X-ray fluorescence (XRF) in the investigation of the composition of earth materials: a review and an overview

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ABSTRACT

X-ray fluorescence (XRF) spectrometry is a well-known, well-established and widely applied technique in the determination of many major elemental compositions of earth materials. XRF confers the ability to analyse solid samples non-destructively through X-radiation. The orderliness and clarity of its emission spectrum, its great accuracy and precision make this technique a geochemical method of choice in mineralogy and investigation of the chemical composition of earth materials. There are limitations regarding the age and calibration of instruments, costs of setting up, matrix effects to be considered and the stringent sets of standards; however, XRF laboratory analyses remain the standard technique for providing high-quality geochemical data analyses in the investigation of earth elemental composition. With further improvements in XRF technology, it is expected that this technique will be of continued importance/utility in geological and geomorphological investigations.

1. Introduction

X-ray fluorescence (XRF) spectroscopy is one of the most widely used and well-established methods of routine estimation of geochemical composition of rocks, sediments and earth material samples (Kramar, 1997; Ling et al., 2017; Tolosana-Delgado & McKinley, 2016; Weltje & Tjallingii, 2008; Young, Evans, Hodges, Bleacher, & Graff, 2016). For many years, XRF spectrometry is used in the determination of geochemical concentrations for a range of major and trace elements at parts per million (ppm) level. It has, also, been utilised in the successful investigation of geological, archaeological and industrial samples (Jenkins, Gould, & Gedcke, 1995; Young et al., 2016). One reason why this technique is widely used is because of its ability to analyse solid samples through X-ray radiation (Weltje & Tjallingii, 2008). The geochemistry of many of the Earth’s solid materials is regarded as the product of parent rock, climatic-environmental conditions, and possible anthropogenic interactions with the material (Jalali & Jalali, 2016). Hence, the ability of XRF to determine the major oxide/element composition of many earth materials (either in glass discs, powder pellets or bulk powder samples) has made it useful in many laboratory settings (Jenkins et al., 1995; Kramar, 1997; Young et al., 2016). It remains a standard method of geochemical investigation of Earth’s mineral and chemical compositions. This paper summarises the theories and applications of XRF in geochemical investigations; and highlight the examples of its diverse applications. This is intended as a simple overview of a useful technique for geo-scientific investigations of geological formation and landscapes. Its usefulness is illustrated by analysis of coastal-estuarine sediments, a case study example.

2. XRF

The major elemental composition of Earth material samples can be analysed by various instruments (Baedecker, 1987; Saabou, Ait-Salem, & Zazoun, 2009). However, XRF spectrometry is particularly valuable because of its ability to rapidly provide a high-resolution assessment of relative variations of most Earth elemental compositions (Löwemark et al., 2011). XRF spectrometry is based on the wavelength-dispersive principle, which states that individual atoms emit a relative abundance of X-ray photons of energy or wavelength feature that can be estimated (Weltje & Tjallingii, 2008). This technique has been applied in the examination of Earth materials from a range of settings and environments (e.g., Chalmers & Bustin, 2017; Löwemark, Jakobsson, Mörtth, & Backman, 2008; Oyedotun, 2016; Özkul, Çiftci, Tokel, & Savaş, 2017; Rivera, Giráldez, & Fernández-Caliani, 2016; Saabou et al., 2009). The wide range of XRF’s uses is due to its capacity to provide probable higher precision and accuracy than alternative methods (Taggart, Lindsay,
2.1. Strengths and weaknesses of XRF

The advantages of the XRF technique (after Taggart et al., 1987; Kramar, 1997; Weltje & Tjallingii, 2008) are many. First is its ability to analyse the bulk chemical contents of major elements (e.g., Al, Mn, Ca, Na, K, Ti, P, Si, Mg, etc.) found in Earth materials. The X-ray emission associated with the XRF technique is simple, systematic, relatively independent of the chemical state, and with uniform excitation and absorption dependent on an atomic number. Also, interference in the line of X-ray radiation can be easily corrected thereby enabling high accuracy and precision to be easily attained. Another advantage of XRF, in a geochemical investigation, is sample preparation, which is fast, simple and can be non-destructive.

Although XRF has many advantages, there are some drawbacks that should be considered before embarking on a study using this technique. Firstly, most commercially available XRF instruments are very limited in their ability to accurately and precisely measure the abundance of geochemical elements of the natural earth materials that have minimal levels of elements (generally, fewer than eleven elements) (Taggart et al., 1987), without any form of modification/calibration. Secondly, most elemental variations are measured as counts instead of as concentrations. Calibration of the XRF instruments to measure concentration requires quantitative analysis of bulk sediment chemistry (Löwemark et al., 2011). Thirdly, sensitivity to low isotopes of an element is very poor, and this shortcoming necessitates the use in routine analyses of some other instrumentation – for example, the surface roughness, water content, and grain size variations of a material can influence the sensitivity of XRF measurements (Weltje & Tjallingii, 2008). Fourthly, on many occasions, XRF methods cannot distinguish the inter-element effect within some earth material samples. In the past, this shortcoming has necessitated the implementation of various other geochemical techniques such as Mossbauer spectroscopy (e.g., Günzler & Williams, 2001; Gültlich, 2012). This limitation may be compounded by the age of the X-ray instrument used. An ageing instrument may influence the counts measured, thereby impeding the comparison of results. Fifthly, the initial costs of setting up the XRF instrumentation and equipment are relatively high. Lastly, strict adherence to sets of standards and principles is required with intensive sample preparation and analyses to meet the set standard – although this may appear as a limitation to some, it can also be regarded as essential good practice in an XRF laboratory ethic.

However, despite the weaknesses of this method, XRF laboratory analyses remain the geochemical standard for provision of the highest possible quality of geochemical data analyses of Earth materials (Janssens, 2013; Young et al., 2016).

2.2. Theory of XRF

The XRF procedure involves inter-linked processes (summarised from Sakurai et al., 2004; Weltje & Tjallingii, 2008). The incoming X-rays from an XRF instrument knock the electron of an atom out of the inner orbital. This results in the excitation of the atom and the production of high-energy radiation (photons, protons, electrons, etc.). The third process involves the detection and integration of characterised emitted lines to give varying levels of intensity. The last stage in this process is the conversion of the detected line intensities to elemental concentrations. Earth materials (e.g., natural rocks) consist of diverse elemental minerals at highly variable compositions and structures which affect the behaviour of light in many complex ways, the identification of these elements is vitally possible using X-ray methods, (e.g., XRF) through the characteristic emitted-radiation of these compositions under certain conditions.

2.3. XRF instrumentation

Diverse advances have been made on instrumentation for XRF laboratory analyses and in situ field measurements because of its abilities for geochemical analyses and investigations (Marguí, Queralt, & Van Grieken, 2016; Weltje & Tjallingii, 2008; Young et al., 2016; etc.). Two types of these instruments are in use today and these are reported in literatures. Since the early 1960s, the Wavelength Dispersive (WD) XRF instruments have been widely adapted to geochemical investigations/applications, and these remain common in laboratory analyses of major elemental compositions (Kramar, 1997). The second form of XRF instrumentation that is still in use is based on the energy-dispersive (ED) discrimination principle with its ability to simultaneously discriminate the X-ray spectra of ten to thirty elements (Kramar, 1984). Because of the sensitivity of XRF to background ratio, various modifications have been made to the early ED instruments and these have given rise to many new variants (Vincze, Janssens, Vekemans, Adams, & Lemberge, 2004), such as the Total reflection XRF (TXRF) (Prost, Wobrauschek, & Streli, 2017), Polarised XRF (PXRF) (Sakurai et al., 2004; Zhan, Luo, & Fan, 2007) etc. In laboratories, these have been used for decades with great success (Janssens, 2013; Young et al., 2016). Because of the advantages inherent in mobility of XRF instrumentation, many manufacturers have developed handheld XRF (hXRF) instruments which are now being deployed on the field for in situ measurements (Coccato et al., 2017; Marguí et al., 2016; Young et al.,
2.4. XRF applications

The versatility and rapidity of the XRF technique have given it a wide application in many industrial and scientific fields (Table 1).

2.5. XRF method

2.5.1. Sample collection and preparation

The Earth material samples (liquid or solid) must be collected carefully to prevent contamination of the natural concentrations of the elements in the material. Also, the sample collection and preparation must follow the established standards for the type of investigation being undertaken. Indeed, sample preparation is highly variable and is mostly dependent on the materials being analysed and the goals of the analysis. For the XRF analysis of solid components of the Earth materials, samples must be larger than the largest particle or grain size in the materials (typically larger than 10× the largest particle). This is imperative since, depending on the XRF technique involved, the sampled material may be subjected to a series of preparatory processes, including crushing and grinding to grains of a few millimetres in size or to a fine powder. Full details of sample collection and preparation can be found in Marguí et al. (2016).

2.5.2. Analysis

XRF results can be reported both qualitatively and quantitatively. Although the energy-dispersive (ED) XRF can be used to generate quantitative data if appropriate standard-controlled calibration exists, often it is ideally suited for qualitative elemental analysis since the peak assignment for the XRF spectrum is easy and each element occurs at a fixed position. XRF can be readily utilised as a quantitative method of elemental composition analysis since the peak height of an element is often related to the concentration in the sample. Quantitative XRF analysis generally uses two main techniques, the Fundamental Parameters Method (FPM) and the calibration with standards method. These two techniques are always incorporated in the XRF instrument software (Horiba, URL). The FPM is used to calculate the element concentration based on the peak intensities, while the Calibration Standard is used to relate peak intensities to element concentration by deriving calibration curves from materials of known/certified composition.

2.5.3. Precision and accuracy in XRF

Two basic quality principles with XRF analysis are precision and accuracy. These are necessary for unbiased analysis. The ability of a method to give the same result on a repeated analysis of the same sample is stated to be precise. Precision is the deviation of a set of determinations from their random error (mean), while accuracy is the level of conformity with the elimination of systematic and random error (Taggart et al., 1987). Although a highly precise technique can yield unbiased results, these results may be inaccurate especially if impurities have been introduced during sample preparation or because of calibration errors. To achieve high-quality and acceptable XRF results, attention must be given to achieving both precision and accuracy. In addressing the drift (imprecision, whether short-term or long-term), multiple variables must be taken into consideration. These include stability of the XRF instrument, precision in sample preparation, calibration of the instrument to the most appropriate and acceptable reference standard, monitoring and management of room temperature, monitoring of voltage changes because of fluctuating power supply, and giving attention to barometric pressure and other external factors.

Table 1. Recent applications of XRF spectrometry.

| Field of application | Examples |
|----------------------|----------|
| Ecology/ecosystem    | Rodríguez-Zorro, Enters, Hermanowski, Lima da Costa, and Behling (2015) |
| Metallurgy           | Mighall, Timberlake, Martínez-Cortizas, Silva-Sánchez, and Foster (2017); Turner and Filella (2017) |
| Forensics            | Castillo-Peinado and Luque de Castro (2017); Rim et al. (2017) |
| Polymers             | Bull, Brown, and Turner (2017); Guo, Ye, Li, Han, and Loh (2017); Turner and Filella (2017) |
| Archaeology          | Hunt and Speakman (2015); Turco, Davit, Cossio, Agostino, and Opetti (2017) |
| Environmental analysis | Tolosana-Delgado and McKinley (2016); Rivera et al. (2016) |
| Geology              | Jalali and Jalali (2016); Ling et al. (2017); Özkul et al. (2017) |
| Mining               | Chalmers and Bustin (2017); Pavlilonis, Grassman, Johnson, Díaz, and Caravanas (2017) |
| Soils/landscapes     | Hartemink and Minasny (2014); Kitchel (2016) |

3. Case study: identifying patterns of major elemental composition using XRF

The Hayle, the Gannel and the Camel estuaries, within St Ives, Crantock, and Padstow bays, respectively (Figure 1), have received considerable attention in terms of the impacts of mining on estuarine sedimentation (e.g., Oyedotun, 2016; Pirrie, Power, Payne, & Wheeler, 2000; Pirrie, Power, Wheeler, & Ball, 2000). The effects of mining on sediment supply, sedimentology and mineralogy were explored extensively in those studies. Here, XRF is used to compare the composition of major elements in the sediments of these three coastal-estuarine systems with the aim of identifying the anthropogenic influences on the geological landscapes and explore the sedimentary connectivity of the individual systems.
3.1. Method

X-ray Fluorescence Spectrometry (XRF) was used to determine the major elemental composition of 21 sediment samples from the estuarine and coastal systems. The major elements in their oxidised state were determined as a percentage of composition (Oyedotun, 2015, 2016). The samples used in the XRF analyses were obtained from 0 to 5 cm sediment depth randomly collected from

Figure 1. Southwest England showing three estuarine systems (Hayle, Gannel, and Camel) where sediments were sampled. Source: Contains OS data © Crown copyright and database right (2015).

Figure 2. Major element composition (%) of intertidal sediments of three estuaries determined by X-ray fluorescence of 21 samples.
the intertidal locations around the Hayle, Gannel, and Camel systems of southwest England between 24 and 27 October 2011 (Figure 1).

Samples were prepared at the Coastal and Estuarine Research Unit of the Department of Geography, University College London (Oyedotun, 2015). The sediments were freeze-dried at ~60 °C in a Modulo 4 k Freeze Drier for 5 days. The dried samples were pulverised into a fine powder with an agate mortar and pestle. To avoid contamination and the mixture of samples during preparation, both faces of the compression die for each of the samples were well covered. Each pulverised ground sample (powder pellet) was then weighed prior to analysis; weights of samples ranged from 4 to 6 grams. These samples were analysed with a Spectro XLab Pro 2000 which produces high X-ray intensity and permits quantitative analysis of elements in the ng range (after Jenkins et al., 1995).

3.2. Comparison of major element (XRF) composition (%) of intertidal sediments

The elements analysed were Ca, Si, Al, Fe, Cl, Mg, Na, K, Ti, S, P, Mn, V, and Cr. The total base cation percentages (Si, Mn, P, Cl and Fe) of the Hayle estuary was high compared to total content for the other estuaries; whereas Mg, Al, S, and K were higher in the Camel Estuary (Figure 2). The total base cation content (Na, Mg and K) was low (<5% in total) in all the sites but Ca was much higher (~20%) compared to all the other elements investigated. Patterns in Ca distribution were broadly similar across the sites. Shell material was clearly present in the sediments, and shell fragments contributed to the medium and coarse sand sizes. In all the estuaries, Na, Mg, Si, S, and K had a relatively low percentage (0.1–6%). XRF examination has enabled the easy identification of differences in the chemical composition and comparative examination of these systems. These have enabled the identification of the different anthropogenic mining activities whose impacts have affected the landscape of each system, even beyond their years of cessation. Detailed results of these differences and investigations of sediment sources at the study sites are reported in Oyedotun (2016).

4. Conclusion

Analysis of Earth materials for multivariate purposes will continue as humans seek to understand the Earth’s composition and search for new uses for such compositions. Certainly, XRF spectroscopy will continue to hold an important position in geochemical analyses of the earth’s multifarious components. Despite its limitations, the technique remains relevant in the field of Earth and environmental sciences because it provides highly accurate and quality data analyses in quick and often non-destructive manner – the qualities which are vital in the understanding the composition of the earth’s material and landscapes. With the continuous developments and improvements in XRF equipment, this technique will continue to flourish in the future.

Acknowledgement

I sincerely appreciate the supervisory assistance and support of Dr. Helene Burningham and Professor Jon French when XRF analysis was undertaken as part of my Ph.D. Geography programme at University College London, UK. I also appreciate the guidance and assistance of Janet Hope with the laboratory analyses; Dan Shuman and Ann Grant with reading through and commenting on the drafts of this article.

Disclosure statement

No potential conflict of interest was reported by the author.

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