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**XRF OVERVIEW**

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**INTRODUCTION**




- X-Ray Fluorescence spectroscopy is a well-established analytical technique, its use and development spanning decades. It's a technique that can be utilized to quantify/Identify the chemical composition of a wide range of materials.
- Non-destructive or destructive techniques can be utilised dependent on the accuracy and precision of the analysis required. The technique is employed in many industries and applications WDXRF is widely used in the mining, metals and minerals analysis sectors.
- It is capable of elemental analysis of a wide range of materials including solids, powders, and liquids. As with any analysis the quality of the analytical data produced is reliant on the method, suitable equipment and the skills, expertise and experience of the analytical specialists performing the analysis.
- X-Ray Fluorescence Spectrometers can be divided into two main categories; Energy dispersive X-Ray Fluorescence and Wavelength dispersive X-Ray Fluorescence the main difference between the systems is in the detection systems. There are multiple manufacturers and suppliers, who offer a wide range of spectrometers and applications, across a range of industries and sectors.
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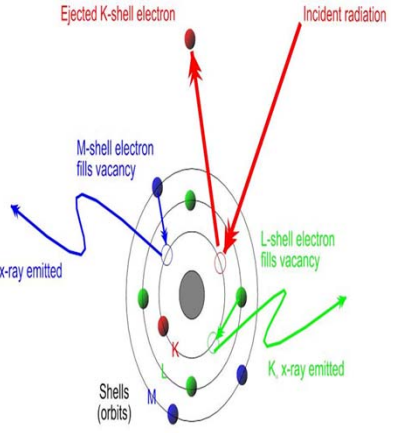
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- With regards to this booklet and the analysis of Molybdenum Concentrate we will be referring to Wavelength dispersive X-Ray Fluorescence.
- WD-XRF works as follows: a source X-ray strikes an inner shell electron. If at high enough energy (above absorption edge of element), it is ejected from the atom. This causes a hole in the orbital and instability within the atom as it wants to restore the original configuration. Higher energy electrons cascade to fill the vacancy, giving off characteristic fluorescent X-ray photons. Each atom has its own specific energy levels so this emitted radiation is characteristic to each specific element.



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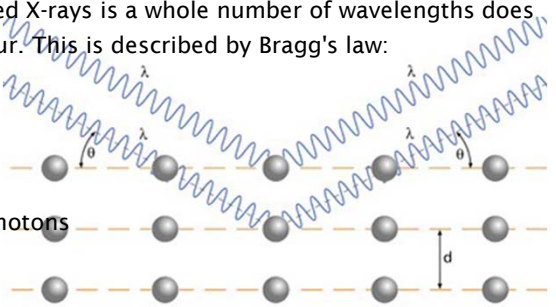
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In wavelength dispersive XRF (WDXRF) spectroscopy, X-rays are separated by means of a diffracting crystal and a detector that are placed in positions complying with Bragg's law. The placement is either by turning of a goniometer, measuring the energies one after the other (sequential) or in fixed positions, measuring the energies all at the same time (simultaneous). The layers of a crystal act like weak reflecting mirrors for X-rays. Only if the path difference of the reflected X-rays is a whole number of wavelengths does constructive interference occur. This is described by Bragg's law:

$$n\lambda = 2d\sin\theta$$

$\lambda$ : wavelength of the X-rays  
 $d$ : the spacing of the layers  
 $\theta$ : the incident angle of the photons



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- As with any analytical technique a good analysis starts with a well-prepared sample, the sample must be finely divided, homogeneous and representative of the entire material.
- Most XRF analysis requires the sample to be in oxidic form before fusion, this can be achieved before analysis utilising calcination and or by the addition of a pre-oxidation step during the fusion.
- Most Molybdenum methods will follow the steps below;
- A portion of the test sample is weighed accurately on an analytical balance
- The sample is combined with a suitable flux and fused at high temperature to destroy its mineralogical and particulate composition. Fusion also gives a defined density and particle size effects
- A wide variety of fluxes, fluxing reagents and internal standards can be utilised as required.

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- The mixture is fused in a crucible at high temperatures and cast onto a suitable receptacle (Crucibles are normally Pt/Au 95%/5%, casting dishes can be a range of materials dependant on temperature of the fusion)
- The resultant melt is now a glass bead which is presented to the XRF spectrometer.
- As the spectrometer is only analysing the surface layer of the bead the bead should be totally transparent and show no signs of devitrification.
- If bead is not transparent it could be due to the grain size of the sample, solubility of the sample in the flux, temperature of the fusion, temperature of the casting dish, requirement for the addition of a releasing agent.
- The glass bead should also be free from blemishes/scratches on the measurement surface. Glass beads must not be picked up using bare hands as even fingerprints and elements contained in oils and sweat can disturb the analysis.

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- XRF is a relative method and it is always necessary to calibrate using samples with known element concentrations. During measurement each element in the sample emits characteristic fluorescence x-ray lines which are read against the calibration
- Various calibration strategies can be implemented, but all should be prepared exactly the same as the sample being analysed
- Use of Certified Reference Materials(CRM's) with the same background matrix as the sample of interest. These are normally commercially available and analysed by several independent laboratories with the average concentrations and associated uncertainties given on a certificate. ( Very easy to set-up if enough of these standards can be obtained) NB most errors occur when the analysis instructions are the certificate are not followed ie the drying temperature/times
- SeRM Secondary standards made from high purity oxides 99.95-99.99% can be used to prepare multi-element or single element synthetic calibration standards. NB These must be dried or the hygroscopic moisture if any accounted for. The correct oxidation state of the reagents being used must also be ensured. Failure to do so will result in erroneous results.

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- A mixture of Certified reference materials and synthetic calibration standards can be used
- Calibration standards are run for the requested elements and a regression calculation is performed to construct the calibration curve. Normally the calibration is a function of intensity of the given element on the Y axis and the concentration on the X axis
- Where the matrix is not consistent matrix corrections need to be performed utilising empirical alphas, theoretical alphas or fundamental parameters. Your XRF method developer can give more information on which if any applies to your application.
- XRF is characterised by having very high long term reproducibility and stability, however small changes can occur over the long term due to degradation of the detector or tube. This means that the calibration is only valid for a set amount of time. This effect can be overcome by re-calibrating by analysing all calibration beads anew or using a drift correction. A drift correction monitor bead is run and the relative change in intensity from that bead is applied to the samples being analysed, thus saving time.

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