



Portable X-ray fluorescence analysis of mineral and organic soils and the influence of organic matter



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ABSTRACT

Portable X-ray fluorescence (PXRF) spectrometers with tube X-ray source are being used to determine the elemental composition of soils in the laboratory and the field. Most studies with PXRF have been with mineral soils and there is a need to assess PXRF applications to organic soils and peats. Using a commercial PXRF instrument and the manufacturer's soils programme we assessed performance by the analysis of various soils with a range of organic matter concentrations up to those of low ash peats. We first analysed seven certified reference mineral soils and a certified, low ash ombrotrophic peat. The data obtained for the certified reference mineral soils was definitive for Ti, Cr, Mn, Fe, Ni, Cu, and As, quantitative for K, Ca, Zn and Sr, and qualitative for Pb. Portable X-ray fluorescence analysis of the ombrotrophic peat gave satisfactory results for Cu ($4.00 \pm 1.00 \text{ mg kg}^{-1}$, certified $5.28 \pm 1.04 \text{ mg kg}^{-1}$) and Pb ($184 \pm 3 \text{ mg kg}^{-1}$, certified $174 \pm 8 \text{ mg kg}^{-1}$) but overestimated the concentrations of Ca, Ti, Cr, Ni and Zn by 2–3 times, and Fe by 5 times. To extend comparison beyond the only available low ash certified reference soil and further exemplify the differences between mineral soils and peat soils we analysed 183 Scottish topsoils that had a wide range of organic carbon (OC) concentrations (1.23 to 48.8% by weight) and compared the concentrations of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr and Pb determined by PXRF with pseudo total concentrations determined by aqua regia extraction and inductively coupled plasma spectrometry. The results demonstrate that to maximise the potential of the PXRF instrument for use beyond mineral soils, to organo-mineral and peats, modifications to the manufacturer's calibrations should be made. We recommend validation using soils on a continuum of OC concentrations from those of mineral soils to peats covering the range required.

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Introduction

X-ray fluorescence (XRF) spectrometry is a non-destructive, rapid, simultaneous multi-element analytical methodology that has been developed to include portable, hand-held devices (Hou et al., 2004). With the miniaturisation of X-ray tubes and developments in silicon drift detector technologies, portable X-ray fluorescence (PXRF) spectrometers that are more affordable and rapid in operation compared with wet chemical based methods (e.g. total dissolution and inductively coupled plasma (ICP) spectrometry) and have detection limits that are sufficient for environmental monitoring of many elements in soils and other geological materials (Potts, 2008; Wiedenbeck, 2013) are available from several manufacturers. There is no standard terminology used to describe such instruments. We choose to use PXRF but similar instruments are often referred to as hand-held, mobile or transportable XRF (West et al, 2013). The use of PXRF spectrometers with tube X-ray sources has superseded the use of those with radioactive sources, which

have decreased X-ray emission output with time as well as additional safety, disposal and transport requirements. Tube source PXRF spectrometers also offer a wider range of excitation energies circumventing the requirement for multiple-isotope, radioactive sources. Portable X-ray fluorescence spectrometers are now finding applications in soil analysis in the laboratory and in the field, and are being used by consultants, local authorities and other bodies interested in monitoring soils. The detection limits of PXRF are poorer than those of large laboratory based XRF instruments, or of ICP related techniques. However, PXRF offers rapid, cost effective, non-destructive analysis suitable for a variety of tasks, although low atomic mass elements, often referred to as "light elements", cannot be easily detected (Jenkins, 1999).

PXRF analysis is a surface/near surface technique and sample preparation is critical. X-rays from PXRF instruments penetrate approximately 2-mm into a mineral soil matrix, and a 5-mm depth of soil is considered infinitely thick (Kalnicky and Singhvi, 2001). Several methods of sample preparation to obtain homogeneous thick masses exist including fusion with a flux or forming pellets under pressure. These time-consuming, laboratory-based procedures defeat the advantage of portable instrumentation as the ultimate focus is on direct application in the field where simple drying and milling are the extent of

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practical operations for sample pre-treatment. Methods involving direct point and shoot at the soil surface have been reported (Carr et al., 2008; Chou et al., 2010; Gutiérrez-Ginés et al., 2013; Weindorf et al., 2012) but the quality of the data is compromised by the horizontal and vertical heterogeneity of the medium, moisture and surface roughness (Argyriaki et al., 1997; Ge et al., 2005). Measurements in the field can also be made with the PXRF instrument placed against the dry, sieved soil held in plastic bags (Peinado et al., 2010). Others prefer to recover samples to the laboratory to avoid effects related to soil moisture and grain size (Dao et al., 2013). The low cost, portability and on-site operation of PXRF makes it a useful tool for environmental survey work, especially in areas affected by the mining of heavy metals (Higuera et al., 2012; Jang, 2010), or for screening waste (Vanhoof et al., 2013). The United States Environmental Protection Agency (USEPA, 2007) and the International Organisation for Standardisation (ISO, 2013) have provided protocols for the analysis of soil and sediments. To our knowledge there have been no studies with peat or peaty soils.

Our objective was to assess the use of PXRF for the analysis of mineral soils and peats in the laboratory, firstly through a preliminary analysis of certified reference mineral soils and a certified reference low ash ombrotrophic peat, and by analysis of 183 topsoils from Scotland. The topsoils from Scotland had a wide range of organic carbon (OC) concentrations and were analysed for inorganic element concentrations by aqua regia extraction and ICP spectrometry. In many soil testing laboratories, extraction of soil with aqua regia is used to provide pseudo totals of the elements because aqua regia extraction is cheaper, safer and more suited to high throughput than total dissolution methods which often involve HF.

Material and methods

Portable X-ray fluorescence

We used a Bruker S-1 Turbo^{SD} instrument (Bruker Nano GmbH, Berlin) with an Rh tube and a Si drift detector. The instrument was set up on a stand and analyses were carried out with the manufacturer's soil programme, which uses a mixture of theoretical and empirical calibration methods. For analysis the dry soil (around 2 g) was held in a 25-mm diameter plastic cup with a 4- μ m thick polypropylene window (TF-240 film from Fluxana, Bedburg-Hau, Germany). After placing the soil in the container it was tapped on a hard surface to settle the particles onto the film window and analysed for a fixed period (120 s). Each sample was analysed at least in duplicate and our study was restricted to the analysis of K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr and Pb.

Soils

The properties of the soils used in testing the PXRF instrument are summarised in Table 1. The certified reference Chinese mineral soils were from LGC, Teddington, Middlesex, UK and had a range of parent materials, a relatively narrow range of OC concentrations (0.3 to 0.8%) and losses on ignition (4.4 to 14.3%), and had a comprehensive suite and concentration range of certified inorganic elements. We had access to only one certified reference peat soil, which was a low ash ombrotrophic peat (NIMT/UOE/FM/001, 95% loss on ignition) obtained from the University of Edinburgh. For the PXRF study we also used 183 topsoils sampled during the 2007–2009 National Soil Inventory of Scotland (NSIS_2). These soils had been sampled on a regular 20-km grid across the country and were from the centre of the genetic horizons (Chapman et al., 2013). The soil samples represented a range of parent materials, organic matter concentrations, and land uses. For aqua regia extraction (described in the Aqua regia extraction section) and PXRF analysis the soils were milled (Pulverisette 5 planetary mill, Fritsch, Germany) using zirconia milling components for approximately 10 min.

Effect of sample weight and milling

To assess the effect of sample weight in the XRF cup on the results of PXRF analysis we used different weights (0.5, 1, 1.5, 2, 2.5 or 3 g) of the MTS and the MAP soils and to assess the effect of milling we used the mineral soil (MTS), (Table 1). The 2-mm sized fraction of the soil was milled (Pulverisette 5 planetary mill, Fritsch, Germany) using agate components for 10 or 30 min. The particle size distribution of the soils before and after milling was measured by laser diffraction (Mastersizer, Malvern Instruments, Malvern, UK) after dispersion by sonication in water.

Aqua regia extraction

The topsoils were extracted with refluxing aqua regia according to a standard procedure (ISO, 1995). The extracts were filtered, diluted with water and analysed by ICP optical or mass spectrometry. To assess the efficiency of extraction of elements from peat soils by aqua regia we used 0.5, 1.0, 1.5 or 2.0 g of the MAP soil with the standard amount of aqua regia (21 ml of 12 M HCl and 7 ml of 15.8 M HNO₃ for each sample).

Table 1
Properties of test soils. For the certified soils, proposed values are given in parenthesis.

Code	Sample type ^a	Description	Organic C (% weight)	Loss on ignition (% weight)
GBW07402	CRM soil	Chestnut soil from Nei Mongol, China	0.49	4.4 ^b
GBW07403	CRM soil	Yellow-brown soil from Shandong, China	0.51	2.67 ^b
GBW07404	CRM soil	Limy-red soil from Guangxi, China	0.62	(10.9) ^b
GBW07405	CRM soil	Yellow-red soil from Hunan, China	(0.32)	(9.1) ^b
GBW07406	CRM soil	Red soil from Guangdong, China	0.81	(10.0) ^b
GBW07407	CRM soil	Laterite soil from Guangdong, China	0.64	(14.3) ^b
GBW07408	CRM soil	Loess from Shaanxi, China	(0.30)	9.12 ^b
LAP	Uncertified	Low ash peat from Kintyre, Scotland	48.8	95.0 ^c
MAP	Uncertified	Moderate ash peat from Hatton, Scotland	NA ^d	78.0 ^c
MTS	Routine quality control test soil	Mineral topsoil derived from granite from Aberdeen, Scotland	3.76	7.72 ^c
NIMT/UOE/FM/001	CRM soil	Ombrotrophic peat from Flanders Moss, Scotland	NA ^d	(95–96) ^c
NSIS_2 ^e	Uncertified	Topsoils from the National Soil Inventory of Scotland (n = 183)	1.23–48.8	0.87–98.3 ^c

^a CRM = certified reference material.

^b Ignition temperature unknown.

^c Ignition temperature 450 °C.

^d NA = not available.

^e NSIS_2 = National Soils Inventory of Scotland, 2nd sampling (2007–2009).

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