X-Ray Fluorescence

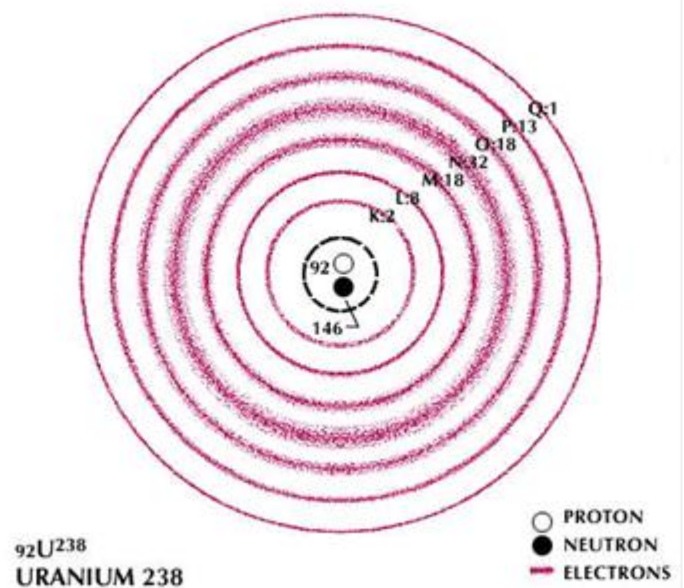
Analytical Background:

X-ray Fluorescence Phenomenon

The X-ray and radiation physics behind XRF spectrometry is described in detail elsewhere (e.g. Shackley 2011; Pollardet al. 2007; Moens, et al. 2000). Presented here is a brief overview of the basic principles.

When atoms in a material are externally excited by high-energy, short-wavelength radiation of sufficient energy, such as X-rays, electrons in their inner atomic shell become dislodged and are replaced by higher energy electrons from an outer shell in order for the atoms to maintain electrical stability. These high-energy electrons must release energy to fill the lower energy vacancies within the atom. This energy is emitted as photons with an energy/wavelength characteristic of the difference between the initial and final energy state of the electron or outer and inner shell energies. The two critical points for our discussion are: (a) the relationship between the energy of the emitted photon and the initial energy/ shell of the substituting electron and (b) the “sufficient” excitation energy to dislodge an electron from the inner shell.

Figure 1.1 Bohr model of a Uranium atom. Electron shells are indicated by the capital letters; adjacent numbers indicate the total number of electrons in the shell. In EDX analysis, only the first four shells (K-N) are typically used.



Atoms of most elements are composed of a nucleus and multiple orbitals of electrons organized into shells of related energies. In XRF spectrometry, we are primarily concerned with electron shells K, L, M and N (Figure 1.1). The K shell is the lowest energy electron shell: it is also the inner most shell, closest to the nucleus. It is the energy requirement of the K shell that must be met by a substituting electron to maintain an atom's electrical stability. Each successive electron shell (L, M, N, O, etc.) is both farther away from the atomic nucleus, i.e., outside the previous electron shell, and composed of higher energy electrons.

When an electron vacancy in the K shell is filled by an electron from the L shell, the characteristic energy/wavelength of the emitted photon is called the K-alpha ($K\alpha$) spectral line, and when the K shell vacancy is filled by an electron from the M shell, the characteristic energy/wavelength of the emitted photon is called the K-beta ($K\beta$) line (Figure1.2). The substitution of an L and/or M shell electron into a K shell vacancy creates a corresponding energy vacancy in the L and/or M shell, catalyzing an electrical cascade as electrons in the M and N shells emit energy/photons in order to fill the energy vacancies in these lower energy shells. The L-alpha ($L\alpha$) line is the characteristic energy of a photon emitted when an M shell electron fills a vacancy in the L shell and the L-beta ($L\beta$) line is the characteristic energy emitted when an N shell electron fills an L shell vacancy.

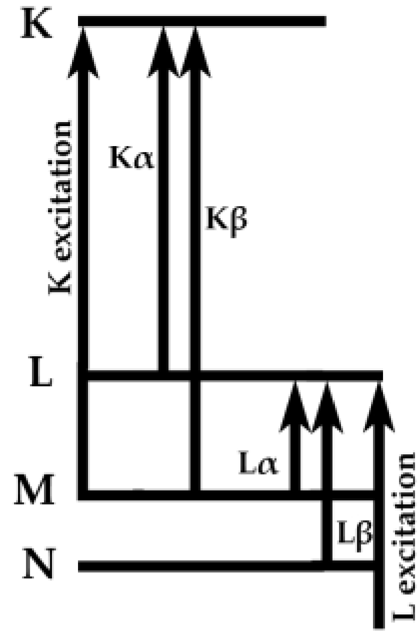


Figure 1.2: Electron energy transitions important for EDX

Alpha lines generally have a higher count rate that beta lines because electrons from the next higher energy level substitute into low energy vacancies with greater frequency than those from energy shells farther away. However, beta lines are a critical component of XRF spectrometry because these spectral lines often have similar characteristic energies to the alpha lines of adjacent elements. For example, the Kβ line of titanium (Ti) is 4.931 keV and the Kα line of vanadium (V) is 4.949 keV (see periodic table at the beginning of chapter). While, theoretically, each of these lines has a unique and characteristic energy related to a specific M-K or L-K electron transition, in practice, detector resolution is not sufficiently fine-grained enough to differentiate these energies. Therefore, the Kβ counts for, in this case, Ti are reported as part of the V Kα peak (Figure 1.6). This spectral line interference is particularly important for the detection and quantification of low and mid Z elements for which there are no L lines ($Z < 30$). We revisit this phenomenon, commonly referred to as spectral overlay below.

L lines have a lower count rate and lower energies than K lines of the same element. The latter results from the smaller energy differential among the L, M and N shells than the energy gap between the K shell and the outer shells. This lower L line energy can be an advantage in XRF spectrometry because, generally speaking, the energy required to dislodge electrons from the K or L shell is twice the energy of the desired K or L spectral line. For example, the Kα line of tin (Sn) is 25.193 keV, which means that an excitation energy of approximately 50 kV is required for its optimal detection. The Lα line of Sn, however, is 3.133 KeV, requiring an excitation energy of only 6 kV for optimal detection.

Laboratory based XRF spectrometers are typically configured with 50–60 kV X-ray tubes and pXRF spectrometers are typically configured with 30–50 kV tubes, which means that there are limitations to the Kα lines which can be adequately and optimally detected: $Z \leq 56$ for laboratory based instruments and $Z \leq 50$ for portable instruments. The L lines of higher Z elements are often used in XRF spectrometry to detect and quantify these elements. Lead (Pb), for example, has a Kα line energy of 74.228 keV and an Lα line of 10.549 keV. The Kα line is out of range for both laboratory and portable XRF spectrometers, however, the Lα line is well within optimal excitation range. L lines are also used to help identify elements with K lines obscured by spectral overlay.

The disadvantages of using L lines include both their lower count rate, which can make them difficult to differentiate from background, and spectral overlay. In the example above, Pb has an Lα line energy of 10.549 keV which 'overlaps' with the Kα line of arsenic (As) at 10.532 keV. Detection and quantification issues related to spectral overlay cannot be avoided by analyzing the L lines of all the elements of interest because not all elements have L lines. Additionally, some elements have spectral overlap energies with both K and L lines. In our example, for instance, the Mα line of Pb 'overlaps' with the Kα line of sulfur (S) at 2.346 and 2.307 keV respectively.

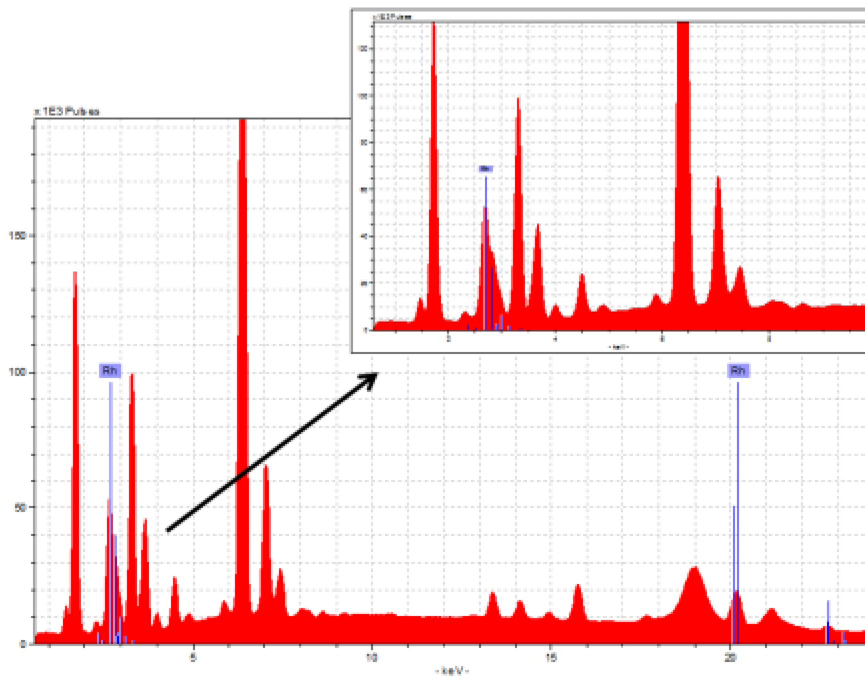
Spectral Interferences

Bremsstrahlung radiation (Background)

"Bremsstrahlung" means, literally, "braking radiation" and is an important phenomenon for ED-XRF spectrometry. When an excited K-shell electron is dislodged by X-rays of sufficient energy it can either escape from the atom entirely or be reabsorbed by the atom into a higher energy electron shell. These 'escaped' electrons are collimated and directed toward a metal anode or target. The purpose of the target is to 'capture' the electrons, which it does by absorbing or converting their kinetic energy (motion) into electromagnetic energy (light), literally acting as a brake.

The photons emitted during this process, the Bremsstrahlung radiation, have lower energy than the 'escaped' electrons since energy is absorbed and lost as heat during their conversion from kinetic to electromagnetic radiation. The decelerated energy of these photons is neither entirely predictable nor characteristic, except for the energy (K lines) associated with the target, because the 'escaped' electrons may 'brake' as a result of direct absorption by an atom in the target, giving off a single pulse of energy, or be deflected by multiple atoms before coming to a rest, giving off multiple pulses of different energies in the process. This Bremsstrahlung radiation or energy scattering is responsible for the continuous nature of the ED-XRF spectrum and the energy shoulders which create 'peaks' around the characteristic K and L lines of elements.

Figure 1.3: Compton scatter peak created on EDX spectra by a Rh



One of the outcomes of this phenomenon is a pronounced scattering of energy or generation of a Compton peak at the characteristic K lines of the target material (Figure 1.3). Rhodium (Rh) is a common target used in the X-ray tubes of ED-XRF spectrometers. The reason Rh is often selected as the target is that the K lines of Rh are 20.167 and 22.759 keV, neither of which overlap with the K or L lines of elements typically of interest in ED-XRF analysis. The smaller Compton scatter associated with Rh L lines, at 2.696 and 2.834 keV, also do not overlap with the K or L lines of elements typically of interest in ED-XRF

analysis. The two elements with radiation overlay interference with the K and L lines of Rh are molybdenum (Mo) and chlorine (Cl), neither of which are informative for geochemical studies.

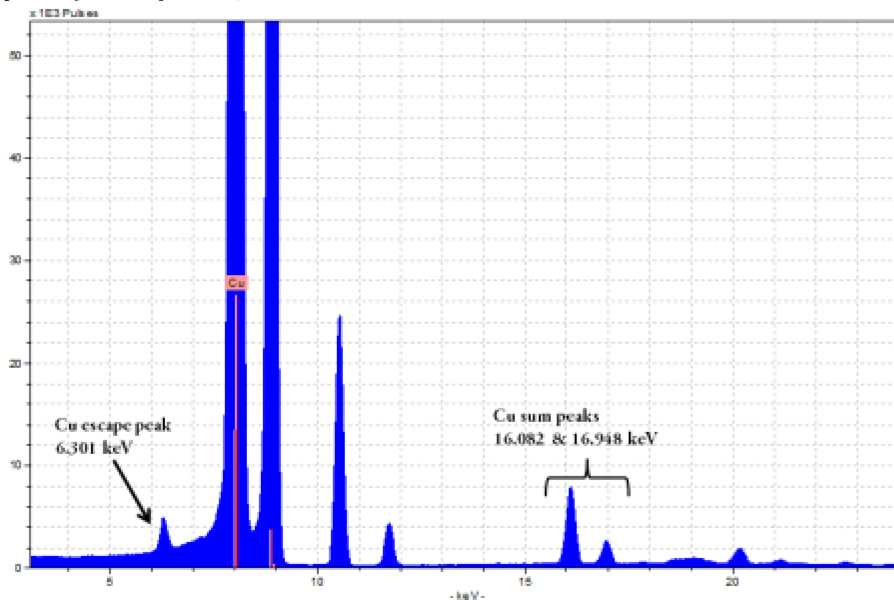
Bremsstrahlung radiation is often referred to as 'background' in ED-XRF spectrometry. The intensity of the energy scatter produced by Bremsstrahlung radiation is inversely proportional to the atomic number of the element from which the electron 'escaped', approximately $1/Z^2$. This means that the background radiation generated by low Z elements is significantly higher than for the mid-high Z elements (elements for which $Z \geq 26$). For elements $Z < 26$, the Bremsstrahlung radiation is so intense that it is often difficult for the detector to differentiate between background and signal and/or counting errors and background. For this reason, ED-XRF is not the best analytical instrument for quantifying low Z/major elements.

There are several way to ameliorate the effects of Bremsstrahlung radiation and reduce background noise. The two simplest and most straight forward for the detection of low Z elements are decreasing the accelerating voltage or excitation energy and increasing the count or analysis time. Decreasing the accelerating voltage limits the range of elements sufficiently excited to fluoresce, preventing the mid-high Z elements from contributing to the Bremsstrahlung radiation and/or creating spectral overlay of their L lines on the K lines of the low Z elements. Increasing the count time enables the detector to measure and report more counts for the low Z elements thus enabling it to more efficiently and effectively differentiate among signal, noise and counting errors.

Another way to reduce Bremsstrahlung radiation is to use a filter. Filters are typically thin foils of metal or a combination of metals placed between the X-ray tube or excitation energy and the sample. The purpose of the filter is to change the energy range of the excitation X-rays. A filter absorbs X-rays with energies immediately above the absorption edge of its material, while allowing X-rays of

lower and very high energies through. Thus, filters create a region of low Bremsstrahlung radiation immediately above the filter's absorption edge energy. For low Z elements, such as phosphorus (P) and sulfur (S), an aluminum (Al) or neutral filter can be used to reduce the noise created by low energy electron scatter. The absorption edge energy of Al is 1.559 keV which means that the Kα lines of Na, magnesium (Mg) and Al will be absorbed by the filter but a background free region will be created between approximately 1.7–3.7 keV facilitating detection of silicon (Si) to calcium (Ca).

Figure 1.4: Escape peak of Cu generated by a SDD on a pXRF



Escape peaks

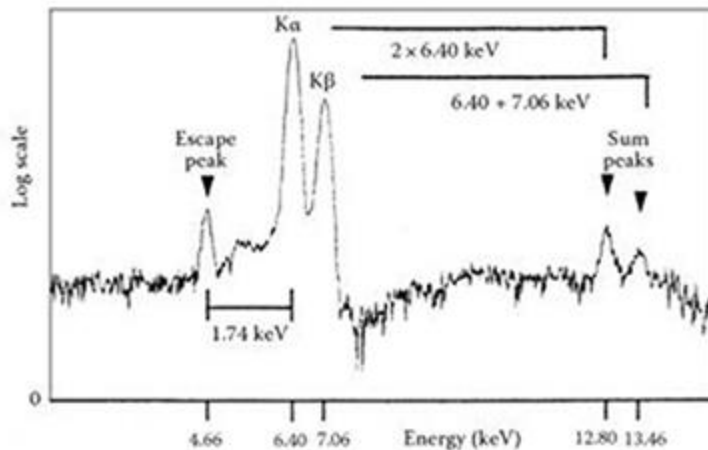
Escape peaks are an artifact of the detector generated by the photoelectric effect. When the energy of an incoming X-ray is greater than the absorption edge of the detector material, in ED-XRF this is typically silicon (Si) at 1.838 KeV, it can stimulate fluorescence of the detector itself. Some of this fluorescence is emitted as characteristic X-rays with an energy equal to the energy of the incoming or parent X-

ray minus the Kα energy of the detector material. For example, when copper (Cu) Kα X-rays, with an energy of 8.041 keV, reach the SDD of an ED-XRF they stimulate the Si in the detector to fluoresce, and the X-rays emitted as a result of this interaction have a characteristic energy of 6.301 keV (8.041 keV (Cu Kα) – 1.740 (Si Kα)). The resulting energy peak is called an escape peak in recognition of the fact that some of the parent X-ray energy is 'escaping' as energy characteristic of the detector material. In the example above, the peak generated at 6.301 keV is referred to as the Cu escape peak, because the parent energy was Cu (Figure 1.4).

The size of the escape peak is a function of the fluorescence quantum yield of both the parent and detector materials. Generally, the escape peak is smaller than the characteristic parental peak of an element because comparatively fewer X-rays excite the detector material than are counted overall. That said, escape peaks can be quite large and completely overwhelm or obscure the signal of characteristic K or L lines of elements with related energies. In our example, the Cu escape peak (6.301 keV) overlaps with the Kα line of iron (Fe) at 6.400 keV, complicating spectral deconvolution and quantification of Fe in samples with a high concentration of Cu.

Unlike Bremsstrahlung radiation, there is no way to ameliorate the spectral interference caused by escape peaks. However, many software packages are able to identify and correct for escape peak radiation.

Figure 1.5: Escape peak and sum peaks of Fe. There is an additional Fe sum peak at 14.12 keV (Fe Kβ + Fe Kβ), but



Sum peaks

Sum peaks are generated when the pulses generated by two high-intensity photons arrive at the detector simultaneously or at least so close in time that the signal processing unit is unable to differentiate them. As a result, the combined energy of the two pulses is recorded as a single peak; that is a single peak is generated at an energy that is the sum of the energy of the two pulses. Sum peaks are more commonly generated by major elements because they have higher count rates, making it more likely that two photons will be detected at the same time. For example, the iron emission spectrum in Figure 1.5 shows both the Fe escape peak at 4.66 keV (Fe Kα 6.400 – 1.740 (Si Kα) and two Fe sum peaks at 12.80 and 13.46 keV. The first sum peak at 12.80 results from the simultaneous detection of two Fe Kα photons, each with an energy of 6.400 keV; 6.400 keV * 2 = 12.80 keV. The second sum peak at 13.46 keV results from the simultaneous detection of an Fe Kα photon and an Fe Kβ photon; Fe Kα 6.400 keV + 7.06 keV Fe Kβ = 13.46 keV.

Some analytical software packages can correct for sum peaks as well as escape peaks, however most do not and so it is critical to evaluate your spectra as well as the elemental concentrations generated from them.

Spectral overlay

Spectral overlay, also referred to as spectral overlap and spectral interference, occurs when the characteristics energies of two or more elements are sufficiently close in energy so that the energy shoulders or peaks for each element, created by Bremsstrahlung radiation, overlap (Figure 1.6). The overlay radiation is recorded by the detector as part of the characteristic peak of higher energy, increasing or enhancing its intensity and reported elemental concentration. For example in Figure 1.6, some of the Ti Kβ radiation is reported as V, and some of the V Kβ radiation is reported as chromium (Cr), etc.

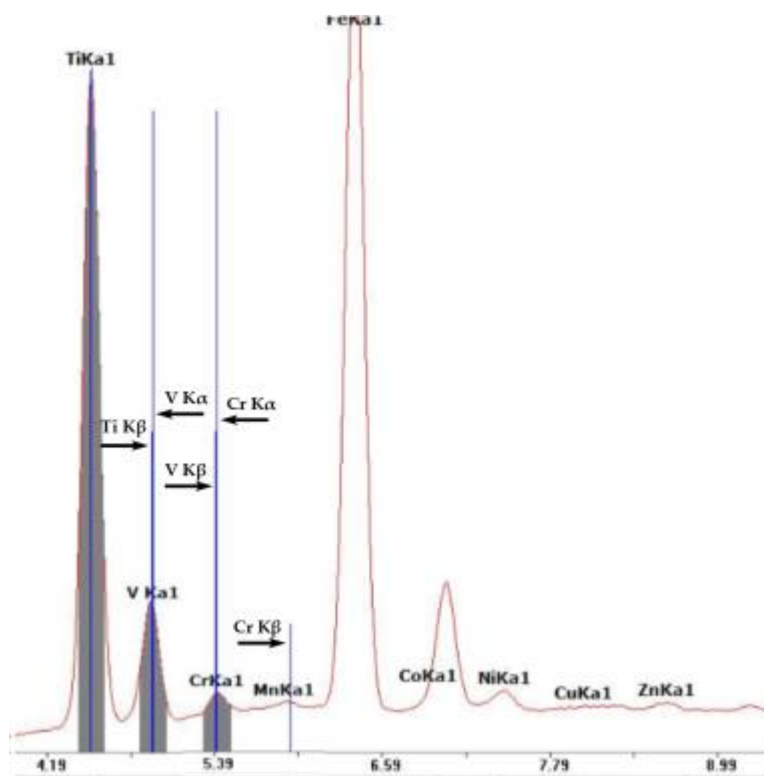


Figure 1.6: pXRF spectrum illustrating overlapping K and L

Overlay radiation effects have a critical impact on the accurate quantification of elemental concentrations, particularly low Z elements for which there are no measurable L lines ($Z < 30$). This is because spectral overlay can only be corrected for or ameliorated by spectral deconvolution in order to improve resolution and/or by calculating K line contribution/intensity from the L line intensity. Both of these corrections are typically performed by analytical software, which is not available for/on all pXRF spectrometers and is highly variable in terms of the accuracy of its algorithms.

Elements & Excitation

In acceleration physics, 'accelerating voltage' is used to describe the effective voltage surpassed by a charged particle along a defined, straight line trajectory. In EDX, accelerating voltage refers to the energy of the incident radiation stimulating the emission of radiation from the sample and it typically measured in kV. As we have seen, the accelerating voltage affects which elements can be excited and measured. An important consideration when selecting the accelerating voltage is whether the target's line energy or the Bremsstrahlung radiation is acting as the incident radiation. If the target lines are used as the incident radiation, then the accelerating voltage needs to be 1.5–2 times the absorption edge energy of the target material. In a Rh tube, a voltage in the 35–45 kV range is required, since the absorption edge of Rh K lines is 23.224 keV. If the Bremsstrahlung radiation is being used as the incident radiation then, generally speaking, the accelerating voltage needs to be 2 times the absorption edge of the highest energy element of interest being analyzed. For example, if we are interested in analyzing low Z element ($Z = 12$–25) using Bremsstrahlung radiation, the highest absorption edge energy of interest is 6.537 keV (Mn). The optimal accelerating voltage for this analysis, therefore, is approximately 13 kV.

Another consideration is that the higher the accelerating voltage, the more Bremsstrahlung radiation is generated and the higher the background. This means that while high energy X-rays are necessary to excite high Z elements of interest, the increased background radiation may make these elements difficult to detect at low concentrations. Therefore, it is important to coordinate accelerating voltage and filter selection.

Current is a measure of the particle flux or the flow rate of an electrical current. Optimal current setting for a given analysis depends upon the fluorescence efficiency of the matrix, the accelerating voltage, and how quickly the detector can integrate signal without flooding. The sample matrix, accelerating voltage and current are instrumental in the number of pulses being generated by the sample. If too many pulses reach the detector, too quickly, the system gets flooded and cannot accurately measure the number of pulses per energy level. This is a similar phenomenon to the generation of sum peaks.

The old school method for determining the optimal current setting is to ensure that the dead time approximates 50%. Dead time is the time it takes the detector to reset after each pulse in counted before it can record another pulse. Current and count rate are directly proportional, a general rule of thumb is that low accelerating voltages require high currents and high accelerating voltages require low currents. Even using modern instruments, running all analyses at the same or a standard deadtime, whether 10%, 30% or 50%, ensures there is one less variable to correct for between the calibration and sample spectra.

Most EDX manufacturers recommend accelerating voltage and current setting for each filter and/or range of elements of interest. With few exceptions, most pXRF spectrometers are pre-programed with automatic current settings for each accelerating voltage preset. Since most of these instruments also select the filter for the end user,

it is difficult to evaluate or manipulate these three variables to ensure they are optimally suited to a particular matrix/analysis.

Instrumentation

Energy Dispersive XRF

Portable X-ray fluorescence spectrometers (pXRF) are smaller, lighter, and more compact than benchtop or laboratory based energy-dispersive X-ray spectrometers (ED-XRF or EDX). Since pXRF spectrometers are relatively small and light weight, most weigh less than 2 kg, they are ideal for field applications where in situ bulk chemical screening is essential, such as environmental toxicity studies and industrial quality control applications. pXRF instruments are cheaper than benchtop instruments and require less technical expertise to operate and maintain, making them a more accessible instrument for many scientists. However, benchtop instruments can operate under full vacuum conditions and can accommodate larger detectors and higher voltage X-ray tubes. This means that even at their best, pXRF spectrometers are not a substitute for laboratory EDX bulk elemental analysis.

Since the operating principles and basic instrumentation is the same for pXRF and benchtop EDX spectrometers, they will be discussed here together.

The x-ray source for EDX spectrometers is generally an x-ray tube with a high Z target, often rhodium (Rh), enclosed in a pressurized, sealed glass capsule. When the filament, often tungsten (W), is heated, it emits high energy electrons. These electrons hit the target, which subsequently emits high energy x-rays (Figure 1.7). These x-rays are directed through an exit window, usually made of beryllium (Be), and out of the nose of the pXRF spectrometer where they interact with the sample.

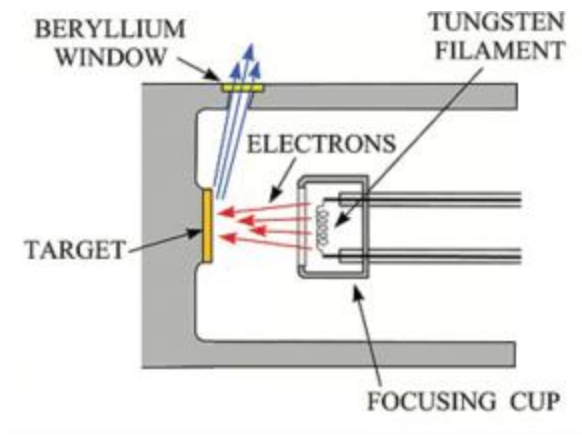
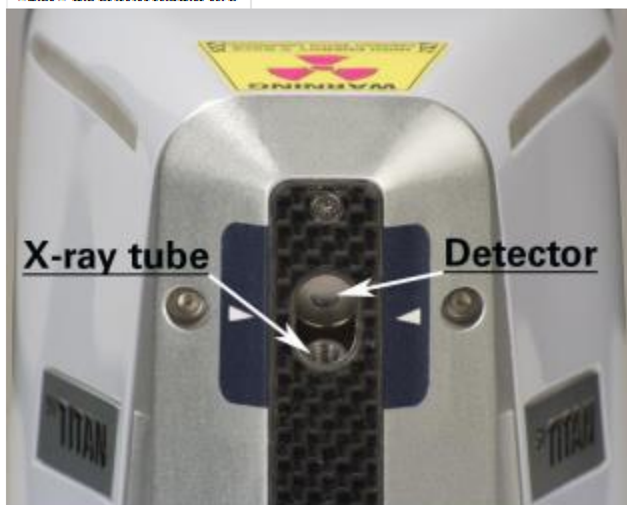


Figure 1.7: Schematic of x-ray generation within the glass bulb of

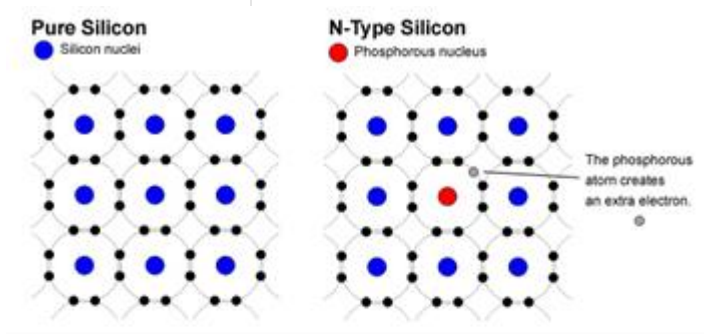
Radiation emitted by the sample as a result of the interactions between these x-rays and the sample is collected by the detector. Typically the opening to the detector is situated at an acute angle to the sample and the x-ray tube (Figure 1.8). Although several types of detectors have been used in portable EDX instruments over the years, most currently available pXRFs use silicon drift detectors (SDD), which have better resolution than PIN diode detectors and are more thermally stable.

Figure 1.8: Typical location and orientation of the x-ray tube exit window and detector entrance on a



In a SDD, the incident x-rays, those emitted by the sample, are directed into the detector core, which is composed of n-Silicon. n-Silicon or negative silicon is silicon ‘doped’ or chemically combined with phosphorus gas to create negatively charged crystals as a result of the ‘free’ or un-bonded electron (Figure 1.9). The incident x-rays interact with the n-silicon, exciting those ‘free’ electrons so that they have enough energy to break free of the silicon nuclei and leave behind electron hole pairs, that is a ‘space’ in the atomic shell of the silicon. The number of electrons ‘freed’ by the incident x-rays is directly proportional to the energy of the x-ray.

Figure 1.9: Conceptual illustration of the atomic structure of pure silicon and n-silicon. Note the free



Once the electrons are free, they move quickly toward the anode on the detector surface, which is held under the influence of an electric field. Once the electrons reach the anode, they generate an electric current signal or ‘pulse’, which is then counted by a digital signal processor. Spectra generated by EDX instruments are a record of pulses or counts for each discrete energy level (keV) measured (Figure 1.10). Once the signal or pulse has been counted, it is placed into energy ‘bins’ or channels by the multi-channel analyzer (MCA). The smaller the range of energies contained in each ‘bin’ or, put another way, the more channels energy can be allocated into, the better the instrument software is able to resolve spectral overlay interferences.

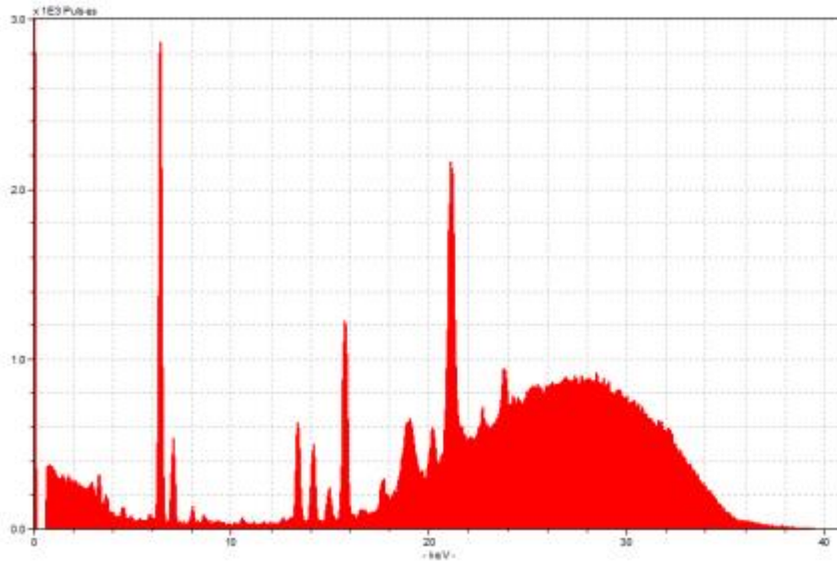


Figure 1.5: EDX spectrum generated
using a pXRF instrument. Note that the

In order for those pulse counts to be converted into elemental concentrations, the central processing unit or CPU references a database of counts for an elements energy lines at known or certified concentrations, commonly called a calibration, and by comparing the number of counts associated with that known concentration it calculates the elemental concentration of the counts generated by the sample using models and algorithms.

Wavelength Dispersive XRF

The photons emitted during X-ray fluorescence can be detected and quantified using wavelength or energy dispersive spectrometry (WD-XRF or ED-XRF). As their names suggest, WD-XRF measures the wavelength of the emitted photons whereas ED-XRF measures their energy. WD-XRF detects and measures the characteristic wavelengths of emitted photons by first separating them according to wavelength using crystal diffraction, so that only a single characteristic wavelength is detected and measured at a time. Because the detector records a single wavelength at a time, WD-XRF spectrometry is not susceptible to Bremsstrahlung radiation, escape peaks or spectral overlay. As a result, WD-XRF spectrometry has a

higher resolution than ED-XRF spectrometry, enabling it to detect and quantify low Z elements (Z = 11–25).

There are two types of WD-XRF spectrometry: sequential and simultaneous. Sequential WD-XRF spectrometry uses a single crystal at a time, oriented to detect a specific wavelength, in order to measure individual elements in sequence. Simultaneous WD-XRF spectrometry uses multiple detectors, each associated with a single crystal, oriented to a specific wavelength, to measure multiple elements at a time: each detector measuring a different, single wavelength/element. In both systems, crystals are rotated or exchanged to facilitate measurement of a broad range of elements.

Once the photons are detected, they are relayed, counted and reported according to the same procedure as EDX pulses described above.