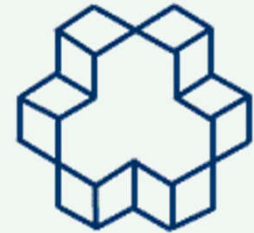




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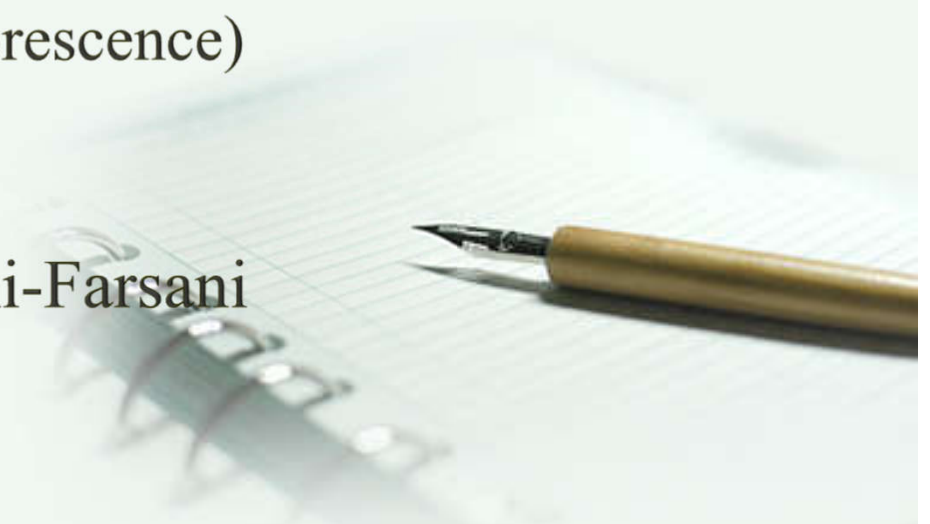
K. N. Toosi University of Technology  
Faculty of Materials Science and Engineering



## Materials Characterization Methods

Eleventh Session  
(X-Ray Fluorescence)

Reza Eslami-Farsani



# XRF



X-ray Fluorescence (XRF) is an analytical technique that uses the interaction of X-rays with a material to determine its elemental composition. The use of a primary X-ray beam to excite fluorescent radiation from the sample was first proposed by Glocker and Schreiber in 1928. XRF is suitable for solids, liquids and powders, and in most circumstances is non-destructive. XRF spectroscopy is an effective method for qualitative and quantitative analysis of material composition.



# XRF



When materials are exposed to short-wavelength X-rays or to gamma rays, ionization of their component atoms may take place. Ionization consists of the ejection of one or more electrons from the atom, and may occur if the atom is exposed to radiation with an energy greater than its ionization energy. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbitals of the atom. The removal of an electron in this way makes the electronic structure of the atom unstable, and electrons in higher orbitals "fall" into the lower orbital to fill the hole left behind.

# XRF



In the fall of electrons, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved. Thus, the material emits radiation, which has energy characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different energy (generally lower).





## Characteristic Radiation

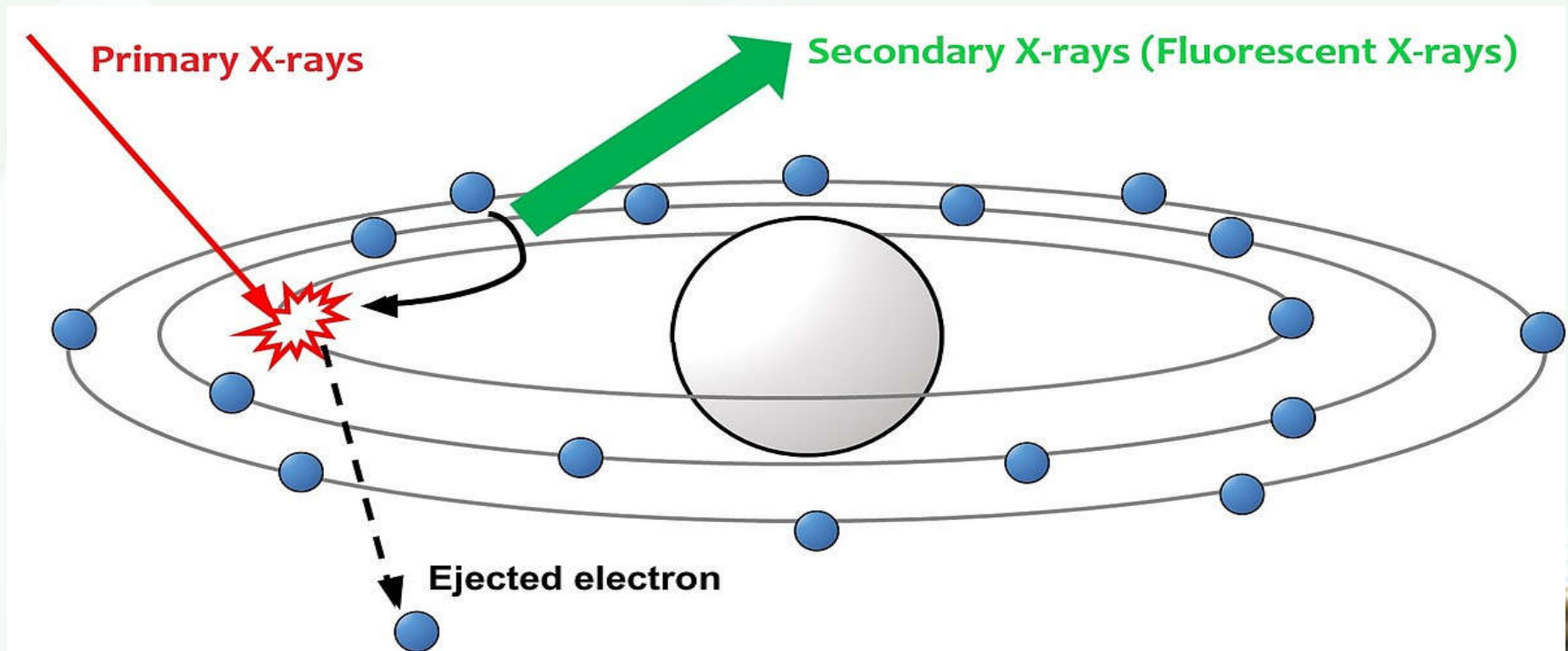
Each element has electronic orbitals of characteristic energy. Following removal of an inner electron by an energetic photon provided by a primary radiation source, an electron from an outer shell drops into its place. There are a limited number of ways in which this can happen, as shown in Figure 1. The main transitions are given names: an L→K transition is traditionally called  $K\alpha$ , an M→K transition is called  $K\beta$ , an M→L transition is called  $L\alpha$ , and so on.

Each of these transitions yields a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital.

# XRF



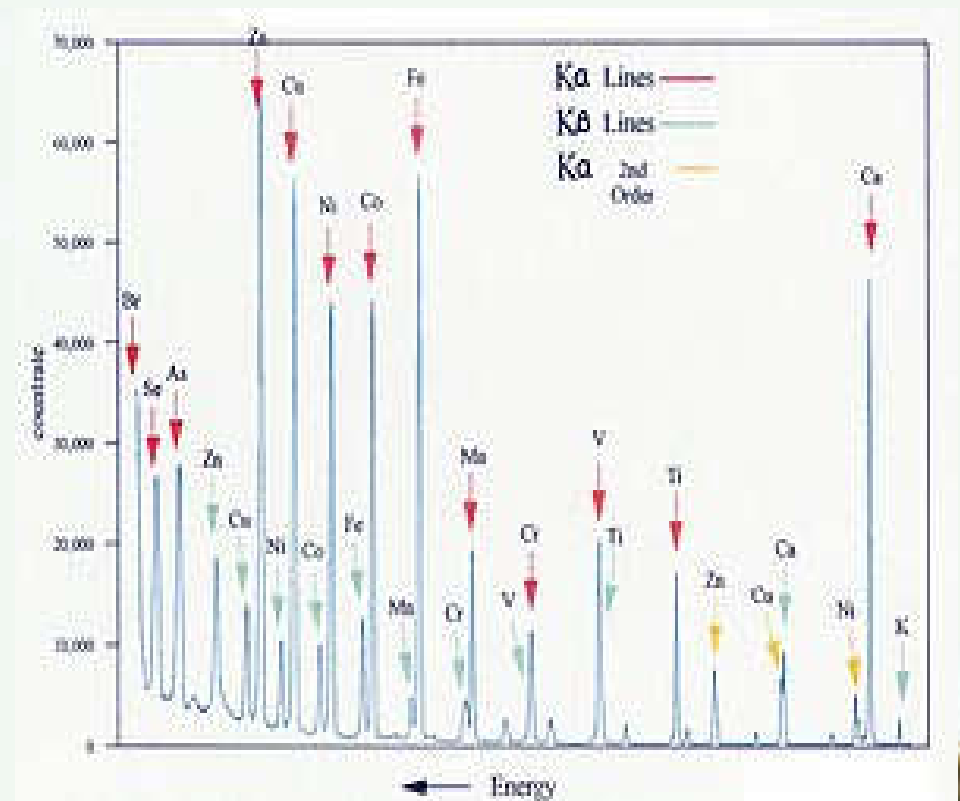
## Principle of Fluorescent X-Rays Emission



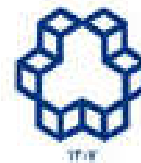


## Characteristic Radiation

The fluorescent radiation can be analyzed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelength-dispersive analysis). Once sorted, the intensity of each characteristic radiation is directly related to the amount of each element in the material.







## Primary Radiation Sources

In order to excite the atoms, a source of radiation is required, with sufficient energy to expel tightly held inner electrons. Conventional X-ray generators, based on electron bombardment of a heavy metal (i.e. tungsten or rhodium) target are most commonly used, because their output can readily be "tuned" for the application, and because higher power can be deployed relative to other techniques.

The continuous spectrum consists of **"bremsstrahlung"** radiation: radiation produced when high-energy electrons passing through the tube are progressively decelerated by the material of the tube anode (the "target").

X-ray generators in the range **20–60 kV** are used, which allow excitation of a broad range of atoms.



## Energy-Dispersive Analysis

- ✓ In energy-dispersive analysis, the fluorescent X-rays emitted by the material sample are directed into a solid-state detector which produces a "continuous" distribution of pulses, the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyzer (MCA) which produces an accumulating digital spectrum that can be processed to obtain analytical data.



## Wavelength-Dispersive Analysis

- ✓ In wavelength-dispersive analysis, the fluorescent X-rays emitted by the sample are directed into a diffraction grating-based monochromator. The diffraction grating used is usually a single crystal. By varying the angle of incidence and take-off on the crystal, a small X-ray wavelength range can be selected. The wavelength obtained is given by Bragg's law.





## Detection

- ✓ Proportional counters or various types of solid-state detectors (PIN diode, Si(Li), Ge(Li), Silicon Drift Detector) are used. They all share the same detection principle. An incoming X-ray photon ionizes a large number of detector atoms with the amount of charge produced being proportional to the energy of the incoming photon. The charge is then collected and the process repeats itself for the next photon. Detector speed is obviously critical, as all charge carriers measured have to come from the same photon to measure the photon energy correctly.



## Detection

- ✓ In wavelength-dispersive analysis, the single-wavelength radiation produced by the monochromator is passed into a photomultiplier (a detector similar to a Geiger counter) which counts individual photons as they pass through. The counter is a chamber containing a gas that is ionized by X-ray photons. A central electrode is charged with respect to the conducting chamber walls, and each photon triggers a pulse-like cascade of current across this field. The signal is amplified and transformed into an accumulating digital count. These counts are then processed to obtain analytical data.

# XRF



**X-ray Fluorescence (XRF) can be considered in a simple three step process occurring at the atomic level:**

1. Primary X-rays knock out an electron from one of the orbitals surrounding the nucleus within an atom of the material.
2. A hole is produced in the orbital, resulting in a high energy, unstable configuration for the atom.
3. To restore equilibrium, an electron from a higher energy, outer orbital falls into the hole. Since this is a lower energy position, the excess energy is emitted in the form of fluorescent X-rays.

# XRF



- ✓ The energy difference between the expelled and replacement electrons is characteristic of the element atom in which the fluorescence process is occurring. Thus, the energy of the emitted fluorescent X-ray is directly linked to a specific element being analyzed. It is this key feature which makes XRF such a fast analytical tool for elemental composition.

# XRF



- ✓ In general, the energy of the emitted X-rays for a particular element is independent of the chemistry of the material. For example, a calcium peak obtained from  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CaCl}_2$  will be in exactly the same spectral position for all three materials. در





## X-Ray Intensity

- ✓ The fluorescence process is inefficient, and the secondary radiation is much weaker than the primary beam. Furthermore, the secondary radiation from lighter elements is of relatively low energy (long wavelength) and has low penetrating power, and is severely attenuated if the beam passes through air for any distance. Because of this, for high-performance analysis, the path from tube to sample to detector is maintained under vacuum.



## Chemical Analysis

- ✓ Today, the method is used as a non-destructive analytical technique, and as a process control tool in many extractive and processing industries. In principle, the lightest element that can be analyzed is beryllium ( $Z=4$ ), but due to instrumental limitations and low X-ray yields for the light elements, it is often difficult to quantify elements lighter than sodium ( $Z=11$ ), unless background corrections and very comprehensive inter-element corrections are made.





## Energy Dispersive Spectrometry

- ✓ In energy-dispersive spectrometers (EDX or EDS), the detector allows the determination of the energy of the photon when it is detected. Detectors have been based on silicon semiconductors, in the form of lithium-drifted silicon crystals, or high-purity silicon wafers.



# XRF



## Usage

- ✓ EDX spectrometers are different from WDX spectrometers in that they are smaller, simpler in design and have fewer engineered parts, however the accuracy and resolution of EDX spectrometers are lower than for WDX. EDX spectrometers can also use miniature X-ray tubes or gamma sources, which makes them cheaper and allows miniaturization and portability.

# XRF



## Usage

- ✓ This type of instrument is commonly used for portable quality control screening applications, such as testing toys for lead content, sorting scrap metals, and measuring the lead content of residential paint. On the other hand, the low resolution and problems with low count rate and long dead-time makes them inferior for high-precision analysis. They are, however, very effective for high-speed, multi-elemental analysis.

# XRF



## Wavelength Dispersive XRF (WDXRF)

- ✓ 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).
- ✓ A detector is placed at a fixed position, and the crystal is rotated so that different wavelengths are picked up by the detector. The XRF spectrum is built up point by point. In this system, a number of crystal/detector units are used so that a range of elements can be detected simultaneously.



## Wavelength Dispersive XRF (WDXRF)

- ✓ The principal difference between ED and WDXRF techniques lies in the achievable energy (spectral) resolution. WDXRF systems can routinely provide working resolutions between 5-20 eV, depending on their set up, whereas EDXRF systems typically provide resolutions ranging from 150-300 eV or more, depending on the type of detector used.



# XRF



## Wavelength Dispersive XRF (WDXRF)

- ✓ The final difference between ED and WDXRF techniques lies in spectral acquisition. With an EDXRF system an entire spectrum is acquired virtually simultaneously, so that elements from across most of the periodic table can be detected within a few seconds. With WDXRF spectrum acquisition is either made in a point by point fashion (which is extremely time consuming), or else has a very limited number of simultaneous detectors (which is an expensive option).





## Wavelength Dispersive XRF (WDXRF)

- ✓ The higher resolution of WDXRF provides advantages in reduced spectral overlaps, so that complex samples can be more accurately characterized. In addition, with high resolution backgrounds are reduced, providing improved detection limits and sensitivity.





## Wavelength Dispersive XRF (WDXRF)

### Useful for

Separating EDS  
peak overlaps,  
for example Al-  
Br or Mo-S-Pb

Trace  
element  
identification

Elemental  
quantification  
using standards  
for increased  
accuracy

Increased  
sensitivity to  
light elements,  
such as Be and B

# XRF



## Wavelength Dispersive XRF (WDXRF)

### Application Include

Alloy  
composition

Defect  
identification

Mapping low  
atomic number  
second phases  
in steels and  
other alloys

Defects in  
electronics and  
electronics  
packaging



## Detectors

- ✓ Detectors used for wavelength dispersive spectrometry need to have high pulse processing speeds in order to cope with the very high photon count rates that can be obtained. In addition, they need sufficient energy resolution to allow filtering-out of background noise and spurious photons from the primary beam or from crystal fluorescence. There are four common types of detector:

Gas Flow  
Proportional Counters

Sealed Gas  
Detectors

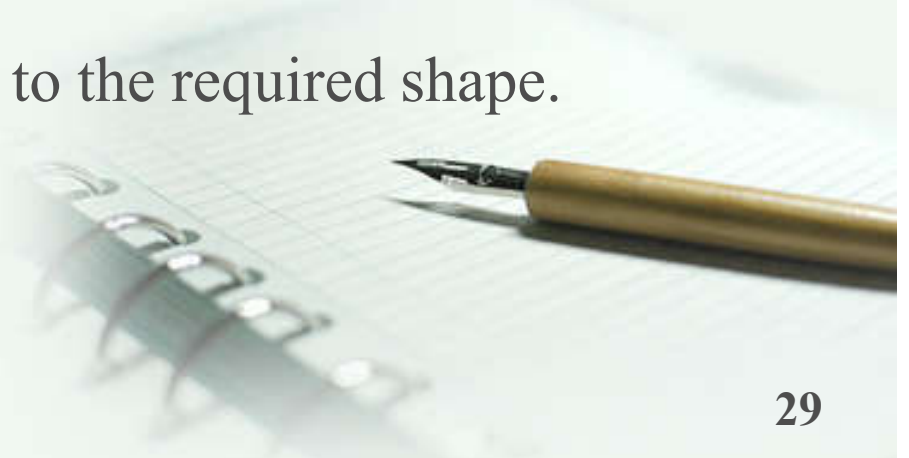
Scintillation  
Counters

Semiconductor  
Detectors



## Sample Preparation

- ✓ In order to keep the geometry of the tube-sample-detector assembly constant, the sample is normally prepared as a flat disc, typically of diameter **20–50 mm**. Ways of obtaining sample discs vary: metals may be machined to shape, minerals may be finely ground and pressed into a tablet, and glasses may be cast to the required shape.





## Sample Preparation

- ✓ A further reason for obtaining a flat sample surface is that the secondary X-rays from lighter elements often only emit from the top few micrometers of the sample. In order to further reduce the effect of surface irregularities, the sample is usually spun at **5-20 rpm**. It is necessary to ensure that the sample is sufficiently thick to absorb the entire primary beam. For higher-Z materials, a few millimeters thickness is adequate, but for a light-element matrix such as coal, a thickness of **30-40 mm** is needed.