

X-ray fluorescence spectrometry: a fast and versatile technique for the analysis of geological samples

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X-ray fluorescence (XRF) spectrometry provides a non-destructive analytical method capable of analysing solids from a few parts per million to near 100% for a wide range of elements (Figure 1). This versatile technique is ideally suited for the analysis of rocks, soils, dust, contaminated land samples, mineral concentrates and products, archaeological artefacts, synthetic materials and metals. The non-destructive nature of the technique allows long term storage of samples, which can

then be re-analysed any number of times for additional elements as necessary. This approach therefore, avoids problems of re-sampling and digestion of separate aliquots.

Since the 1960s XRF spectrometers have been fully automated and today's state-of-the-art machines are compact, self-contained analytical units, capable of running unattended for several days, with the flexibility of rapid transitions from one analytical programme to

another. One of the more recent designs has been the use of end window X-ray tubes, which reduces the coupling distance between the sample and the tube, and this together with upgraded detection systems enhances the sensitivity of the spectrometers.

Sample preparation

Sample preparation is an important procedure in XRF analysis, and this

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Figure 1. Periodic table showing some of the elements which can be determined by XRF spectrometry—light green background. At very low atomic numbers analysis is not possible because the X-rays are absorbed before they can be measured. As the atomic number increases, generally lower detection limits can be achieved, often to the sub-ppm level. Analysis of some of the non-highlighted elements, such as Au, Ru and some of the other Rare Earth elements may be possible in unusual samples where the concentrations are above the normal naturally occurring levels in geological samples. An example would be the analysis of Rare Earth ores, a task ideally suited to XRF spectrometry.

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starts with the initial sample selection and subsequent preparation (i.e. crushing and milling of consolidated materials), with the final product being a fine-grained (ideally $<63\mu\text{m}$) powder. The ideal sample to be presented to the X-ray beam is flat, homogeneous and infinitely thick with respect to the X-rays. It should be capable of withstanding a vacuum, though this constraint can easily be overcome by the use of a helium atmosphere in the spectrometer. There are many methods for preparing bulk materials; two basic types are most suitable for the types of samples under discussion here.

- Fused beads, where the sample is mixed with a suitable flux, which is then fused into a glass and either cast or pressed into a disc.
- Pressed powder pellets, where sample powder, with or without a binding agent, is compressed to produce a solid tablet of powder.

Provided the correct flux is used, the fusion method provides the simplest method for obtaining an ideal sample. The pressed powder method can also provide a suitable sample, but there can be concerns about homogeneity. In general terms this can mean problems concerning particle size effects and chemical/mineralogical homogeneity. For most XRF applications the fusion bead method provides a superior solution, with heterogeneity problems minimised, and with the right matrix corrections, consistent and reliable results are easily achieved. However, in certain situations (e.g. mineral exploration) a number of issues arise whereby the pressed powder pellet method is to be preferred. Some of these issues include:

- Preparation of fusion beads is relatively slow compared to pellet making and the equipment required is more expensive. Fusion is normally undertaken in Pt–Au crucibles, although cheaper alternatives can be used.
- Depending on the analytical problem (i.e. sample composition), it may be necessary to vary the flux mixes. Consequently, where large numbers of samples are to be analysed this may not produce an economic solution.

- Damage can occur to crucibles where the sample types are unknown (e.g. sulphide rich samples can corrode Pt–Au crucibles), but where knowledge of the samples is provided this can be avoided.

- Production of fusion beads inevitably involves the dilution of the original sample, with a corresponding decrease in detection limits or, in some cases to achieve the desirable limits, counting times may have to be significantly increased.

In a commercial setting all of these factors can significantly increase the cost through increased capital costs and increased analytical times. Given these factors, it may be desirable on a job-by-job basis to select pressed powder pellets as the analytical medium, since this may affect the cost for a commercial contract and/or yield lower limits of detection for selected trace elements.

There are numerous methodologies and recipes for preparing pressed powder pellets. Many materials, such as coals, many soils and shales, waxes and some synthetic materials will form stable pellets without the addition of a binder. For routine preparation, however, a binder is necessary to produce a coherent and semi-resistant pellet, which can be handled during loading and XRF analysis. Commonly employed binders include ethyl and methyl cellulose, starch, Moviol (Hoechst Inc.) and polyvinyl binders. In some applications large volumes of binders have been used which act as diluents. Again this dilution procedure has the effect of raising the lower limit of detection, does not diminish matrix effects and does not remove grain size effects. In the case of low-level trace element work this approach is not advised.

Operating conditions

A prerequisite in any analytical scheme is the use of the correct operating conditions. For the vast amount of geochemical work most elements are known to fall within certain ranges and these are considered when selecting operating conditions. In general one set of operating conditions is sufficient for each element, designed initially to avoid

spectral overlaps (on peaks and backgrounds) and to optimise the count rate. In general it is preferable to count for a longer period on a well-separated peak than to introduce a correction for overlapping peaks where the choice exists.

An excellent example of this is illustrated by considering the analysis of zirconium. Many analysts have chosen to analyse Zr using its K_{α} line, using the LiF_{220} crystal. This is the strongest Zr peak, but it does suffer from a Sr ($\text{SrK}_{\beta 1}$) overlap occurring on the short wavelength side. If the Sr concentration is very low ($<50\text{ppm}$), the effect on the Zr peak is negligible, but once Sr attains a few hundred ppm concentration some correction is required. An alternative method avoiding the Sr overlap is to select the $\text{ZrK}_{\beta 1}$ line, which is approximately 15% of the intensity of the K_{α} line, but is free of the peak overlap problem, except where high Mo ($>50\text{ppm}$) occurs. Although in the case of many earth and environmental samples, Mo concentrations are routinely low ($<10\text{ppm}$), whereas Sr concentrations are more variable and often elevated ($>100\text{ppm}$). However, to compensate for the 15% intensity it is necessary to substantially increase the counting time to achieve the same levels of detection.

Quantitative analysis

To a first approximation, the intensity of any given line is proportional to concentration, but modified by a combination of absorption and enhancement effects, which are, in turn, a function of the composition of the sample and the primary spectrum from the X-ray tube. Quantitative analysis involves choosing a calibration strategy that can accommodate or attempt to eliminate these effects, and most methods attempt to achieve a simple linear relationship between the measured spectral line intensity and concentration. There is a very wide range of methods available,¹ two of which are particularly suitable for the analysis of most natural materials.

The (major) elements (Si, Al, Ti, Fe, Mg, Mn, Ca, Na, K, P etc.) that make up the bulk of a rock are normally determined using fused beads; this produces homogeneous samples for analysis, and

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a significant dilution of the original rock powder which, in turn, minimises the absorption and enhancement effects. This is most effective when fusion is achieved together with a heavy absorber (usually La_2O_3) as part of the fusion mix.² Calibration is achieved either by simple straight-line methods, or by multi-element measurement approaches. The software that comes with modern instruments all contain algorithms for the latter, though there are many variations, some of which are not suitable for wide ranges in composition. The most “all embracing” model published in 1984 by Rousseau³ is not always supported.

Minor and trace elements are generally determined using pressed powder pellets to minimise the dilution of the sample. With only a few exceptions, the spectral lines used for trace element analysis in most natural samples lie at shorter (higher energy) wavelengths than those of the associated major elements, and the dominant problem to be overcome is that of absorption. The simplest, and probably the most effective, approach to correcting for absorption makes use of the fact that the intensity of the background, and of the coherent and incoherent scattered lines of the anode element, vary systematically with the mass absorption of the sample matrix. Measurement

of this scattered radiation, usually that of the Compton K_{α} for most anodes, thus provides an absorption correction factor. There are several ways in which scatter corrections can be applied; most involve ratioing the scatter measurement on the sample to the same measurement on a standard at a wavelength shorter than the lines of the elements to be measured.⁴ This method works well, though problems can arise with higher trace element concentrations (1000s ppm) when the ratio relationship may break down with increasing wavelength.

While these methods work well with most rocks and related materials a different approach might be needed for ores or heavily mineralised samples, and for those unusual “one-off” samples. Internal standard and double dilution techniques¹ are recommended for these.

Sensitivity and precision

With optimisation of analytical conditions and stable run conditions, both the lower limits of detection and analytical precision at all levels are a function of counting time and statistics for a particular element and sample.

As an illustration of how long count times can vastly improve precision, we present some previously published work.⁵ The requirement of highly precise

determinations of U, Th and K are now important in a variety of geological applications (e.g. heat flow studies, calibration of spectral gamma wireline logging tools). The calibration of wireline spectral gamma tools is very important, since these tools are often used to measure near continuous elemental profiles in a borehole. The U, Th and K concentrations derived from sedimentary successions can then be used as proxies for climate change signals. The long count operating conditions for the analysis of U, Th and K are presented in Table 1. The measurement for U consists of the U (Up) and Rb (Rbp) peaks and three background positions: (a) b1 immediately to the low-angle side of Up, (b) b2 in the trough between Up and Rbp and (c) b3 at the high angle side of Rbp. Of these, the positioning of b2 is critical, since it is placed to encounter some enhancement from the tail of the RbK_{α} peak, whilst avoiding the UL_{α} peak (Figure 2), further details of which can be found in Reference 5. In measuring Th, a similar method is used as for U,⁵ but the absence of any significant overlaps diminishes the need for interference corrections. An exception is for samples containing elevated Bi (>50 ppm), but since Bi concentrations (<5 ppm) are low in sedimentary rocks this can be ignored. Analysis of K is far easier since this element is abundant in many sedimentary rocks and therefore its peak/background ratio is >100, which reduces any slope in the background. Calibration of each element involves: (i) repeating the measurement

Table 1. Operating conditions and settings employed for high precision U, Th and K analysis.

Scint.: Scintillation; GFPC: gas flow proportional counter; $K_{\alpha(c)}$: K_{α} Compton scatter line. Peak and background angles are given in degrees 2θ .

Element	Analytical line	Wavelength (Å)	Collimator (μm)	Detector	Crystal	kV	mA
Rb	K_{α}	0.927	150	Scint.	LiF_{200}	75	40
U	$L_{\alpha 1}$	0.911	150	Scint.	LiF_{200}	75	40
Th	$L_{\alpha 1}$	0.956	150	Scint.	LiF_{220}	75	40
K	K_{α}	3.744	400	GFPC	PE	40	70
Rh	$K_{\alpha(c)}$	0.614	150	Scint.	LiF_{200}	60	40

Element	Peak	Time (s)	High-angle background	Time (s)	Low-angle background	Time (s)
Rb	26.61	40	27.15	20	25.90	400
U	26.16	800	26.30	400	25.90	400
Th	39.25	800	40.95	400	38.65	400
K	50.65	16	—	—	49.15	8
Rh	18.395	10	—	—	—	—

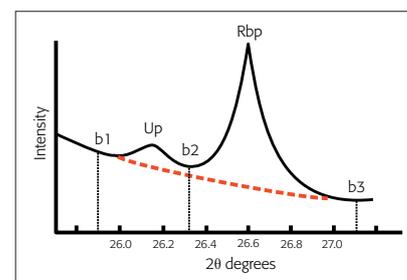


Figure 2. Sketch of the general shape of the X-ray spectrum near to U-La. The dashed red line represents the background spectrum in the absence of Rb. Positions b1, b2 and b3 represent background positions for U analysis, see text for details.

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Table 2. Summary of six standards analysed for U, Th and K, XRF data from Reference 5, Pub is published standard values from Reference 6.

Standard	U (XRF)	U (Pub)	Th (XRF)	Th (Pub)	K (XRF)	K (Pub)
G-2	1.85	2.07	25.8	24.7	3.65	3.72
W-1	0.6	0.57	2.53	2.4	0.53	0.53
AGV-1	1.93	1.92	5.76	6.5	2.41	2.42
GSP-1	2.33	2.54	103.8	106.0	4.51	4.57
NIM-G	15.00	15.00	52.6	51.0	4.13	4.14
NIM-L	13.49	14.00	63.9	66.0	4.61	4.57

of each of the Geochemical Reference Materials six times (Table 2), (ii) for each element determine the mean net intensities $[(I_{pk} - I_{bkg}) \times rc]$, where I_{pk} is measured peak intensity, I_{bkg} is the interpolated background intensity and rc is the intensity of the RhK Compton line]. The 2σ lower limits of detection using total count times of 4800s are 0.2ppm for U and 1.0 ppm for Th. In the case of K, the 2σ lower limit of detection is 0.001%. In comparison, routine rapid analysis of U and Th with 100s total count times yield 2σ lower limits of detection of 1 and 2ppm, respectively. In the case of K, using rapid counting times gives a 2σ lower limit of detection of 0.01%.

Conclusions

XRF is now a well-established analytical tool for the analysis of specimens of geological interest. Modern spectrometers have the capability to provide precise

analysis for a wide spectrum of elements at much reduced lower limits of detection; typically most elements can now be analysed at sub-ppm levels. A major advantage of XRF analysis is that it can be a non-destructive analytical method, whereby pressed powder pellets can be repeatedly re-analysed for a variety of elements, so avoiding the need to re-sample. Furthermore, in this non-destructive mode aliquots of a sample may be recovered from pressed powder pellets and analysed by other techniques (e.g. ICP-MS) for a range of other elements or isotope analysis, ensuring that a data set for an individual sample is derived from the same sample volume. Another recent advance, resulting from spectrometer redesigns, is the ability now to analyse for light elements such as B, C, N and Be, which are important in the assessment of synthetic materials. All of these advances suggest that the XRF spectrometer will retain its importance as

an analytical tool and allow development into new areas as defined by the users.

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