

## **MSE 310 Lecture 10**

### **X-Ray Fluorescence (XRF)**

#### **What is X-Ray Fluorescence (XRF)**

X-ray Fluorescence (XRF) is an analytical technique that uses the interaction of x-rays with a material to determine its elemental composition. XRF is suitable for solids, liquids and powders, and in most circumstances is non-destructive. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays (“a fingerprint”) that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

X-rays form part of the electromagnetic spectrum, and are characterized by energies lying between ultra-violet and gamma radiation. Wavelengths are typically in the range 1nm to 1 pm.

#### **Interaction of X-rays with Matter**

Röntgen’s studies in the late nineteenth and early twentieth centuries quickly established the penetrating nature of X-rays, and the potential for medical imaging was soon realized. However, the interaction of X-rays with matter is more complex than simply ‘passing through’. On reaching a material, some of the x-rays will be absorbed, and some scattered – if neither process occurs, the X-rays will be transmitted through the material.

When absorption occurs, the X-rays interact with the material at the atomic level, and can cause subsequent fluorescence – it is this X-ray Fluorescence which forms

the basis of XRF spectroscopy. In addition to the absorption/fluorescence process, the X-rays can also be scattered from the material. This scattering can occur both with and without loss of energy, called Compton and Rayleigh scattering respectively.

The ratio of absorption/fluorescence, Compton and Rayleigh scatter and transmission depends on the sample thickness, density and composition, and the X-ray energy.

### **Fundamental Principles of X-Ray Fluorescence (XRF)**

The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behavior of atoms when they interact with radiation. When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample.

### **X-Ray Fluorescence (XRF) Instrumentation - How Does It Work?**

XRF spectroscopy is the technique of analyzing the fluorescent X-rays in order to gain information on the elemental composition of a particular material.

The key components of a typical XRF spectrometer are:

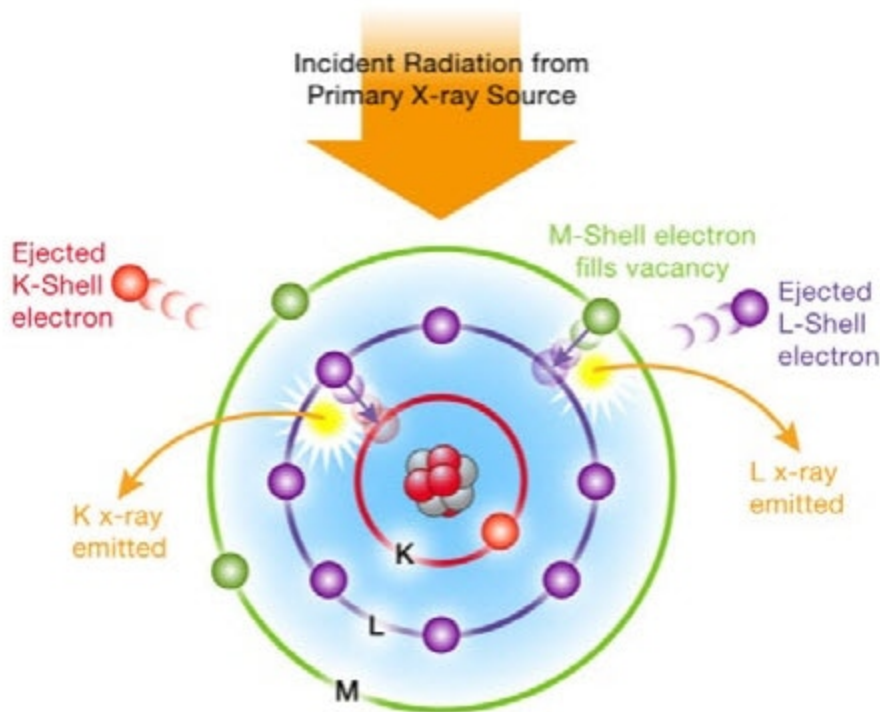
- Source of X-rays used to irradiate the sample.
- Sample.
- Detection of the emitted fluorescent X-rays.

The resulting XRF spectrum shows intensity of X-rays (usually in counts per second) as a function of energy (usually in eV)

The analysis of major and trace elements in geological materials by XRF is made possible by the behavior of atoms when they interact with X-radiation. An XRF spectrometer works because if a sample is illuminated by an intense X-ray beam, known as the incident beam, some of the energy is scattered, but some is also absorbed within the sample in a manner that depends on its chemistry. The incident X-ray beam is typically produced from a Rh target, although W, Mo, Cr and others can also be used, depending on the application.

### **The X-ray fluorescence process**

1. A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube.
2. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's K or L shell binding energy), an electron from one of the atom's inner orbital shells is dislodged.
3. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells.
4. The electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis



### Interpretation of XRF spectra

Most atoms have several electron orbitals (K shell, L shell, M shell, for example). When X-ray energy causes electrons to transfer in and out of these shell levels, XRF peaks with varying intensities are created and will be present in the spectrum, a graphical representation of X-ray intensity peaks as a function of energy peaks. The peak energy identifies the element, and the peak height/intensity is generally indicative of its concentration.

### X-ray Fluorescence - Multiple Transitions

Since most atoms comprise a number of electron orbitals (eg, K shell, L shell, M shell) a number of possible fluorescent transitions are possible.

For example, interaction of X-rays with an atom with K, L and M shells could result in a hole forming in the K shell, which is then filled by an electron from the L shell or from the M shell. In either case, these are termed K transitions. Alternatively, a hole could be formed in the L shell, subsequently filled by an electron from the M shell (termed an L transition).

Thus, for a single element, a number of XRF peaks are possible, and typically these will all be present in the spectrum, with varying intensities. They form a characteristic fingerprint for a specific element.

There are two types of XRF: Energy dispersive and Wavelength Dispersive XRF:

### **Energy Dispersive XRF**

An energy dispersive detection system directly measures the different energies of the emitted X-rays from the sample. By counting and plotting the relative numbers of X-rays at each energy an XRF spectrum is generated. In **energy-dispersive** spectrometers (EDX or EDS), the detector allows the determination of the energy of the photon when it is detected.

### **Wavelength Dispersive XRF**

A wavelength dispersive detection system physically separates the X-rays according to their wavelengths. The X-rays are directed to a crystal, which diffracts the X-rays in different directions according to their wavelengths (energies). In **wavelength dispersive** spectrometers (**WDX** or **WDS**), the photons are separated by **diffraction** on a single crystal before being detected.