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Portable X-ray fluorescence analysis

Portable X-ray fluorescence analysers (PXRF) represent a category of hand-held instrumentation that is capable of *in situ* simultaneous multielement analysis outside the confines of a laboratory. The instrument is placed in contact with the sample to be analysed, and analytical results are immediately available for review by the operator. The technique can, therefore, be used to analyse large immovable artefacts such as museum samples that cannot be taken to the laboratory. Similar instrumentation, the "Beagle 2 PXRF", of mass 280 g, has been used for analysis of the rock and soil on the surface of Mars.

Some expertise is required to interpret results from PXRF analysers, especially when an *in situ* surface measurement is being used to represent the inaccessible bulk composition of a test item. However, PXRF provides unique opportunities that cannot be matched by conventional laboratory techniques. The immediate availability of analytical results allows the investigator to undertake a comprehensive assessment of a complex problem within a single visit to, for example, a contaminated field site.

PXRF in action

Many analytical techniques may be considered 'portable' in the sense that they can be operated in a mobile laboratory that is capable of being transported to a field site to provide an immediate laboratory analytical facility. However, the particular advantage of PXRF is the capability of the technique to undertake *in situ* analytical measurements where the PXRF analyser is taken to, and placed in direct contact with the test item. No sample preparation is involved, although care may need to be taken during selection of the test area. An analytical measurement is undertaken and the result is immediately available to the operator. The operator may then decide what to analyse next, giving rise to the concept of an interactive-sampling-and-analysis capability that laboratory-based techniques are incapable of delivering. PXRF is normally used as a surface analytical technique, as in applications such as alloy sorting.

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Principle of operation and instrumentation

Portable X-ray fluorescence analysers operate on a principle similar to laboratory-based energy dispersive X-ray fluorescence analysers. They have recently benefited from developments in the miniaturisation of components to make them compact, light weight, hand held devices. The principle of operation is that X-rays from an excitation source interact with the test surface causing the emission of secondary fluorescence X-rays that have energies characteristic of the atoms of the excited material. Two configurations for radioactive isotope excitation sources (^{55}Fe, ^{109}Cd and ^{241}Am) used in some instruments as shown in Figure 1 (A and B). Miniature X-ray tubes dissipating a few watts are now widely used (Figure 1(C)).

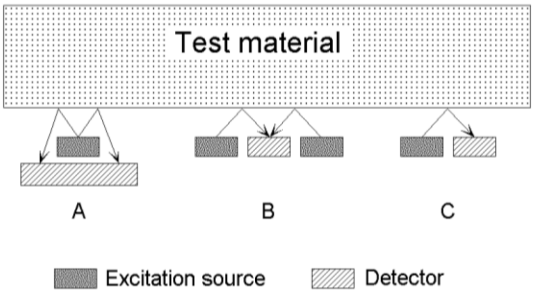

Figure 1. Excitation/detection configurations for portable X-ray fluorescence spectrometers, with radioactive isotope excitation (A and B) and miniature x-ray tube excitation (C).

Fluorescence X-rays are detected using an energy dispersive system, which in modern instruments is usually either a silicon PIN device or a silicon drift detector (SDD). The former devices are relatively cheap and robust. The more expensive SDD devices allow a more sophisticated design that provides a much higher resolution with little degradation in spectrum quality (*e.g.*, count rate-dependent peak broadening or drift). As in conventional XRF, the intensity of fluorescence X-rays is affected by inter-element ('matrix') effects, normally manifested by an absorption or enhancement that is dependent on the matrix composition. However, modern PXRF analysers benefit from miniaturisation and advances in computing power. These allow the use of sophisticated software that compensates for background variation and line overlap and provides a comprehensive matrix correction. Quantitative analytical results can be obtained, either while an analysis is being undertaken or immediately after the end of a count, which typically needs less than 200 s.

Applications

Some typical applications of PXRF analysers are as follows.

- *Contaminated land*. Monitoring spatial distribution of elements, *e.g.*, Pb, As.
- *Workplace monitoring*. Generating health and safety information.
- *Particulates on filters*. Monitoring hazards in air.
- *Surfaces and coatings*. Determining Pb in paint, and coating thickness.
- *Metal and alloy sorting*. Enhancing value during recycling.
- *Architectural buildings and monuments*. Monitoring deterioration from atmospheric pollution.
- *Geochemical prospecting*. Locating new economic ore deposits.
- *Archaeological investigations*. Provenancing of lithic artefacts.
- *Works of art and cultural heritage*. Evaluating restoration techniques and detecting forgeries.
- *Extra-terrestrial exploration*. Characterising planetary surfaces.

Analytical performance

In theory the PXRF technique is capable of exciting all but the low atomic number elements, depending on the efficiency of the excitation source. Because measurements are made in air, the absorption of low energy fluorescence X-rays makes the determination of the low atomic number elements problematic (those below potassium in the periodic table). Some instruments incorporate a helium flush or miniature vacuum system, which extends detection capability down to silicon. Instruments with SDD detectors now enable users to measure Al, Mg, and Si in air.

Detection limits depend on the excitation source chosen for an application, but for some elements (and matrices) they extend down to the low $\mu g\ g^{-1}$ range. These elements can be measured from the K-line series with absorption edges just below the energy of the emissions from the excitation source (that is, usually elements lighter than molybdenum). Elements of higher atomic number can also be determined but at a lower sensitivity, as the L-series lines must be used for detection.

Interpretation of results

The mass of test material analysed depends on the energy of the characteristic fluorescent X-ray and its associated critical penetration depth within the sample. As a guide, for the lower atomic number elements, critical penetration depths are in the μm range, but for higher atomic elements determined from the K-line, 1-2 mm or more is the relevant figure. The best estimate of analysed mass is, therefore, in the mg to g range.

Some expertise is required in the interpretation of the results obtained from PXRF analysers, especially when surface measurements are used to estimate the bulk composition of an artefact or where PXRF data are to be compared with results obtained by conventional sampling and laboratory analysis. In these circumstances, surface alteration effects (*e.g.*, patinas, contamination or weathering) must be taken into account. Furthermore, when instruments are used for applications such as the analysis of soil, the presence of moisture that influences *in situ* PXRF results must be considered in any comparisons with the results of the laboratory analysis of dried samples.

Further Reading

The purchase of instrumentation requires a critical evaluation of a wide range of instrumental features in relation to the intended application, which are comprehensively evaluated in a recent report of the Instrumental Criteria SubCommittee[1]. Further information on analytical capabilities for *in situ* analysis may be elsewhere[2].

References

1. *Accred Qual Assur*, 2008, **13**, 453-464.
2. *Portable X-ray fluorescence spectrometry*, P J Potts and M West (eds), RSC Publishing, Cambridge, 2008. ISBN 978-0-85404-552-5

This Technical Brief was prepared for the Analytical Methods Committee by the Instrumental Criteria Subcommittee (Chair: Prof S. Greenfield) and drafted by P.J .Potts and M. West.

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