Ciência e Agrotecnologia 41(3):245-254, May/Jun. 2017
http://dx.doi.org/10.1590/1413-70542017413000117

REVIEW

Portable X-ray fluorescence (pXRF) applications in tropical Soil Science

Aplicações da fluorescência de raios-X portátil (pXRF) na Ciência do Solo tropical

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Received in March 10, 2017 and approved in May 26, 2017

ABSTRACT

The X-ray fluorescence (XRF) is an analytical technique for determination of elemental composition of different materials. In soils, the XRF has many pedological, environmental and agronomic applications, mainly after the emergence of portable equipments (pXRF). This technique has been recently adopted and successfully used for soil characterization worldwide, but very rare works have been carried out in soils of developing countries. The soil characterization includes the complete elemental composition determination (nutrients, trace and rare-earth elements) and allows estimating some soil physical and chemical properties. In Brazil, this technique is still incipient, mainly the use of pXRF, however, it can greatly contribute to soil characterization in-field or in-lab conditions and also replacing methods of soil analyses considered non-environmentally friendly. This review summarizes the XRF technique including principles and the main applications of pXRF in soils highlighting its potential for tropical Soil Science.

Index terms: Soil analyses; soil morphometrics; soil characterization.

RESUMO

Fluorescência de raios-X (FRX) é uma técnica analítica para determinação da composição elementar de diferentes materiais. Em solos, a FRX apresenta muitas aplicações pedológicas, ambientais e agronômicas, principalmente após a emergência de equipamentos portáteis (pXRF). Essa técnica tem sido utilizada com sucessso no mundo todo para caracterização do solo, entretanto, são raros os trabalhos em solos de países em desenvolvimento. A caracterização do solo inclui a determinação completa da composição elementar (nutrientes, elementos-traço e terras-raras) e permite a estimativa de atributos químicos e físicos do solo. No Brasil, a FRX é ainda incipiente, principalmente o uso do pXRF, entretanto, essa técnica pode contribuir grandemente para a caracterização do solo no campo, em condições laboratoriais e, também, substituindo alguns métodos de análise do solo considerados não prejudicial ao ambiente. Esta revisão sumariza a técnica de FRX incluindo princípios e as principais aplicações do pXRF, destacando seu potencial de uso na Ciência do Solo tropical.

Termos para indexação: Análise do solo; morfometria do solo; caracterização do solo.

INTRODUCTION

Historically, in Soil Science the analyses of soil physical, chemical and mineralogical properties are characterized by using a great amount of chemical reagents, being time-consuming, costly and, in most of cases, non-environmentally friendly methods since they generate chemical residues. However, soil analyses are required for more detailed soil characterization and, hence, development of several soil-related studies.

The X-ray fluorescence (XRF) is a technique capable of identifying and quantifying elemental composition of several solid materials with the use of X-rays, allowing for a chemical characterization of the analyzed material and correlation with other properties (Gazley; Fisher, 2014; Weindorf et al., 2014a). Atoms that compose the structure of the analyzed materials are reached by high energy X-rays, promoting a dislodgement of electrons from their original orbit. As the electrons return to their original orbit, they emit energy in fluorescence form that is characteristic of each element. Thus, the elements present in the analyzed materials can be identified (Weindorf et al., 2014a).

Technological advances enabled the emergence of portable equipment of X-ray fluorescence (pXRF), which has been showed to be a precise, accurate, low cost, rapid, non-destructive and environmentally friendly method to determine elemental composition of soils and other

2017 | Lavras | Editora UFLA | www.editora.ufla.br | www.scielo.br/cagro

materials (Radu; Diamond, 2009; Zhu; Weindorf; Zhang, 2011; Bastos; Melquiades; Biasi, 2012; Weindorf et al., 2012a; Weindorf et al., 2012b Weindorf et al., 2014a; Weindorf et al., 2014b; Stockmann et al., 2016a, 2016b).

Worldwide, the pXRF has been recently adopted and successfully used for pedological, agronomic and environmental purposes (Weindorf et al., 2014a), showing adequate correlations to other standard laboratory methods (Weindorf et al., 2012b). In USA, the US Environmental Protection Agency (US-EPA, 2007) recognized the pXRF for the determination of elemental concentrations in soils and sediments (method 6200) and the USDA established the protocol method for using it (Soil Survey Staff, 2014). More recently, Weindorf and Chakraborty (2016) published the chapter *Portable X-ray fluorescence spectrometry analysis of soils* in the Methods of Soil Analysis by the Soil Science Society of America. A complete historical description about XRF and pXRF can be found in Weindorf et al. (2014a).

In Brazil, the use of pXRF equipments for in-field or in-lab soil characterization is still incipient and needs further studies in order to assess the effects of different tropical soil conditions on pXRF results, such as soil moisture, particle size distribution, structure, mineralogy and organic matter content. One of the available works with pXRF in Brazil is that of Terra et al. (2014), who checked the accuracy of pXRF using some certified reference standard materials for soil characterization purposes and found significant and good correlation ($R^2 > 0.90$) for K, Ca, Mn, Fe and Si. However, until now, pXRF has not been applied in natural conditions to Brazilian soils characterization. Wastowski et al. (2010), assessed the soil elemental composition using energy dispersive X-ray fluorescence spectrometry (EDXRF). This technique was sensible to detect the effect of different land use and management. Simabuco and Nascimento Filho (1994) used EDXRF in a Red Latosol and Red Yellow Argisol under influence of vinasse. A complete elemental composition distribution down soil profile was obtained. Using XRF technique it was possible to study the pedogeochemical processes and mobility of trace and rare-earth elements in a lithochronosequence of soils from Lavras, Minas Gerais State, Brazil (Lacerda; Andrade; Quéméneur, 2002).

For the following 30 years, Brazil has a great challenge to mapping its territory in a large-scale (1:25,000) through the Brazilian Soils National Program – PronaSolos (Embrapa, 2016). Undoubtedly, the pXRF can substantially contribute to rapid, accurate, low cost, in-field and environmentally friendly analyses of soils, giving insights of their properties after tests with Brazilian soils have been carried out.

This review summarizes pXRF technique including principles and some pedological, agronomical and environmental applications, highlighting the opportunities for tropical soils characterization.

PRINCIPLES OF X-RAY FLUORESCENCE ANALYSES

X-ray fluorescence (XRF) spectroscopy is a technique that has been widely used in industrial activities that require rapid analytical routines to control the quality of products (Santos et al., 2013). According to Weindorf et al. (2014a), currently XRF spectroscopy is the most applied X-ray technique in environmental sciences, mining, chemistry, metallurgy, archeology, Soil Science and agronomy. XRF offers some advantages over other methods of determining chemical elements, as it is inexpensive, fast, requires minimal or no sample preparation, does not generate an environmental liability and is non-destructive, besides determining simultaneously or sequentially the concentration of several chemical elements (Weindorf et al., 2014a).

The XRF is based on the measurement of the intensities of X-ray emissions characteristic of each chemical element that makes up the sample. For this emission to occur, the sample must receive enough energy to excite the electrons of the elements that compose the sample. The technique requires that species be irradiated with very energetic photons and the excitation of the atom happens when it is struck by particles such as electrons, protons or ions produced in particle accelerators, electromagnetic waves or through X-ray tubes of Ta/Au, Rh or Ag (Kalnicky and Singhvi, 2001; Gazley and Fisher, 2014; Sharma et al., 2014; Weindorf et al., 2014a), this latter being the most common process.

When X-rays reach the surface of soil particles, the electrons are displaced from inner to outer shell and, as a consequence, the outer shell electrons move to fill inner-shell vacancies and energy is released in form of fluorescence (Sharma et al., 2014; Weindorf et al., 2014a). Each element has a characteristic spectral signature and the intensity of the energy is proportional to the element concentration in the material, thus the characteristic energy value (keV) is used for elemental identification, and the intensity of fluorescence allows for quantification (Gazley and Fisher, 2014; Weindorf et al., 2014a). Table 1 summarizes different X-ray energies of elements, from Beryllium (Be) to Americium (Am).

Table 1: X-ray energies (keV) of elements.

E	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$	E	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$	E	$K\alpha_1$	$K\beta_1$	$L\alpha_1$	$L\beta_1$	$M\alpha_1$	$M\beta_1$
Be	0.108	---	---	---	Se	11.224	12.497	1.379	1.419	Tb	44.482	50.385	6.273	6.975	1.240	1.269
B	0.183	---	---	---	Br	11.924	13.292	1.481	1.526	Dy	45.999	52.113	6.498	7.248	1.293	1.325
C	0.277	---	---	---	Kr	12.648	14.112	1.585	1.636	Ho	47.547	53.877	6.720	7.526	1.348	1.383
N	0.392	---	---	---	Rb	13.396	14.961	1.692	1.751	Er	49.128	55.674	6.949	7.811	1.404	1.448
O	0.525	---	---	---	Sr	14.165	15.835	1.806	1.871	Tm	50.742	57.505	7.180	8.102	1.462	1.503
F	0.677	---	---	---	Y	14.958	16.739	1.924	1.998	Yb	52.388	59.382	7.416	8.402	1.526	1.573
Ne	0.849	---	---	---	Zr	15.775	17.668	2.044	2.126	Lu	54.070	61.290	7.655	8.710	1.580	1.630
Na	1.040	---	---	---	Nb	16.615	18.625	2.169	2.260	Hf	55.790	63.244	7.899	9.023	1.646	1.700
Mg	1.254	1.302	---	---	Mo	17.480	19.606	2.292	2.394	Ta	57.535	65.222	8.146	9.343	1.712	1.770
Al	1.486	1.557	---	---	Tc	18.367	20.626	2.423	2.535	W	59.318	67.244	8.398	9.672	1.775	1.838
Si	1.740	1.837	---	---	Ru	19.279	21.656	2.558	2.683	Re	61.141	69.309	8.652	10.010	1.843	1.906
P	2.010	2.139	---	---	Rh	20.216	22.724	2.697	2.834	Os	63.000	71.414	8.911	10.354	1.907	1.978
S	2.309	2.465	---	---	Pd	21.177	23.818	2.838	2.990	Ir	64.896	73.560	9.175	10.708	1.980	2.052
Cl	2.622	2.812	---	---	Ag	22.163	24.941	2.983	3.150	Pt	66.831	75.570	9.442	11.071	2.050	2.127
Ar	2.958	3.190	---	---	Cd	23.173	26.093	3.133	3.315	Au	68.806	77.982	9.713	11.443	2.123	2.203
K	3.314	3.590	---	---	In	24.210	27.275	3.286	3.487	Hg	70.818	80.255	9.989	11.824	2.195	2.281
Ca	3.692	4.013	0.341	0.345	Sn	25.271	28.485	3.444	3.663	Tl	72.872	82.573	10.269	12.213	2.271	2.363
Sc	4.093	4.464	0.395	0.400	Sb	26.359	29.725	3.604	3.842	Pb	74.970	84.939	10.551	12.614	2.342	2.444
Ti	4.512	4.933	0.452	0.458	Te	27.473	30.993	3.768	4.029	Bi	77.107	87.349	10.839	13.023	2.423	2.526
V	4.953	5.428	0.510	0.518	I	28.612	32.294	3.938	4.221	Po	79.291	89.803	11.131	13.446	2.499	2.614
Cr	5.415	5.947	0.572	0.582	Xe	29.775	33.620	4.110	4.418	At	81.516	92.304	11.427	13.876	2.577	2.699
Mn	5.900	6.492	0.637	0.648	Cs	30.973	34.982	4.285	4.619	Rn	83.785	94.866	11.727	14.315	2.654	2.784
Fe	6.405	7.059	0.705	0.718	Ba	32.194	36.378	4.466	4.828	Fr	86.106	97.474	12.031	14.771	2.732	2.868
Co	6.931	7.649	0.775	0.790	La	33.442	37.797	4.647	5.038	Ra	88.478	100.130	12.339	15.236	2.806	2.949
Ni	7.480	8.267	0.849	0.866	Ce	34.720	39.256	4.839	5.262	Ac	90.884	102.846	12.652	15.713	2.900	3.051
Cu	8.046	8.904	0.928	0.947	Pr	36.027	40.749	5.035	5.492	Th	93.351	105.605	12.968	16.202	2.996	3.149
Zn	8.637	9.570	1.012	1.035	Nd	37.361	42.272	5.228	5.719	Pa	95.868	108.427	13.291	16.703	3.082	3.240
Ga	9.251	10.267	1.098	1.125	Pm	38.725	43.827	5.432	5.961	U	98.440	111.303	13.614	17.220	3.171	3.336
Ge	9.886	10.982	1.188	1.218	Sm	40.118	45.414	5.633	6.201	Np	101.059	114.234	13.946	17.751	3.250	3.435
As	10.543	11.726	1.282	1.317	Eu	41.542	47.038	5.849	6.458	Pu	103.734	117.228	14.282	18.296	3.339	3.534
					Gd	42.996	48.695	6.053	6.708	Am	106.472	120.284	14.620	18.856	3.438	3.646

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$K\alpha_1$ and $K\alpha_2$ represent the electron transition energy from shell LII to K and from LIII to K, respectively (Figure 1). Kβ1 corresponds to electron transition from MIII shell to K. Lα1 and Lα2 energies correspond to the transition from MV to LIII and from MIV to LIII, respectively, and Lβ1 corresponds to the transition from MIV to LII shell. Different manufactured pXRF and their descriptions were summarized and can be found in Weindorf et al. (2014a).

The X-ray technique is widely used in the world in various fields of science. X-ray diffraction (XRD), widely used in Soil Science, uses the dispersion technique and determines the crystalline composition of minerals in soils and sediments, whereas XRF is an example of an X-ray absorption/emission technique used for determine the chemical composition of the sample (Kalnicky; Singhvi, 2001; Gazley; Fisher, 2014; Weindorf et al., 2014a). There are two types of XRF available today: wavelength dispersion X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF).

Until 1970's, the XRF analyses were performed by using WDXRF equipments. This technique is based on Braggs's Law and needs a synchronized and precise system between the diffractor crystal and the detector. There are some advantages of WDXRF compared to EDXRF, such as: higher spectral resolution, optimum wide range determination, and the measurement of light elements (atomic number smaller than 13, such as C, N, O, F, and Na). However, there are also some disadvantages of WDXRF: lower detection efficiency and higher power X-ray sources (Kalnicky; Singhvi, 2001; Weindorf et al., 2014a).

From the development of superconducting detectors, which are able to discriminate near-spectral lines of energies (Kα and Kβ), emerged the energy dispersive X-ray fluorescence (EDXRF) (Kalnicky; Singhvi, 2001; Weindorf et al., 2014a). These high-resolution detectors can produce electronic pulses proportional to X-ray energies. The most used detectors are the silicon drift detectors (SDD) and the semiconductors Si (Li), Ge (Li) and Ge hyperpure. When using these detectors it is not required the synchronous movement of the diffraction crystal and detector, therefore, there are no moving parts. The EDXRF system has the advantage of producing smaller equipment since it uses low-power X-ray tubes and/or radioactive sources of excitation. Some disadvantages of the EDXRF compared to WDXRF are: low efficiency for low energy X-rays, and EDXRF is not recommended for detection of light elements.

For several decades, XRF has been used in many laboratory analyses, but the development of portable X-ray fluorescence (pXRF) equipments using EDXRF contributed for a wide range of scientific investigations. For example, the pXRF became a useful tool to identify contaminated areas, allowing the determination of total elemental composition in-situ easily and rapidly (Peinado et al., 2010; Weindorf et al., 2012a, 2012b, 2014a; Hu et al., 2014). Some ways to use the pXRF equipments and applications in Soil Science are described below.

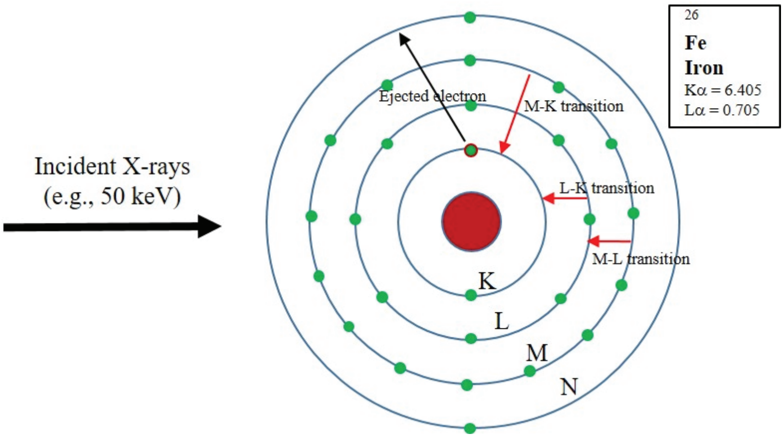

Figure 1: Shell electron distribution of Fe and scheme showing the excitation of electrons when subjected to high energy X-rays.

HOW CAN THE pXRF EQUIPMENT BE USED?

The pXRF equipments can be easily used in field or lab conditions. For in-field measurements, soil characterization can be performed on surface or directly in the soil profile (Figures 2a and 2b). In lab conditions, normally, it has been used for analyses of disturbed soil samples (e.g., dry soil samples passed through a 2 mm sieve), clay or other size fractions (Figure 2c). Also, it is possible to scan on the surface of undisturbed soil core samples. Normally, each measurement takes up to 60 s, although the time of scanning can be defined by the user. The elemental composition of plant leaves can be also determined by using pXRF equiments (Figure 2d).

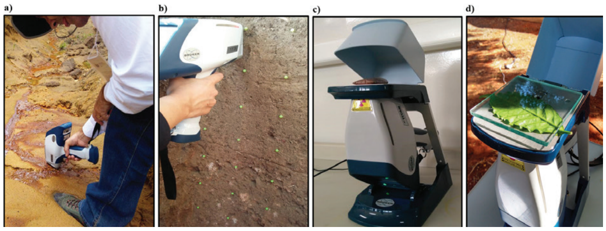

Figure 2: Details of different uses of pXRF equipments: a) directly on soil surface; b) down the soil profile; c) using disturbed dry soil samples packed into plastic bags (*see below factors affecting the XRF results*); and d) scanning a coffee plant leaf. Photos from authors.

FACTORS AFFECTING THE XRF RESULTS

Some factors may affect the XRF results and must be strongly taken into account, as summarized below:

a) Soil moisture content: In wet soil samples, water absorbs part of the X-rays that would hit soil particles or scatter the primary X-rays (Stockmann et al., 2016b). According to these authors, the effect of soil moisture also depends on soil texture and mineralogy, and a general correction factor cannot be established. Weindorf et al. (2014b) evaluated the concentration of several elements obtained by pXRF in samples of 13 pedons of Gelisols, in situ and in laboratory conditions, and compared results with oven dry samples, noticing that most element contents were underestimated in relation to the dry samples. Sahraoui and Hachicha (2017) evaluated four soil moisture conditions, in situ and in the laboratory, to study the differences in element contents resulted from pXRF scanning and observed underestimation of values on wet samples in relation to dry samples, being these underestimation rates variable according to the element being analyzed. Bastos, Melquiades and Biasi (2012) proposed a procedure for decreasing the moisture influence on soil analyses by pXRF. They utilized the background radiation as a parameter for low energies and concluded that, after this correction, the obtained results were satisfactory. These findings emphasize that, correcting the moisture effect, the field-use of the pXRF is feasible. Kalnicky and Singhvi (2001) suggested drying the soil samples if the water content is greater than 0.20 g g^{-1}.

b) Particle size fraction: When a soil sample is grounded and sieved, the particle size distribution obtained may influence the results. For smaller soil particles, the XRF intensity is increased due to smaller incident angles (Maruyama et al., 2008). Then, for fine soil particles it may be expected a higher elemental concentration. For in-lab determination, it is recommended to use air-dried soil samples passed through a 2 mm sieve (Laiho; Perämäki, 2005). The pXRF data obtained in field conditions (e.g., directly in the soil profile) can significantly differ from the results obtained using disturbed soil samples in lab conditions. Stockmann et al. (2016a) quantified the elemental composition at different depths in three soil profiles in-field and in-lab conditions. Mainly for K, Fe, Mn and Ti, the concentration obtained directly in the soil profile was lower than when it was used ground samples.

c) Spectral interference: Some elements may have their spectral lines overlapped, such as: S and Mo; Cl and Rh; As and Pb; V and Cr; Fe and Co. For example, the As Kα peak (10.543 keV) is close to the Pb Lα peak (10.551 keV). Much attention must be driven to adjacent elements (Z-1 or Z+1), which show similar excitation energies (see Table 1). Also, a given element may absorb or scatter the fluorescence of another element. The energy emitted by one element may excite another (Kalnicky; Singhvi, 2001).

d) Scanning through polyethylene plastic bags: Polyethylene plastic films may absorb part of incident X-rays energy (see Figure 2c). So, if soil samples are packed into thin plastic bags and scanned by pXRF the results may be influenced (see Figure 2c). To avoid this interference it is recommended to use 0.2 mil Mylar or polypropylene X-ray film (Kalnicky; Singhvi, 2001).

e) Scanned area and penetration depth of X-rays: Normally, the area scanned by pXRF is about 1 cm^2 and the penetration from 2 to 5 mm (Kalnicky; Singhvi, 2001). So, the heterogeneity (e.g., particle size distribution, mineralogy, organic matter content) of the total soil volume will affect the results. For example, Hangen and Vieten (2016) found that simple soil pore length influenced on pXRF results.

APPLICATIONS OF pXRF FOR TROPICAL SOIL CHARACTERIZATION

In recent years, diverse works have been published in several research areas, such as geology, archeology, and paleontology, whereas regarding soil characterization for varying purposes not too many works are found worldwide. In this review we emphasize the potential application of pXRF in soils for environmental, pedological and agronomic applications, as an effort to provide insights and stimulate future tests mainly in tropical countries with lack of detailed soil information.

Environmental applications

For environmental purposes, the determination of heavy metals and rare-earth elements in different materials can be greatly favored by the use of pXRF (Kalnicky; Singhvi, 2001), and this method can help in-field recognition and fast decision making. Traditionally, metal analyses for environmental studies require acid digestion in microwave oven and subsequent determination by ICP-OES or atomic absorption spectrophotometer (USEPA 3051A method). For instance, in a mining area in Ireland, high correlation was observed between the As, Cu, Pb and Zn concentrations determined by pXRF and those obtained through atomic absorption spectrophotometer after digestion in aqua regia (Radu; Diamond, 2009). Rouillon and Taylor (2016), studying soils contaminated with heavy metals and comparing element data obtained from both pXRF and inductively coupled plasma atomic emission spectroscopy (ICP-AES) with certified reference materials, found that pXRF provided adequate results for Ti, Fe, Cu, Zn, Mn, Cr, Sr, Cd, and Pb after careful sample preparation and pXRF calibration. These findings stimulate similar environmental studies in tropical conditions.

Pedological applications

Considering that pXRF is capable of obtaining the total content of many elements in soils and other materials, diverse elements distribution can be accessed by scanning the soil profile in the field, providing adequate results. Weindorf et al. (2012a) showed the applicability of using pXRF in 10 soil pedons as a manner to quantitatively differentiate soil horizons of alluvial soils from Lousiana (USA) based on differences of elemental concentration, clay content and laboratory analyses results.

For the purpose of this work, aiming to illustrate the potential of pXRF also in tropical conditions, we created a graphic showing the varying Fe contents in depth and among soil profiles obtained by pXRF scanning (Figure 3). This element was chosen since Fe has an important role in soils, influencing soil aggregation, and, hence, soil structure, porosity, bulk density, etc. (Kämpf; Marques; Curi, 2012), adsorption of anions (anion exchange capacity), such as phosphate in more weathered soils (Motta et al., 2002), indicative of pedogenic processes that occurred in soil, reflected by the color associated to the presence of Fe oxides (hematite and goethite) (Resende et al., 2014), drainage conditions (Schaetzl; Anderson, 2005), soil parent material, etc. It can be noticed in Figure 3 that pXRF could differentiate Fe contents in depth within a profile and among soil profiles rapidly and at low cost. Spatialization of such information to the entire soil profile, as illustrated in Hartemink (2015), can also be performed using interpolation techniques and may be of great importance in future works involving the so-called digital soil morphometrics (Hartemink; Minasny, 2014).

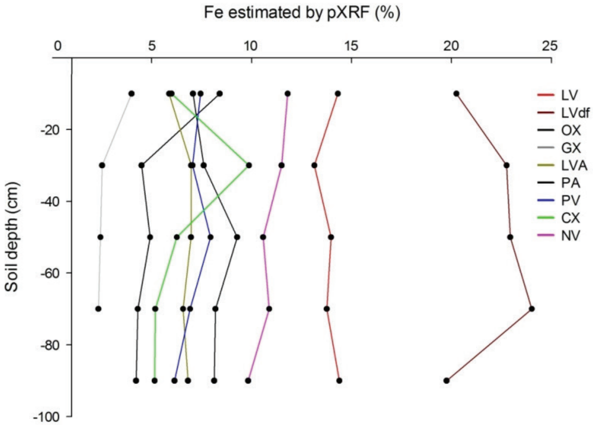

Figure 3: Fe content (%) down soil profiles. LV – Red Latosol; LVdf – Dystroferric Red Latosol; OX – Haplic Organosol; GX – Haplic Gleysol; LVA – Red-Yellow Latosol; PA – Yellow Argisol; PV – Red Argisol; CX – Haplic Cambisol; NV – Red Nitosol. Approximate taxonomic correspondence between Brazilian System of Soil Classification (Embrapa, 2013) and Soil Taxonomy (Soil Survey Staff, 2014): Latosol = Oxisol; Organosol = Histosol; Gleysol = Acquent; Argisol = Ultisol; Cambisol = Inceptisol; and Nitosol = Oxisol.

Stockmann et al. (2016a) used pXRF in three soil profiles in the field in order to help determining soil parent materials and pedogenesis according to calculations of elemental ratios (e.g. Ti/Zr) and weathering indices, such as Ki (SiO_2/Al_2O_3) and desilication index ($SiO_2/Al_2O_3 + Fe_2O_3 + TiO_2$). The authors also compared the results obtained using the pXRF in the field with those using it in the laboratory, and some differences in the results were found. In this sense, Weindorf et al. (2015) used visible near-infrared diffuse reflectance (VisNIR DRS) and pXRF to investigate differences in soil parent material from soils of three countries and pXRF was more efficient in capturing soil properties variability.

Hseu et al. (2016) compared Ni and Cr contents in soil profiles derived from serpentinite obtained by pXRF and aqua regia digestion followed by ICP-AES and an adequate correlation between the methods was found, although there were slightly differences between the absolute values obtained by each method. Aldabaa et al. (2015), studying soil salinity, evaluated the feasibility of predicting electrical conductivity from VisNIR DRS, pXRF and remote sensing data and found adequate results by combining the three sources of data to make predictions.

Most works using pXRF for soil characterization regards mineral soils and few reports of element contents have been made evaluating the effect of organic carbon on pXRF results. Among those works, Shand e Wendler (2014) evaluated element concentration through pXRF and ICP spectrometry after aqua regia digestion in topsoil samples collected in Scotland, with a wide range of organic carbon content, and noticed that specific pXRF calibration for bog soils should be necessary.

In Amazonia, Söderström et al. (2016) studied the effectiveness of proximal sensors used in the field, such as pXRF and a sensor that obtains both the electric conductivity and magnetic susceptibility, to predict, separately and in combination, cation exchange capacity, soil organic carbon, A horizon depth and P content in Amazonian dark earths. The authors found that combining data of the sensors promoted better predictions, but pXRF and the magnetic susceptibility were considered the most powerful single predictors, in this order.

Regarding soil survey, classification and digital mapping perspectives, Silva et al. (2016) employed pXRF elemental data in addition to soil magnetic susceptibility and high resolution digital terrain models (slope gradient, topographic wetness index, etc.) to aid in distinguishing four types of Latosols (Oxisols) according to their chemical properties related to parent material, and mapping their spatial distribution over the study area, in Minas Gerais (Brazil). The authors found that pXRF could capture differences of element contents among soils and, in association with magnetic susceptibility, these data had greater contribution to soil classes differentiation than the high resolution digital terrain models used.

Among soil analyses performed in the laboratory in Brazil, one widely used for several purposes is the sulfuric acid digestion analysis (Embrapa, 1997; Embrapa, 2011). This analysis consists of determining contents of Fe_2O_3, TiO_2, Al_2O_3, SiO_2, P_2O_5, and MnO. Based on preliminary tests, soil weathering indexes can be calculated, such as Ki ($Ki = SiO_2/Al_2O_3$) and Kr ($Kr = SiO_2/(Al_2O_3 + Fe_2O_3)$), in which greater values are expected to be found in low weathered soils (Birkeland, 1999). In addition, Fe_2O_3 content in soils is a key value for classification purposes in the Brazilian System of Soil Classification (Embrapa, 2013).

Despite of the variety of inferences allowed by results of sulfuric acid digestion analysis, it is time-consuming, costly, only performed by very few laboratories in Brazil and it generates large amounts of chemical residues that require careful handling and treatment prior to final disposal. For the purpose of this review and aiming to furnish some application examples, we conducted comparisons of pXRF elemental data with Fe_2O_3 results from sulfuric acid digestion analysis. A Cambisol (Inceptisol) profile located at Federal University of Lavras campus, Minas Gerais, Brazil, was scanned using a pXRF (Figure 4) and the results were compared to sulfuric acid digestion results. For the A horizon, the Fe_2O_3 content was equal to that obtained by sulfuric acid digestion analysis, although for B and C horizons the Fe_2O_3 content by pXRF underestimated the results of the conventional method. Further investigations are required for better evaluation of these results.

Agronomic applications

Several soil physical and chemical properties have been predicted based on pXRF elemental data solely or in association with other variables, such as remote and proximal sensors data, laboratory results of soil samples, geology information, etc. Here we compiled published works on this nature aiming to draw attention to the pXRF potential of use.

Particle size distribution can be estimated based on the results of pXRF, taking into account that there is a characteristic chemical and mineralogical composition of each size fraction (sand, silt, clay) (Zhu; Weindorf; Zhang, 2011). These authors found a significant correlation between Fe and clay content ($R^2 = 0.94$) in soils of the state of Louisiana (USA). This relationship was also found in Latosols, highly weathered tropical soils, developed from gabbro and gneiss, in Minas Gerais State, Brazil, for sand and clay contents using ordinary least square multiple linear regression (Silva et al., 2016).

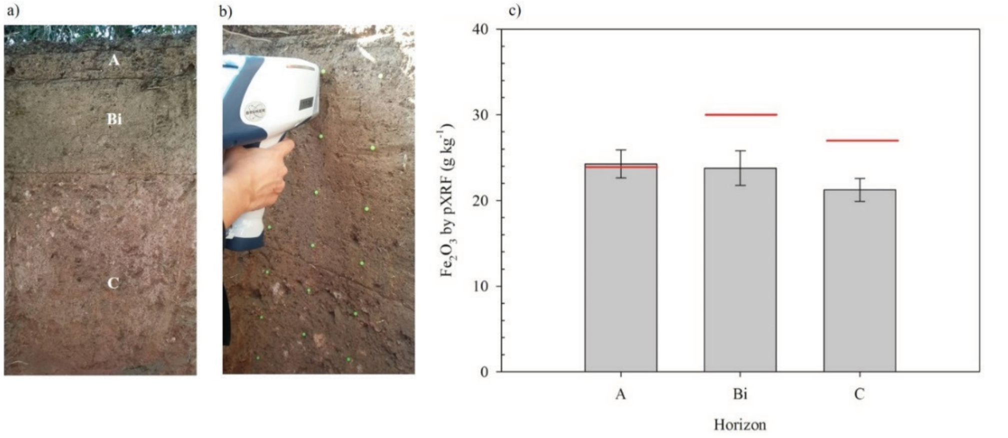

Figure 4: Cambisol (Inceptisol) profile located at Federal University of Lavras campus, Minas Gerais State, Brazil: a) and b) scanning detail of the soil profile; c) comparison between Fe_2O_3 content estimated by pXRF and that obtained after sulfuric acid digestion. Error bars indicate the standard deviation (n = 13 for A horizon; n = 10 for B horizon; and n = 26 for C horizon). Red lines indicate the Fe_2O_3 content obtained by sulfuric acid digestion method (Embrapa, 1997; Embrapa, 2011). Photo: Cortesy of Maxmiller Alvarenga.

Weindorf et al. (2013) satisfactorily determined the calcium sulphate content in soils using pXRF. This can be especially interesting in the monitoring and management of many areas in Brazil with gypsum application for reducing the exchangeable Al^{3+} contents in depth of cultivated soils. Additionally, another work showed that, by means of multiple linear regression, cation exchange capacity could be adequately estimated from the results of the pXRF, using 450 soil samples from California and Nebraska, USA (Sharma et al., 2015). Similarly, Sharma et al. (2014) obtained a significant correlation between soil pH and the elemental composition of soil samples measured by pXRF, since low soil pH values are associated with elements such as Al, and high pH values are associated with elements such as Ca and Mg.

Another possibility of using pXRF is the direct measurement of the elemental composition of plant tissues (leaves) and grains by using pXRF (McLaren; Guppy; Tighe, 2012; Paltridge et al., 2012). Towet, Shephred and Drake (2015) evaluated the composition of leaves of several plants by using pXRF and found a high correlation ($R^2 > 0.90$) for Mg, P, S, K, Ca and Mn contents with those obtained by the traditional acid digestion followed by determination by ICP-OES.

CONCLUDING REMARKS AND FURTHER RECOMMENDATIONS FOR TROPICAL REGIONS

This review intended to draw attention to the potential uses of pXRF for works of varying nature. This equipment has been recently adopted by Soil Science community and, thus, additional tests should be performed under varying tropical conditions to better understand and extrapolate its applicability.

Under tropical conditions, especially in developing countries, pXRF may contribute to increase and gather soils information in a rapid, low cost and environmentally friendly way. Thus, future projects aiming to characterize soils both spatially and locally may have in pXRF a practical and useful tool.

DISCLAIMER

In this review we do not endorse any pXRF manufacturer or model over another.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Nilton Curi (Department of Soil Science of the Federal University of Lavras) for motivating us to elaborate this review and for his precious suggestions and corrections that greatly improved the quality of the manuscript. Also, we thank the following Brazilian funding agencies: CNPq, Fapemig and Capes.

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