

Energy-dispersive X-ray fluorescence spectrometry (EDXRF)

EDXRF offers significant advantages for multi-element applications in the analysis of a wide range of inorganic materials for R&D, production and quality control/trouble shooting applications, despite the better detection limit levels achieved by some competing techniques. EDXRF systems are particularly appropriate for the analysis of geological, environmental, metallurgical, ceramic, and a wide range of other inorganic materials. The technique offers rapid, non-destructive analysis of test materials presented as solids, powders, particulates collected on filter substrates and liquids. Portable EDXRF systems provide the ability to take the spectrometer to the sample, thereby providing a powerful tool for field survey investigations. These portable systems do not offer a vacuum path between the sample and the analyser, thus limiting their use to elements from Ca upwards in the periodic table.

XRF is the technique of choice for many specific applications where simple dedicated instruments can meet regulatory requirements (*e.g.*, S in fuel; Na, Al, Si, and Ca in cement). In addition there are specialised applications, such as the analysis of liquors and brines, which are difficult to handle by competitive solution techniques with insufficient sensitivity for analytes such as halogens or other electronegative elements of interest.

Basic principles

X-ray fluorescence (XRF) is the phenomenon in which X-rays of energy characteristic of an element are emitted following excitation of the test material by energetic X-rays. X-ray fluorescence occurs when an atom is excited by a process of sufficient energy to eject an electron from an inner orbital shell. Electronic transitions then occur in the resultant unstable ionised atom, during which an electron from an outer orbital shell fills the vacancy left by the ejected electron. Loss of energy must occur to accompany this transition, usually by the emission of fluorescence (also called characteristic) X-radiation. When a test material is excited by X-rays, the resultant XRF spectrum contains discrete lines characteristic of the elements present. The intensity of these lines is proportional to the concentrations of individual elements in the matrix. XRF is capable of measuring the elemental concentrations of almost all the elements in the periodic table (by convention from Na to U) to detection limits that, under optimum conditions, fall below the mg kg^{-1} level.

XRF Instrumentation

Traditional wavelength dispersive X-ray fluorescence (WD) spectrometers comprise a high power X-ray tube (typically 3-4 kW power dissipation), a sample presentation device and an X-ray monochromator to measure the fluorescence spectrum. Rapid advances in semiconductor technology in the 1970's led to the development of the lithium-drifted silicon detector, a compact device capable of detecting X-ray spectra from the electronic charge deposited when X-rays interact with atoms of the Si crystal. Although Si(Li) detectors require liquid nitrogen cooling to provide acceptable resolution, the development of these devices provided new opportunities for the design of compact energy dispersive instrumentation based on low power X-ray tubes (*e.g.*, 300 W). These instruments were often originally used for less-demanding qualitative and semi quantitative applications but, with the development of improved software for spectrum analysis and matrix correction, they are now fully competitive with WD-XRF in many applications. Further refinements in detector technology have led to the introduction of alternative detector types including Si(PIN) detectors (which do not require cryogenic cooling), Si-drift detectors (expensive, but with a very high count rate capability), and various semiconductor materials of higher atomic number (Ge, CdZnTe, HgI₂) that can extend the detection efficiency beyond the 20 keV limit typical of Si detectors.

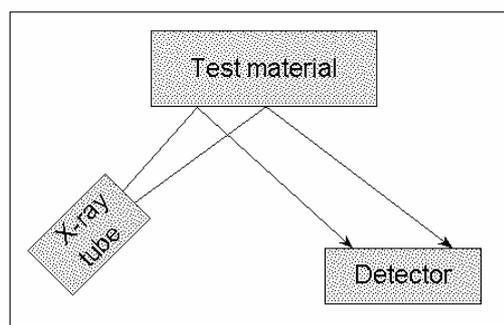


Figure 1 Direct tube excitation

Although ED detectors have the potential to detect the full spectrum of XRF energies, the analytical performance is usually optimised by modifying the excitation efficiency so that specific groups of elements, in particular energy ranges of the fluorescence spectrum, can be preferentially excited

and detected. These modifications include the use of primary beam metal foil filters (which modify the source spectrum reaching the sample to optimise detection characteristics) and a number of developments in excitation geometry. One of these advances is the secondary target excitation geometry in which a Cartesian optical path (Figure 2) is used, namely: tube - secondary target – test material - detector. With this geometry, a significant reduction in the continuum in the fluorescence spectrum is achieved, because the exciting radiation is polarised when scatter occurs through a right angle and cannot then be scattered a second time into the detector. The continuum is a component of the spectrum emitted from an X-ray tube that, when scattered off the test material, causes a general increase in background intensities and a consequent degradation in detection limits. If a low atomic number material is substituted as a secondary target [e.g., boron carbide, corundum or highly ordered pyrolytic graphite (HOPG)], the sample is then excited by the scattered tube spectrum (without additional characteristic lines from the secondary target). This arrangement leads to a further reduction in detected continuum referred to above and improved detection limits. A final refinement in the Cartesian arrangement is a configuration in which the sample is excited using the Bragg diffraction phenomenon. A few substrates are fortuitously capable of diffracting certain low energy characteristic lines from the X-ray tube (e.g., a Pd-L line) through a total diffraction angle of 90°. In this way, excitation of low atomic number elements by the tube L-line is enhanced because the efficiency of diffraction is significantly higher than scatter, whilst at the same time the benefit of background suppression associated with a polarised excitation source is retained. The advantages of all these polarised excitation geometries can only be achieved effectively using an ED detector.

A further technical issue that requires consideration is that like WDXRF, the EDXRF signal (fluorescence intensity) is not usually linearly proportional to concentration, because of small X-ray absorption and enhancement effects brought about by other elements present in the sample. These so-called 'matrix effects' can be overcome by the same correction procedures used in WDXRF spectrometry, where effective software and computer power are integrated into the instrument configuration.

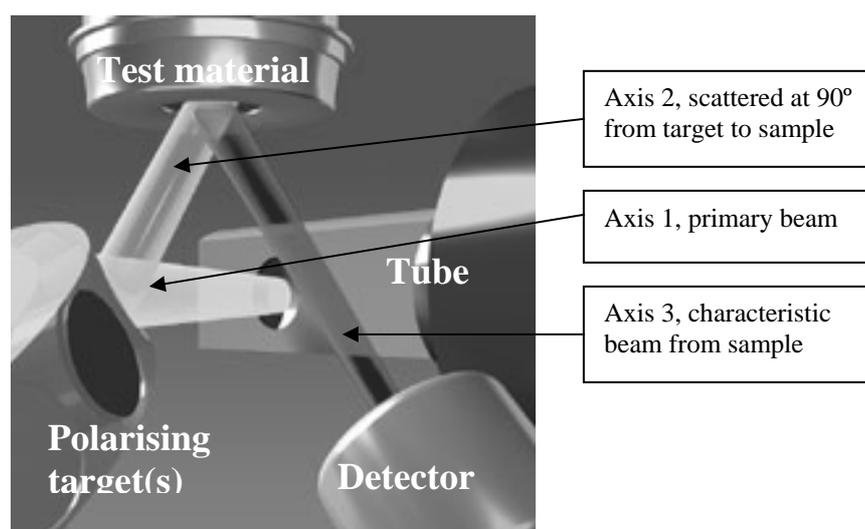
Further reading

Developments in XRF instrumentation, including applications, can be found in an annual review published each November in *Journal of Analytical Atomic Spectrometry*¹. Purchase of instrumentation requires critical evaluation of a wide range of instrumental features in relation to the intended application and these are comprehensively covered in a recent report of the Instrumental Criteria Subcommittee².

References

1. Potts P J, Ellis A T, Kregsammer P, Marshall J, Strelci C, West, M and Wobrauschek P. Atomic spectrometry update: X-ray fluorescence spectrometry. *J. Anal. At. Spectrom.* 2004, **19**, 1397-1419
2. Instrumental Criteria Subcommittee (2005). Evaluation of Analytical Instrumentation - Part XX: Instrumentation for Energy Dispersive X-ray fluorescence Spectrometry. (to be published on www.rsc.org/amc).

This Technical Brief was prepared for the Analytical Methods Committee by the Instrumental Criteria Subcommittee (Chairman Prof S Greenfield).



The Instrumental Criteria Subcommittee supports laboratory managers by providing reports with tabulated features of analytical instruments to help them when choosing between competing systems. The guidelines are intended as a checklist of instrument features to be considered, including service requirements and the relationship between user and manufacturer. The over-all object is to assist purchasers in obtaining the best instrument for their analytical requirements. The reports and this technical brief are also designed as teaching aids.

Figure 2 Cartesian excitation geometry (3 dimensional) polarised excitation

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