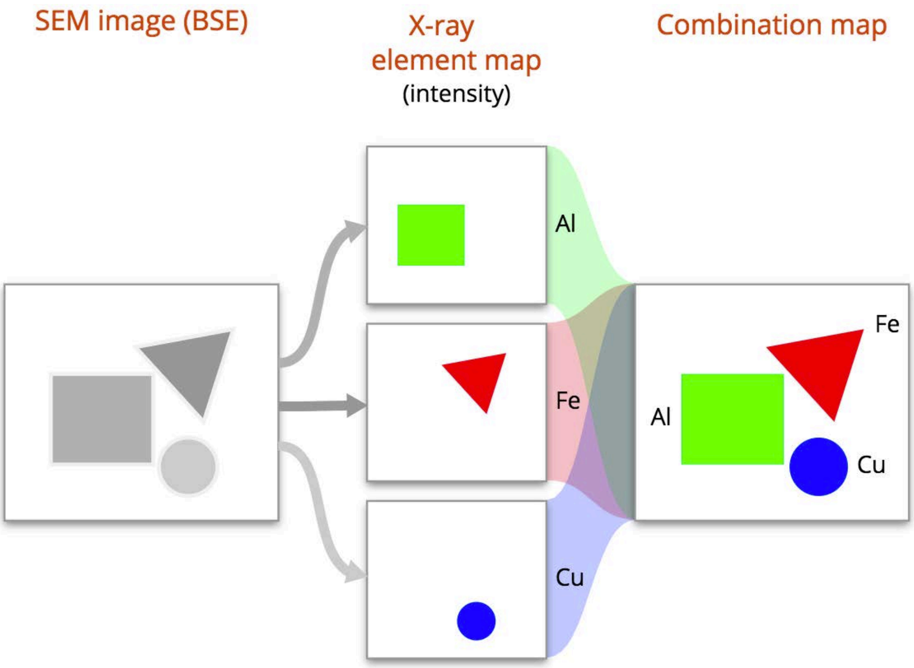
Generation of X-ray element distribution maps by rastering the beam over the area to be mapped.

An image is generated by converting the number of X-ray photons of specified energy detected at each point into a brightness value for a pixel on the screen or digital image. The raw data for the image is a matrix of integers corresponding to the number of X-rays counted at each point and these are mapped to a single-band image with 0-255 levels. The image can be displayed as a grayscale image or assigned false colours based on a look-up table.



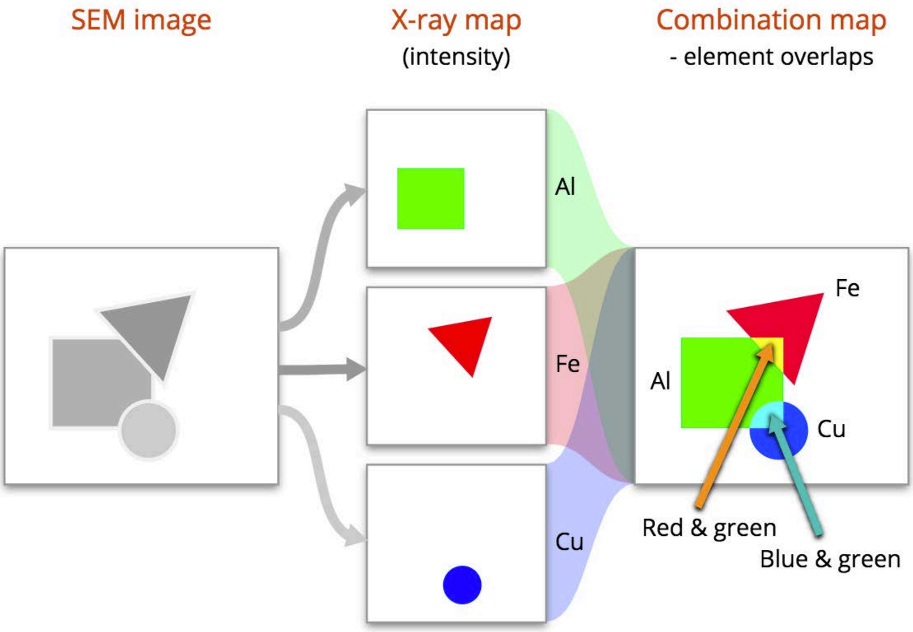
BSE image and element distribution map for Ca Kα displayed with 256 levels of red.

Three single-band images, representing X-ray maps for three different elements, can be assigned different colours (red, green and blue) and combined to form a coloured three-band image. Combining maps from different images can highlight different phases in the area being scanned.

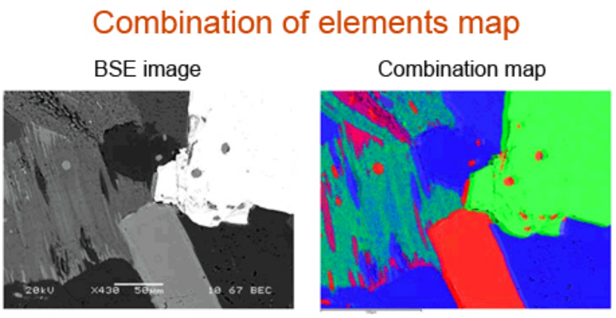


Distribution map for three different elements, in this case Al, Fe and Cu, can be combined in a three-band image to highlight different phases mapped in the area of interest.

Phases containing a combination of more than one of the elements being mapped will be displayed with composite colours.



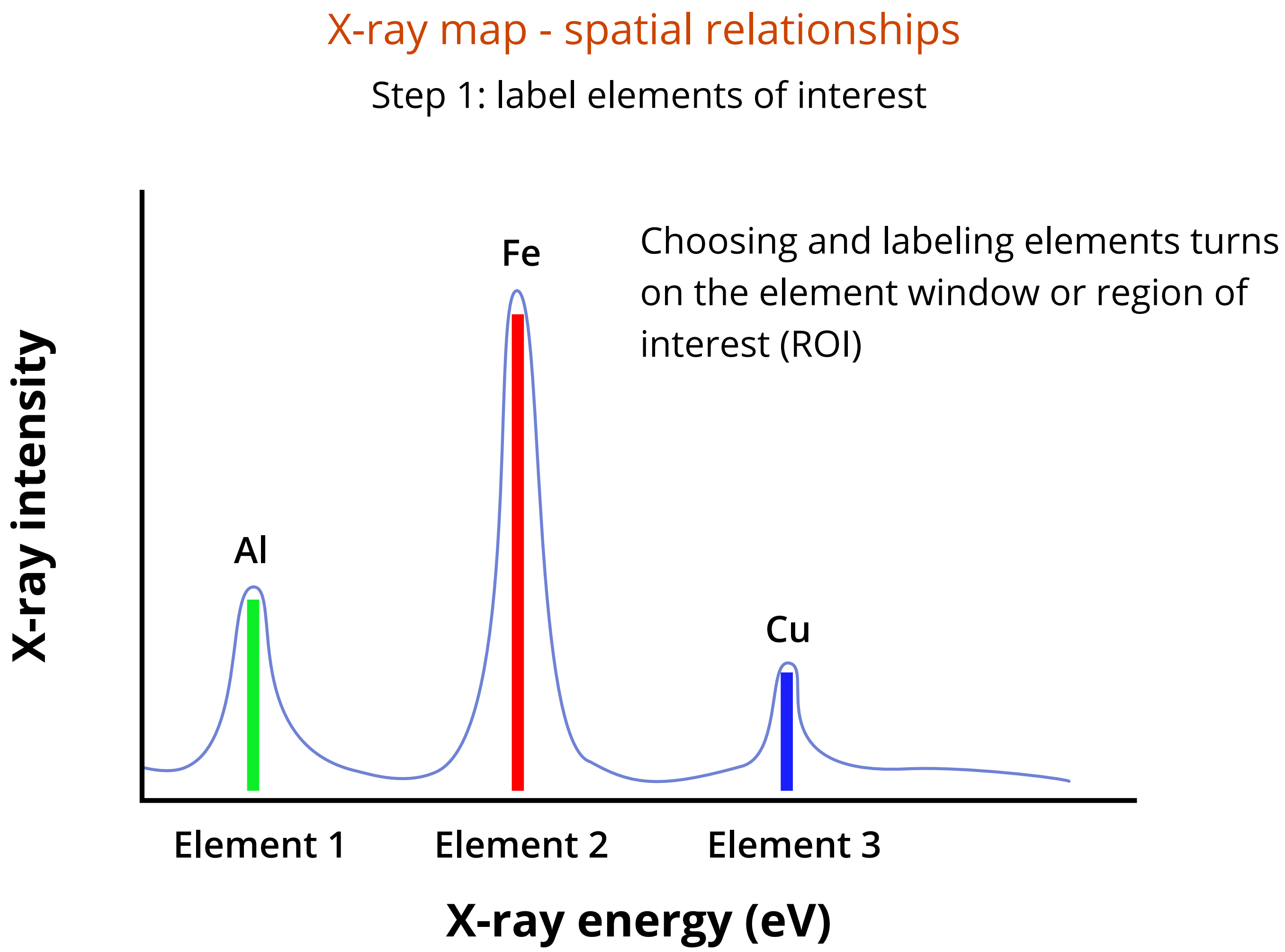
Distribution map for three different elements, in this case Al, Fe and Cu, can be combined in a three-band image. Composite colours are produced where different combinations of the elements are present in different phases in the sample.



A combination map for phases in a sample of granite.

Parameters for X-ray mapping

In older X-ray mapping systems, regions of interest, corresponding to the energy ranges of the Characteristic X-ray peaks of the elements to be mapped, need to be specified before collecting maps.



Choosing and labeling elements turns on the element window or region of interest (ROI)

Labelling the element to be mapped, or defining regions of interest that include the Characteristic X-ray peaks of the element, may be required to generate an X-ray map.

In more recent packages, a complete ED spectrum is collected at every pixel in the image. This allows a map to be generated for all elements in the area mapped. More detailed mining of the data cube is possible after the data have been collected.

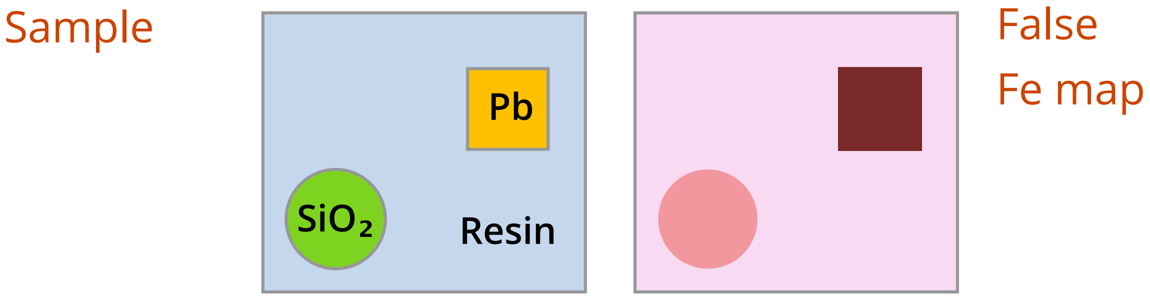
Maps are generally collected at magnifications of 50 to 1000 times. At magnifications less than 50 times, geometrical error is possible, while at magnifications greater than 1000 times oversampling is likely.

The dwell time for each pixel can range from a millisecond to a second or more. These times are much less than those used for point analysis (30-60 s), so mapping is ideal for major elements but is not going to reveal minor or trace element distributions as not enough X-rays will be collected.

The total acquisition time for the map will depend on the resolution of the collected maps (the number of pixels) and the dwell time per pixel. The acquisition time may range from ~0.5 h to >12 h (an overnight run). A very stable beam is required for long acquisition times, although means of adjusting for drift of the beam are available in newer software packages.

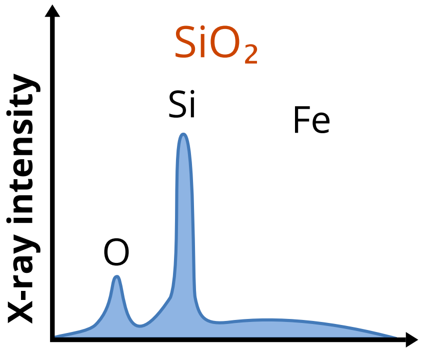
Artifacts in X-ray mapping

The sample to be mapped should be flat and polished to avoid shadowing of parts of the sample.
Some X-ray maps show the number of X-ray photons of a specified energy generated from each point over a fixed counting time (raw X-ray counts) and do not apply any corrections for background or overlapping peaks. The background counts are proportional to mean atomic number (Kramers' Law) so phases in the map with higher Z will give higher background counts which will show up in the element maps, even if there is none of the element present in the high-Z phase.
More recent software packages apply corrections for background, but if this is not available, collect a map from an area of the spectrum where there will be no characteristic X-ray peaks, e.g. Ar Kα. This will be a 'background' map and can be subtracted from the element maps to minimize background artifacts.



Mapping doesn't strip the background.
Maps auto scale from highest to lowest intensity.
This can lead to a false intensity map.
The avobe sample has no Fe, yet we still get a Fe map (all background).
Solution, map an element that will never be there in sample
- that is the background; substract that from everything.

SiO_2



Resin

Pb

Above Detection Limits

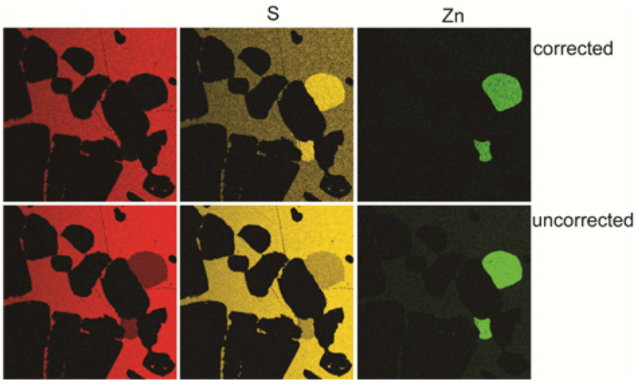
Specimen 1

Specimen 2

The denser the material, the bigger the background

Artifacts can result if the element maps are not corrected for variations in atomic number between different phases.

If there are elements with overlapping peaks in the mapped area, e.g. Pb and S or Ba and Ti, the maps for these elements will be a combination of the counts for both elements and will appear the same. In the example below, the uncorrected maps for Pb and S give the same information, but the corrected maps show the true distribution of Pb and S in the mapped area, i.e. there is no Pb in the Zn-bearing phase but there is S.



Artifacts can result if the element maps are not corrected for overlapping Characteristic X-ray peaks.

Again, more recent software packages are able to deconvolute the spectra to produce maps showing the true distributions of both elements.

Credits

Microscopy Australia acknowledges the huge input of time and expertise by the many staff members and associates who have contributed to the development of MyScope over the years.

For EDS we thank: Ron Rasch, Karen Privat, Pat Trimby, Angus Netting, Ben Wade, Janet Muhling.