MODULE II

ENERGY DISPERSIVE ANALYSIS OF X-RAYS (EDAX)

Energy dispersive analysis of X-rays (EDAX)

Also known as energy dispersive spectroscopy, and can be abbreviated as EDS, EDX, EDXS or XEDS sometimes it is termed energy dispersive X-ray microanalysis(EDXMA) or energy dispersive X-ray analysis (EDXA). It's an investigative method which is widely employed in elemental or chemical characterization of objects. The sample may be of any form such as solid thin films, solid powder, liquid sample or even a pellet etc.

Basic analysis principle of EDS-

A typical set up of the EDAX is similar with that of SEM set up. More specifically, EDAX is actually inbuilt within the SEM set up. The working of EDX is based on electron focusing same as in SEM. Electron beam excitation is employed in SEM and scanning transmission electron microscopes (STEM) whereas the X-ray beam excitation is present in X-ray fluorescence (XRF) spectrometers. A detector converts X-rays into voltage signals; which feed a pulse processor, to measure the signals and pass them to data analyzer for display and investigation. Si(Li) detector cooled at cryogenic temperatures by liquid nitrogen is often emploed; additionally, some modern systems come with silicon drift detectors (SDD) employing Peltier cooling systems.
To produce characteristic X-rays from an object, it is bombarded by either a highly energetic beam of charge carriers (electrons or protons) or X-rays. The atoms of the sample contain ground state (unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. An electron from an inner shell may be excited by an incident beam, thereby removing it from its shell and generating a hole where electron was present before excitation. This hole can be occupied by an electron of a higher-energy shell. The difference in energies of the higher- and lower- energy shells is emitted as an X-ray. Quantitative measurement of the energy and number of these X-rays can be done with energy-dispersive analysis of X-rays. Since the energy of these X-rays is characteristic feature of energy difference between two shells and atomic structure of discharging element, EDAX can be employed to identify the elemental composition of an object.

Advantage of EDS:broad range of elements, i.e., from Boron to Uranium can be examined synchronously.

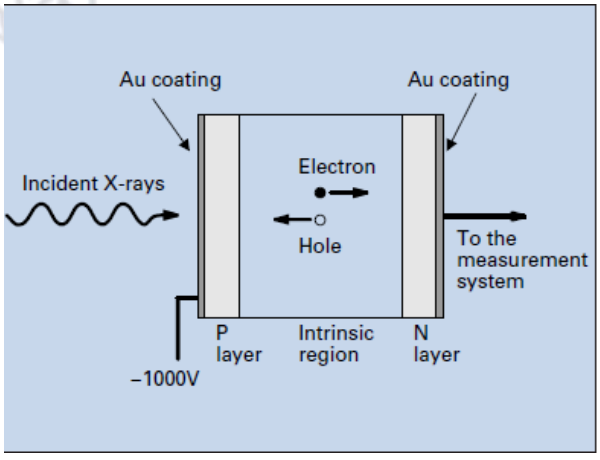

Figure 1 EDS semiconductor detector assembly.

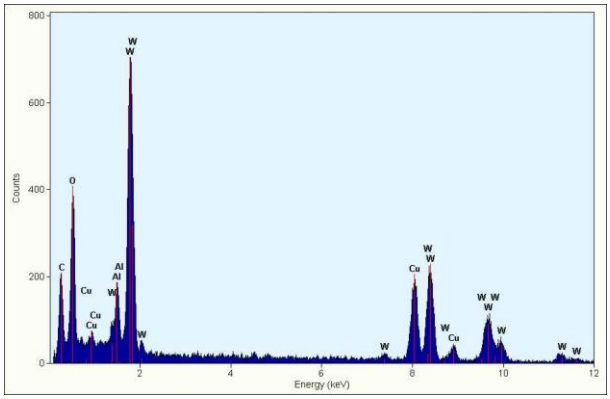

Figure 2 Example of EDS spectrum.

In **Figure 2**, X-axis represents the X-rays energy and the Y-axis depicts the X-ray counts. It is a valuable tool for Qualitative as well as Quantitative analysis. The above figure showing unique peak positions of various elements corresponds to the feasible transitions in its principal energy level.

Characteristic X-Rays Generation-

When a sample is irradiated with highly energetic beam of electrons then a characteristic X-ray is generated. Due to irradiation when an electron is excited from the inner shell of its parent atom, the vacant place is occupied by the higher energy electron from the outer shell and the energy difference between the two shells is emitted as an X-ray. The joule of energy liberatedin electrontransfer is dependentupon from which shell it is transferring to which shell. Emitted X-rays energy as well as number through specimen is obtainable by an energy dispersive spectrometer.

These emitted X-rays are known as characteristic X-rays because their energies (wavelength) are specific to the element from which it is emitted. Thus, this technique can be used for elemental analysis. When K-shell electrons are excited, they emit characteristic X-rays which are termed as “K Lines” and those emitted from L and M shells are called “L Lines” and “M Lines” respectively. When the element is heavy then its characteristics X-rays energies are also higher, therefore incident electrons of higher energy are required. Different types of X-rays are emitted when incident electrons strike the atomic nucleus and these are known as “continuous X-rays”, “white X-rays” and “background X-rays”.

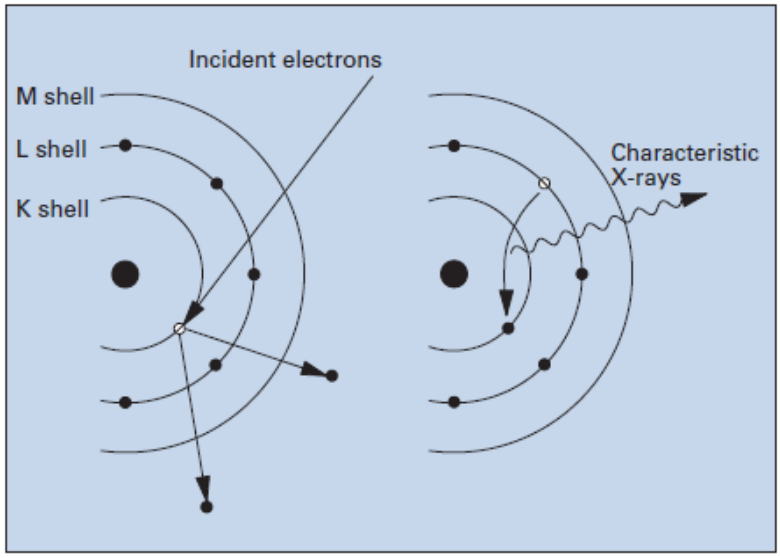

Figure 3 Principle of characteristic X-Rays Generation.

Sample's qualitative compositional data can be known from the respective peak positions with appropriate energies. The X−ray quantanumber measures the concentration of the elements, i.e., the height of thepeak, but there is no linear connection between quantum numbers and elemental concentration portions. The concentration calculation requires the net count rates and characteristic X-ray energy of a specimen is the marker of the specimen atomic number.

Instrumentation of the EDAX-

Figure 4shows the working arrangement of EDS with SEM. This instrument is mainly composed of four components:

- Electron beam source
- X−ray Detector
- Pulse Processor
- Analyzer

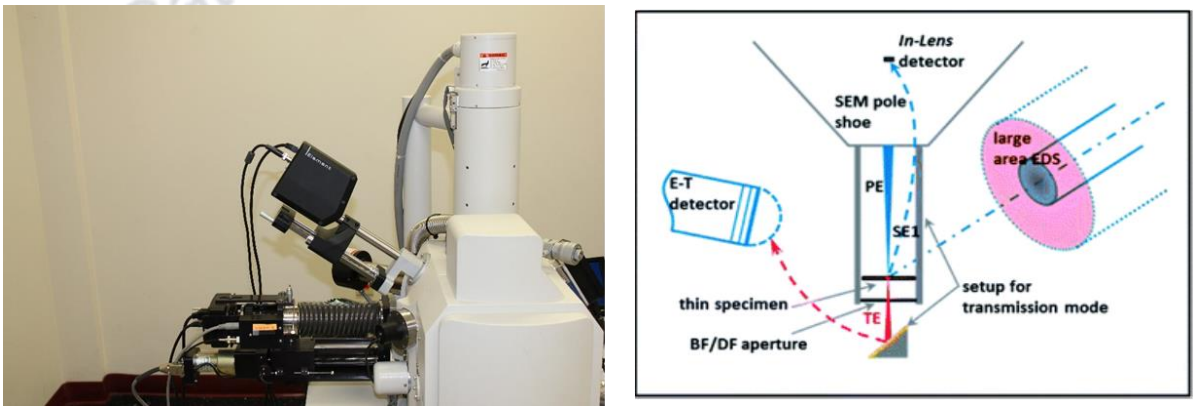

Figure 4 Working arrangement of EDAX (Energy dispersive analysis of X−rays)

Brief Description of Components-

- **Electron beam source:**As EDS is employed with the scanning electron microscope therefore the same electron gun (Field Emission) is used as the incident electron source and to focus the beam lenses are used along with aperture. The energy of the electron beam has to be carefully selected to overcome the compromise between the resolution requirements and the production efficiency of X-rays. The produced X-rays are detected bytwo crystal spectrometers.

- **X−ray Detector:** The X-rays counts (which is the abundance of emitted X-rays) versus X-rays energies are measured by the EDS detector. Detector, a solid state device which is based on lithium drifted silicon. As X−rays strike thesurface of the detector, a charge pulse is created.This charge pulse is directly proportional to theenergy of the incident X−ray.

Parts of Detector:

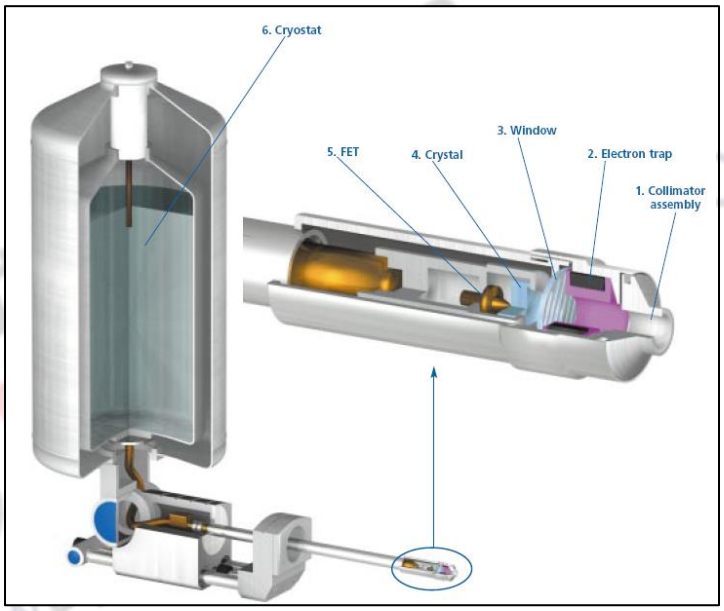

Figure 5Illustrative diagram of X-Ray Detector showing its components.

- **Collimator assembly:** The purpose of the collimator is to providerestrictiveaperture through which X-rays should pass in order tomake a way to detector. The collimator ensures that only X-rays from the region being excited by the beam of electron are detected**.**

- **Electron trap**: Background artefacts are created when electrons penetrate the detector. The purpose of the electron trap is to guarantee that only X-rays should enter the detector.It comprises a pair of permanent magnets to strongly deflect the passing electrons.

- **Window:** The purpose of the window is to provideisolationfrom the microscope chamber tomaintain vacuuminside the detector,at the same time being as transparent as possible forallowinglow energy X-rays. CharFaccomprises a thin window composed of polymer and transmits X-rays from elements which are heavier in comparison to Beryllium.

- **Crystal:**In detector crystal material used is silicon (Si), drifted with lithium (Li) [around 3mm thickness] for small levels of impurity compensation. When X-rays are incident on the crystal of detector then its energy gets absorbed by a series of ionizations within the semiconductor to generate electron-hole pairs. The absorption of every 3.76eV of X-ray radiation generates an electron-hole pair. Therefore, 1,966 electrons are generated by a Ni Kα X-ray photon (7,471 eV). The electrons promotedto the conduction band can freely move in the crystal lattice. Every excited electronleavesbehind a 'hole' in the valence band, which actsas a free (positive) charge carrier within the crystal. When the front and back face of the crystal are biased with high voltage, these electrons and holes areswept towards the opposite poles,therebygenerating a charge signal, whose size is proportional to the incident X-rayenergy.

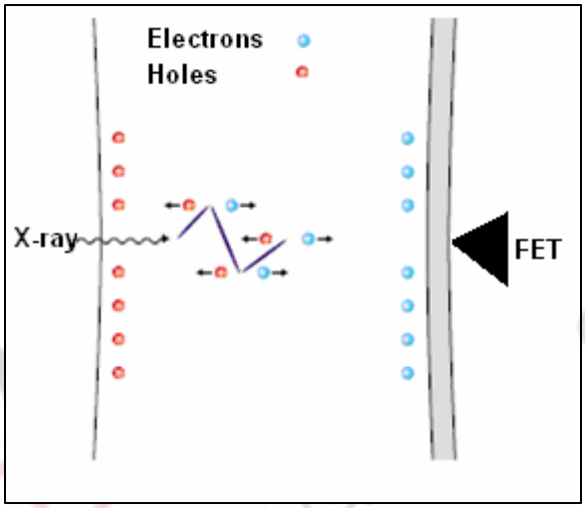

Figure 6 Diagrammatic illustration of X-ray interaction with crystal.

- **FET:** The FET (Field Effect Transistor)performs first stage amplification which measures the charge releasedwithin the crystal bythe incident X-ray and converts it to a voltage output. FET is nowadays integrated with the chips in order to greatly enhance the resolution along with the throughput which is achieved by reducing noise throughminimizing the capacitance between FET and anode. During operation, charge is accumulatedby each incident X-ray on the feedback capacitor,thereby producing sharp voltage steps. Thestep size of this voltage is proportional to theenergy of the incident X-ray. Restoration of the build-up charge is required periodically to avoid preamplifier saturation.

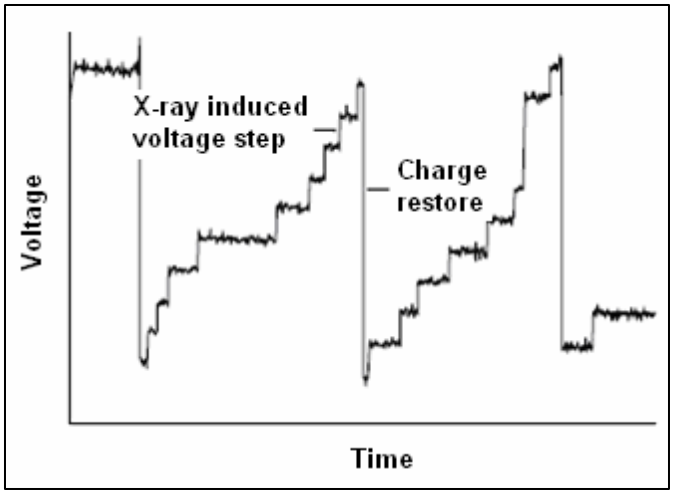

Figure 7 Graph showing Voltage step size.

- **Cryostat:**EDS detector is a self-enclosed vacuum system (called cryostat) with liq. N_2, or a cryogenic pumping. The crystal and FET are mounted on cold finger within cryostat to reduce the noise by cooling. The cooling is necessary as thedetector produces small charge pulses. At low voltages, theresolution of the detector depends upon the noise. The X-ray peaks are typically 2-10 eV wide (FWHM). However, due to noise, this width can increase by at leastan order of magnitude. The vacuum level should be maintained such that the condensation of molecules on crystal can be avoided.

  - **Pulse Processor:**Acharge−sensitive preamplifier is employed to convert the charge pulse to a voltage pulse**.**

  - **Analyzer:**Multi-channel analyseris used to sort pulses by voltage in the signals which are received by the analyser.The energy of the X-ray can be obtainedby measuring the voltage of the charge pulses. This energy is then sent for display and data processing. Here, data is displayed as histogram of intensity vs voltage.

Table 1: Features of EDS

Features	EDS
Measurable element range	B ~ U
Measurement method	Energy dispersive method with a Si (Li) semiconductor detector
Resolution	E≒130 ~ 140eV
Measuring speed	Fast
Multi-element simultaneous measurement	Possible
Damage/contamination of specimen	Little
Detection limit	1500 ~ 2000ppm
Detectable X-rays per current	Many

Qualitative Analysis-

X-rays generated EDS spectrum helps to carry out qualitative analysis to identify whatever elements are present in the sample when it is irradiated with high energy beam of electron. There are 3 methods of examination:

- **Point Analysis:** Spectrum is obtained from a point which is radiated with electron probe.
- **Line Analysis:** Spectrum is obtained from a specified line displaying one–dimensional desired elemental distribution.
- **Mapping:**Spectrum is obtained from a specified area displaying two-dimensional desired elemental distribution. It is often called as "Area Analysis".

X-Ray Mapping-

It is used to study particular elemental distribution. For analysis purpose, electron beam is scanned over a particular area and the related characteristics X-rays are acquired. If the peak to background ratio is very low then X-ray Map does not show the distribution of desired element, i.e., it shows the distribution of continuous X-rays. Sometimes X-Ray Map may not show the distribution of elements which are not of interest because characteristics X-Rays of elements of interest are close to those of not desired. It happens when energy difference between the desired element and undesired element is equal to the spectrometer energy resolution. It takes more time to acquire one X-ray picture as intensities of X-rays are less in comparison to that of secondary and backscattered electrons.The resolution of X-Ray Mapping is limited by "Area Analysis".**Figure 8** shows an example of X-Ray Mapping.

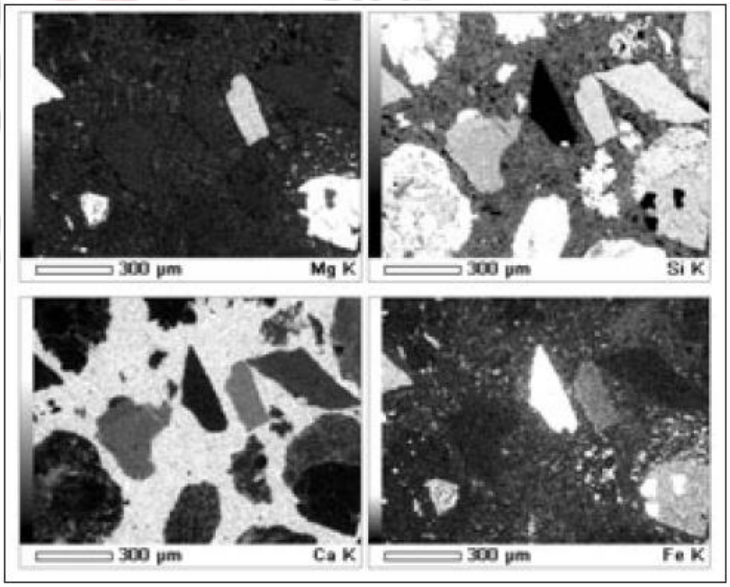

Figure 8Illustration of X-Ray Mapping of a concrete sample.

The procedure which quantitatively evaluates the points upon the sample gradually while scanning the electron beam is called "Quantitative mapping". Precise elemental distribution can be acquired using

“quantitative analysis” method even if Peak to Background ratio is low. It is a great advantage of this method.

Analysis Area-

Incident electrons when strike the specimen surface, get diffused and lose their energy bygenerating characteristic X-rays. This X-ray generation is spread over an area of around a few micrometersunderstandard operating condition. Thus, a larger area needs to be analyzed in order to examine theparticle of the order of few nm range in a SEM image. The analysis area can be decreased by reducing the accelerating voltage. However, accelerating voltage cannot be reduced below a certain level, since the generation of X-rays requires high accelerating voltages.Another strategy to reduce the analysis area is by reducing the thickness of the sample under investigation.

Quantitative Analysis-

As characteristic X-rays intensities are proportional to the particular element’s concentration, therefore quantitative analysis can be performed. The concentrations of unknown elements in a sample can be obtained by matching the intensities of characteristic X-ray of standard sample with that of the unknown sample. However, X-Ray generated in the sample may be either absorbed within thesample or excite the X-rays from other elements before being emitted in vacuum. Therefore, correction is required in this analysis method for which the following requirements are prerequisite:

- Flat specimen surface
- Electron probe should enter the samplein perpendicular direction
- Distribution of elements in the X-ray generation area should be uniform

There are always some appreciable errors in this analysis method because some specimens do not meettheserequirements.

Non-Conductive specimen Analysis-

For non-conducting sample, metal coating is required in order to prevent the charging but if requirement is to detect light element then it is suggested to use thin coating film, as heavy metal coating can block the X-ray emission through the sample because the X-ray intensities are less in comparison to secondary and backscattered electrons.

Analyzing sample with low incident accelerating voltage can cause some problems like:

- High excitation energy based characteristics X-rays cannot be detected
- Quantitative analysis accuracy is degraded
- While performing “line analysis” or “X-ray Mapping” – position shift in incident electron probe occurs

Suggestion for such problem: low vacuum SEM can be used to analyze non-conducting sample because residual gas molecules present in the sample chamber scatter the high energy electron beam thereby increasing the analysis area.

Review your learning:

1) EDS analysis is applicable for which element?

    a) Heavier element
    b) lighter element
    c) atomic number more than boron
    d) atomic number less than boron

2) What is the current range for Beam?

    a) 30 μA
    b) 160 μA
    c) 100 μA

3) Which electron carries highest energy?

    a) Back scattered electron
    b) Secondary electrons
    c) Auger electrons

4) In Energy dispersive system, the energy level and the number of pulses is related to which of the following?

    a) Amount of sample, element involved
    b) Element involved, concentration of the element
    c) Concentration of the element, element involved
    d) Number of atoms, amount of sample

5) Energy dispersive system uses which of the following detectors?

    a) Optical detector
    b) Semiconductor detector
    c) Thermistor
    d) Bolometer

Long question types:

1) Why is Copper used as standard for calibration in EDS detector?
2) Explain working principle of EDS?
3) Explain generation of characteristic X-Rays?
4) What is the preferential form of the specimen for electron probe x-ray microanalysis? How accuracy of elemental analysis degrades if the sample is rough or in the form of particles?
5) List three major types of artificial peaks that can appear on the EDS x-ray spectrum and briefly explain causes for their formation.

References

1) http://www.jeolusa.com/RESOURCES/Electron-Optics/Documents-Downloads/EntryId/598
2) Hafner, Bob. "Energy Dispersive Spectroscopy on the SEM: a primer." Citing internet sources http://www. charfac. umn. edu/instruments/eds_on_sem_primer. pdf (2006).
3) Reimer, L. (1985) Scanning Electron Microscopy, Springer-Verlag, Berlin .
4) Russ, J. C. (1984) Fundamentals of Energy Dispersive X-ray Analysis, Butterworths. London.
5) Scott, V. D. and Love, G. (1994) Quantitative Electron Probe Microanalysis, 2nd edn. Ellis Horwood, Chichester.