

Influence of Compression on Soil Characterization by X Ray Fluorescence

Influência da compressão em caracterização de solo por Fluorescência de Raios X

Yasmin Vieira¹; Mara Regina Linck²; Delton Luiz Gobbi³;
Lucas Brandalise Menezes⁴; Fernanda Da Silva Vilasboas⁵

Abstract

The study of soil mineralogy has been highlighted in recent years, as well as the search for alternative analytical techniques for soil analysis. The classical methods for determination of total oxides in soil expose the analyst to chemical hazards and require time-consuming sample preparation and decomposition. XRF is being employed for this type of analysis, since it does not require the use of chemical solvents. However, the technique requires samples with a smooth and homogeneous surface. The objective of this study was to verify if the soil compression (in 5 t, 10 t and 15 t) influenced the determination of the oxides content in soils of different municipalities of the state of Rio Grande do Sul (Passo Fundo and Cruz Alta). The experiments and the analysis of the data showed that the XRF technique presented low coefficients of variation and low standard deviation and did not have statistical difference between the samples of the same type of soil. The lower variations of these analytical criteria were obtained for soil analysed in the form of powder. Therefore, the most suitable form for the analysis of these soils is in the sedimentary form, however, it is still recommended the use of statistical tools to verify the reliability of the data obtained.

Keywords: Chemometry. Sample Preparation. Soil, XRF.

Resumo

O estudo referente a mineralogia do solo tem sido destaque nos últimos anos, bem como a procura por técnicas analíticas alternativas para análises de solo. Os métodos atuais para as determinações dos teores totais de óxidos no solo expõem o analista à riscos químicos e demandam preparo e abertura demorados. A Fluorescência de Raios X (FRX) está sendo muito empregada para esse tipo de análise, pois não se faz necessária a abertura das amostras do solo com solventes químicos. No entanto, a técnica requer amostras com superfície lisa e homogênea. O objetivo foi verificar se a compressão do solo (em 5 t, 10 t e 15 t) influenciava na determinação dos teores de óxidos em solos de diferentes municípios do estado do Rio Grande do Sul (Passo Fundo e Cruz Alta). Os experimentos e a análise dos dados mostraram que a técnica FRX apresentou baixos coeficientes de variação e baixo desvio padrão e não teve diferença estatística entre as amostras de um mesmo tipo de solo. As menores variações destes critérios analíticos se concentram no solo em pó. Sendo assim, a forma mais adequada para a análise destes solos é na forma sedimentar, contudo, ainda é recomendado o uso de ferramentas estatísticas para verificar a confiabilidade dos dados obtidos.

Palavras-chave: Quimiometria. Preparo de Amostra. Solo. FRX.

¹ Química, Instituto de Ciências Exatas e Geociências, UPF, Passo Fundo, RS, Brasil; E-mail: y.cortinavieira@gmail.com

² Dra. Profa., Instituto de Ciências Exatas e Geociências, UPF, Passo Fundo, RS, Brasil; E-mail: linck@upf.br

³ Me. Prof., Instituto de Ciências Exatas e Geociências, UPF, Passo Fundo, RS, Brasil; E-mail: gobbi@upf.br

⁴ Químico, Instituto de Ciências Exatas e Geociências, UPF, Passo Fundo, RS, Brasil; E-mail: lucasbmenezes@hotmail.com

⁵ Me., Centro Tecnológico de Pedras, Gemas e Joias do RS (CT-Pedras), RS, Brasil; E-mail: fernandavilasboas@gmail.com

Introduction

It is referred to as soil a collection of natural substances, consisting in solid, liquid and gaseous parts, formed by mineral and organic materials, which occupy most of the surface of the planet (EMBRAPA, 2013). From the point of view of soil science, it is the extent of the planet capable of being vegetated by nature as much as a material to be analyzed. Soil formation is a very slow process influenced by environmental factors, called soil formation factors, that are identified as the parental material, climate, relief, living organisms and the time of action of these factors (STRECK et al., 2008). The soil samples studied are from the city of Passo Fundo and Cruz Alta, in the state of Rio Grande do Sul. They are classified, according to the Brazilian Soil Classification System (from portuguese Sistema Brasileiro de Classificação de Solos), as typical dystrophic red latosols (EMBRAPA, 2013). Latosols are deep and homogeneous, highly weathered. Also, they are classified by colouring (reddish) and by the presentation of high saturation of bases (dystrophic). Both soil types have argisol characteristics, however, they vary in their parent material: basalt and sandstone, respectively (STRECK et al., 2008). The great variability of the soil is a result of factors that lead to weathering and the different pedogenetic conditions. Soils have different depths, colors, textures, nutrient contents, acidity and organic matter (GIASSON, 2012). As an alternative form for soil characterization X Ray Fluorescence (XRF) is presented. XRF is a fast, simple, non destructive and low cost analytical technique for a simultaneous chemical determination of oxides in different types of soil. This technique stands out as an important alternative, with detection limits of the order of 1 to 20 ppm. Several studies in soils use this technique for determination of their elemental contents or total oxides. According to IUPAC (1991), X radiation is the radiation resulting from the interaction of high energy particles or photons with matter: when a particle or a photon with high energy reaches an electron from the inner layers of an atom, and the energy of that particle is greater than the energy of the electron connected to the atom, it is ejected with equivalence to the difference between the initial energy and the electron binding energy (TERRA et al, 2014, p. 208). This phenomenon assign the atoms of chemical elements characteristic X ray emissions, releasing certain energy in the process described previously (JENKINS, 2006, p.3). Sampling variables, such as sieving and compression, were studied in non-anthropomorphic soils from different source materials, for XRF analysis. The size of the particles is relevant because the incidence of X rays

must comprise the largest area within which all the particles that make up the sample are available (BRISOLA and FERNANDES, 2008). Considering the importance of the granulometric fractions of the soil, the clay, sand and silt contents are established through physical and chemical parameters. (ALLEONI et al., 2005). The availability of metal ions in the soil is conditioned by their constituents and their chemical nature, which interfere with the adsorption and complexation reactions. Most of the metal ions, in the soil, complex with the oxides present in the clay fraction. Soils with higher clay content tend to complex more metal ions (LAIR et al., 2009).

Materials and Methods

Sampling preparation

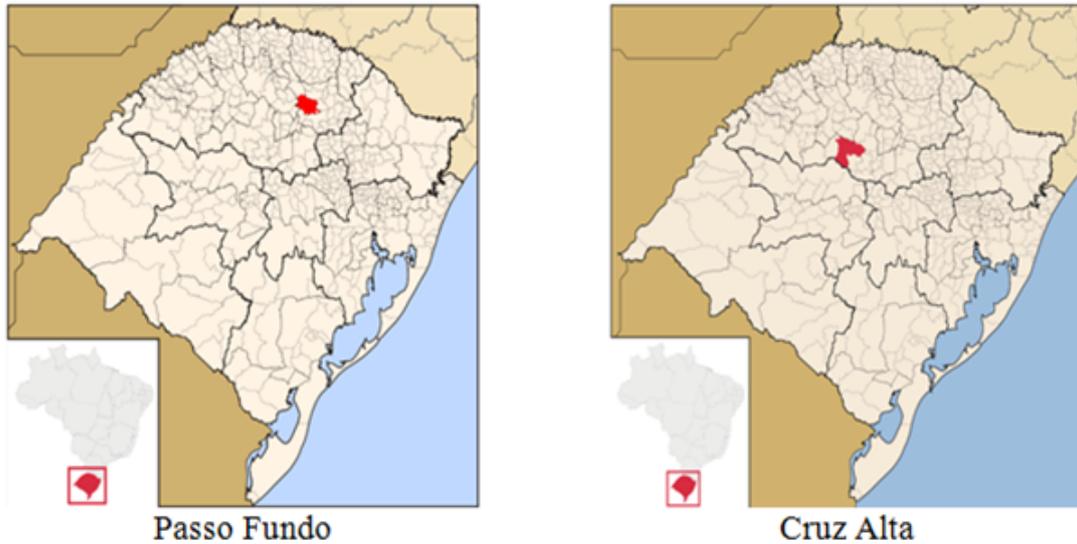
Soil sampling areas were selected according to the distance of cities (> 5.0 km), agricultural production (> 1.0 km), highways and residences (> 0.5 km). Considering the uniformity of vegetation, relief and other factors that indicate soil with homogeneous characteristics, sampling was limited to a surface of 1 ha. The soil was sampled in a native field, depth of 0 to 20 cm, according to the procedure of the Manual of Fertilization and Liming for the states of Rio Grande do Sul and Santa Catarina (from portuguese, Manual de Fertilização e Calagem dos Estados do Rio Grande do Sul e de Santa Catarina) (SBCS, 2012), in the area of Passo Fundo, RS and Cruz Alta, RS (figure 1).

Samples were oven dried at 40°C for 48 hours, crushed with agate mortar and pestle, and sieved to 2 mm prior to analysis. pH was determined according to Tedesco (1995). Soil compression was performed in the laboratory of Ensaios Mecânicos of Faculdade de Engenharia e Arquitetura (Fear) of UPF, in a universal traction machine model UPM, with 7 g of soil. The samples were compressed (figure 2) at 5 t, 10 t and 15 t. A total of 108 samples were analysed, in triplicates.

XRF analysis

The chemical compositions of the soils were determined by XRF in a Bruker S2 Ranger model X Flash, with Pd tube and power of 50 W, located in the gemology laboratory of the Centro Tecnológico de Pedras, Gemas e Joias do Rio Grande do Sul, located in the city of Soledade, RS. The reading range of the equipment goes from sodium to uranium (Na-U). The soil pressed samples were placed directly in the sample holder, with a membrane to protect the detector.

Figure 1: Location of the cities of Passo Fundo and Cruz Alta in the State of Rio Grande do Sul.



Source: IBGE, (2008).

Figure 2: Soil pellet.



Source: The authors.

Statistical Analysis

In this study, the data were analyzed by descriptive statistics, comparison between groups (ANOVA, Student's t-test) and Correlation Tests (Pearson for parametric and Spearman data for non-parametric data), with significance level set at $p \leq 0,05$.

Results and Discussion

Results

Equipment calibration

S2 Ranger (Bruker) was calibrated, first, with certified materials to verify its functioning. Standard samples (0.1 mg g^{-1} to 1 g g^{-1}) of each element analysed were used to verify linearity as well as detection and quantification limites (LOD and LOQ, respectively) ($R^2 = 0.999$).

Spectral information

Spectral information was obtained for each analysis, as energy versus intensity. It can be observed the spectral shift for the energies and intensities for several elements analysed when the compression is increased.

Soils characterization (difference between basalt and sandstone soils)

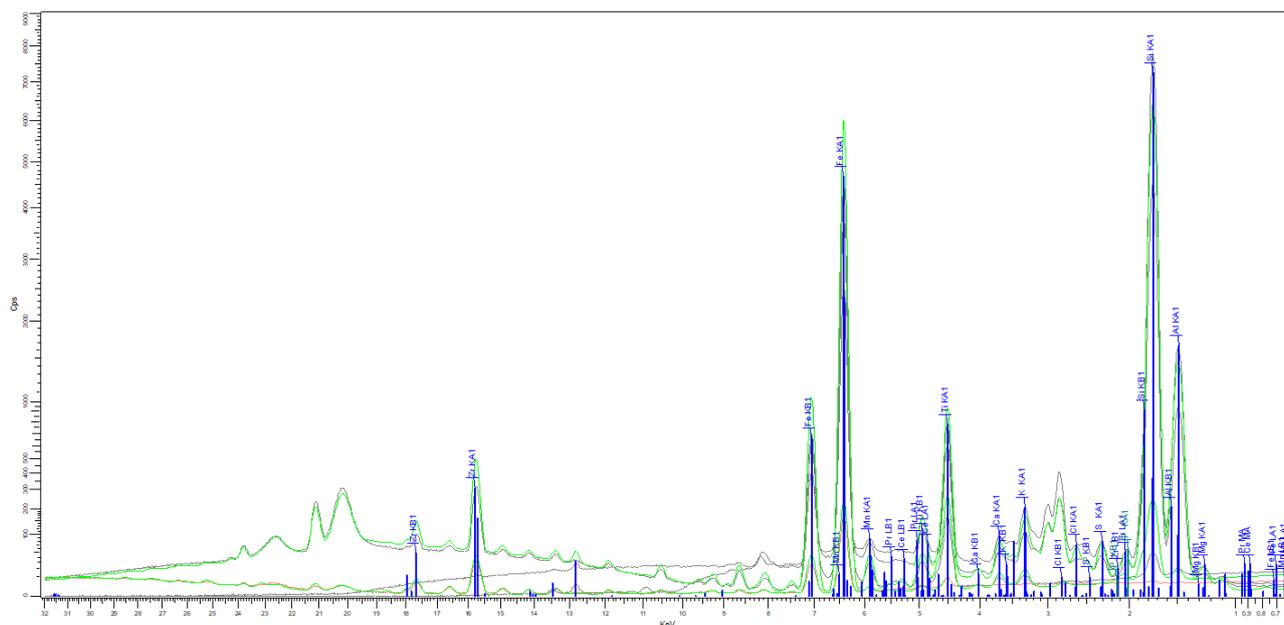
It is observed that the samples derived from the sandstone, collected in Cruz Alta, presented the highest SiO_2 and Al_2O_3 contents. Thus, the total SiO_2 content, quantified with the X Ray Fluorescence, present in this textural fraction, should be the largest part from minerals such as quartz (WILSON, 2017). There is variability of Fe content in soil samples from different parental materials.

Table 1: Soil characterization.

Oxides	Content in basalt (%)	Content in sandstone (%)
SiO_2	61.26	68.96
Al_2O_3	16.75	19.47
Fe_2O_3	14.93	7.35
TiO_2	3.11	2.0
MgO	0,0	0,8
K_2O	0,66	0,50
SO_3	0.75	0.18
P_2O_3	0.88	0.11
MnO	0.14	0.08

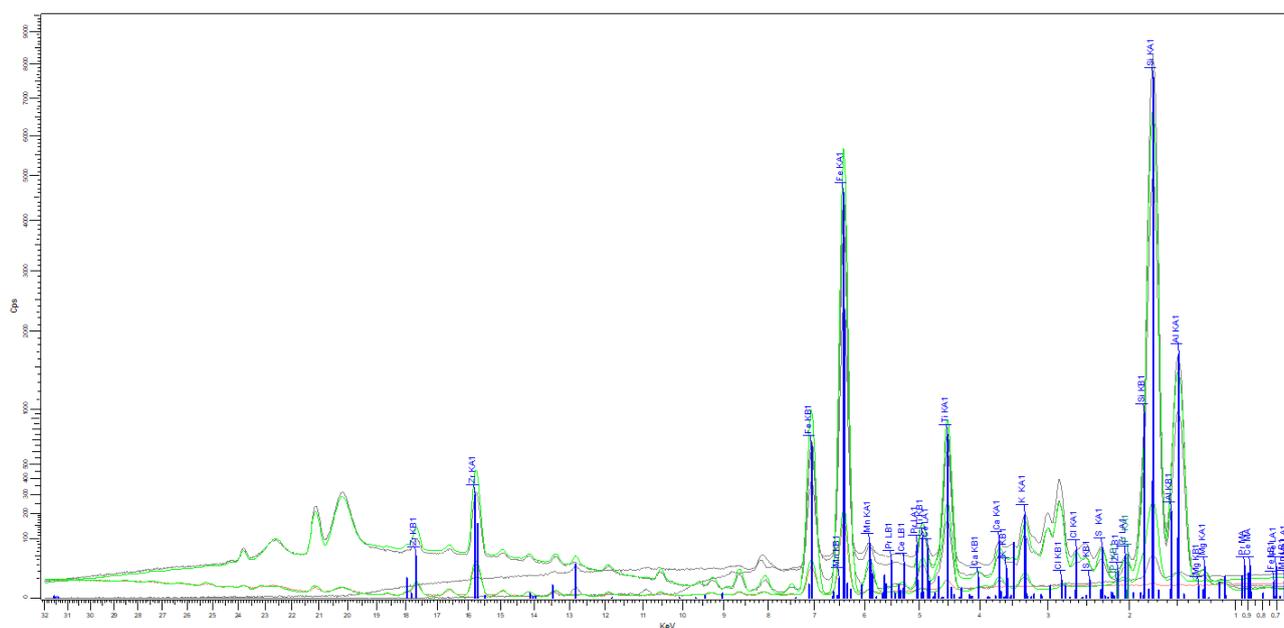
Source: The authors.

Figure 3: Espectral information for basaltic soil compressed in 5 t.



Source: The authors.

Figure 4: Espectral information for basaltic soil compressed in 15 t.



Source: The authors.

Influence of compression

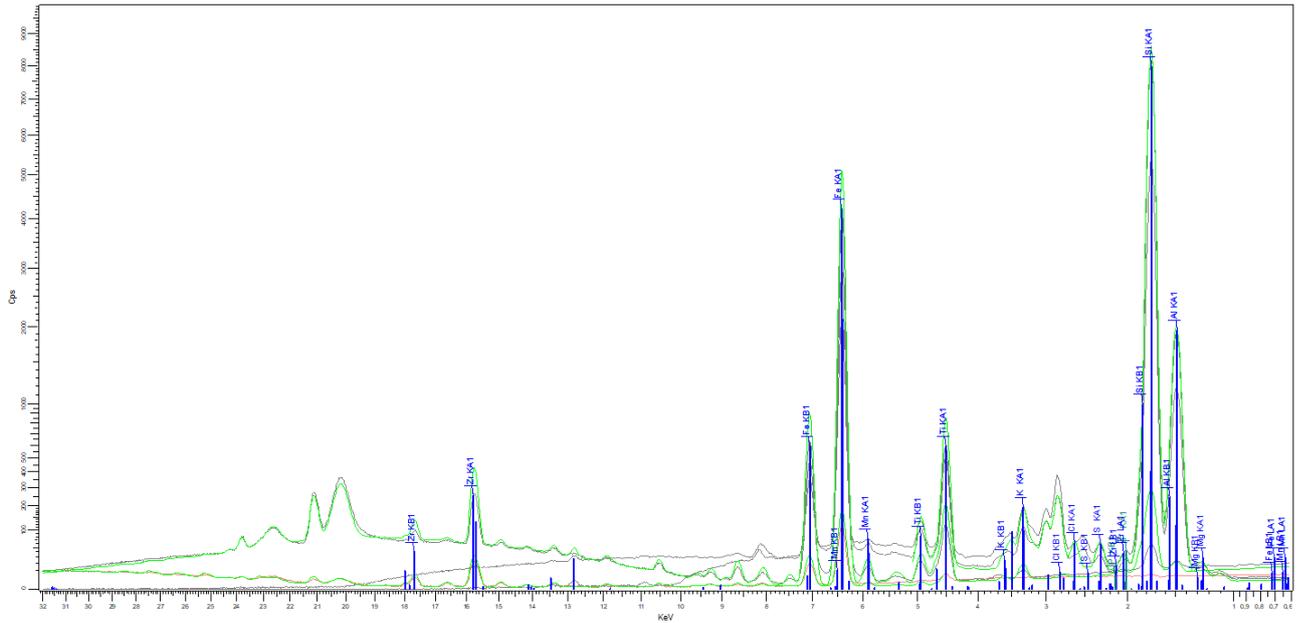
There was no significant variation between samples of the same parent material that were compressed (5 t, 10 t and 15 t). For MgO, SO₃ and P₂O₅ a significant difference between the percentages of oxides in uncompressed and compressed soil samples was observed (table 2).

The samples that were submitted to compression presented, in their majority, high coefficients of variation in comparison to the samples that were analyzed in the form

of powder. The compressed samples that presented lower coefficients of variation were those submitted to 10 t for basaltic soil and 15 t for sandstone soil (table 3).

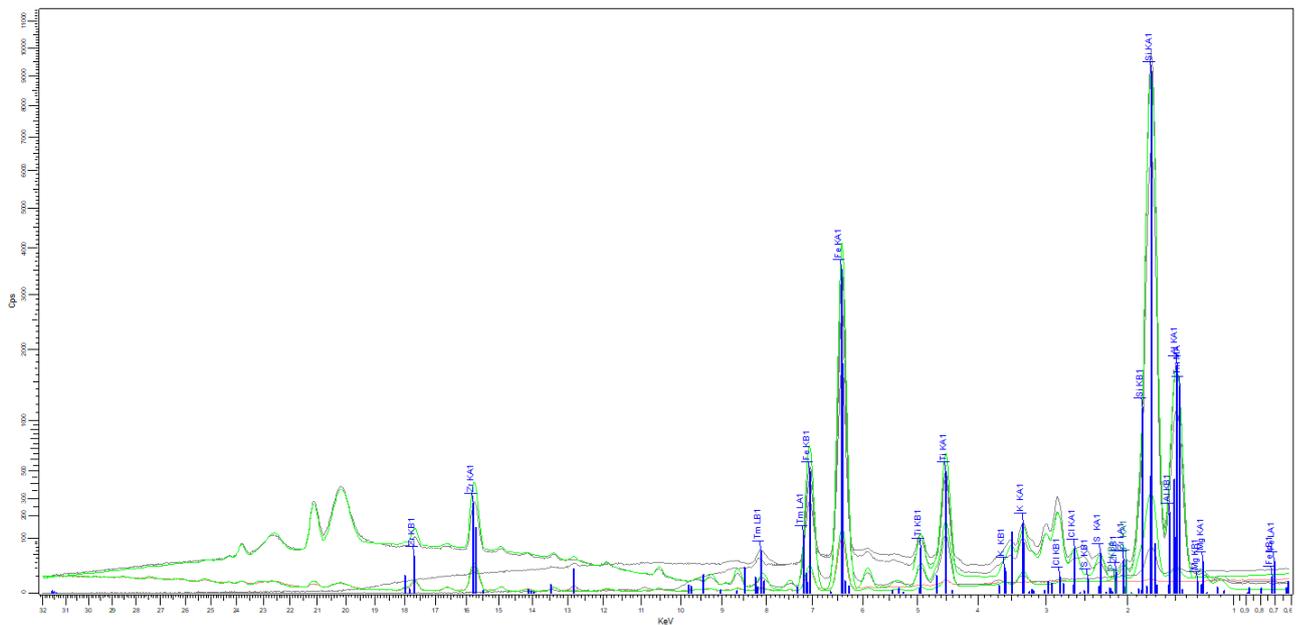
Also, all the treatments were compared through ANOVA test: among the compressed samples there was no significant difference. When the pellets (in all compressions) and the powder were compared they showed a great difference (table 4).

Figure 5: Spectral information for sandstone soil compressed in 5 t.



Source: The authors.

Figure 6: Spectral information for sandstone soil compressed in 15 t.



Source: The authors.

Discussion

XRF instrumentation allows the characterization of samples with a high degree of sensitivity in short time frames compared to other analytical techniques. Conciliated with chemometric studies, it provides better information on multivariate data (TERRA et al., 2010). Although the technique requires samples with uniform surface and homogeneous granulometry, the compression of the samples was not a significant factor for the determination of

the oxides contents in the same soil type ($p>0.05$). The difference between the oxides content of chemical elements between the samples of the two types of soil analyzed, especially the hematite contents (14.93% for basaltic soil and 7.35% for sandstone soil), indicates different mineralogical compositions as a function of material, which is a factor of significance when the variances between the triplicates of the soil pellets are analyzed. The basaltic soil has a greater granulometry in relation to the sandstone

Table 2: Percentage of oxides in relation to different compressions.

Oxides	Content in basalt (%)				Content sandstone (%)			
	0 t	5 t	10 t	15 t	0 t	5 t	10 t	15 t
SiO ₂	61.26	61.64	62.74	63.64	68.96	63.97	64.12	65.60
Al ₂ O ₃	16.75	20.96	20.69	20.48	19.47	23.16	22.81	22.00
Fe ₂ O ₃	14.93	11.54	10.98	10.38	7.35	8.72	8.38	8.66
TiO ₂	3.11	2.81	2.65	2.59	2	1.98	1.94	1.99
MgO	0.0	0.94	0.97	0.91	0.80	0.81	0.76	0.93
K ₂ O	0.66	0.66	0.61	0.61	0.50	0.60	0.59	0.61
SO ₃	0.75	0.39	0.36	0.36	0.18	0.26	0.27	0.34
P ₂ O ₅	0.88	0.20	0.18	0.22	0.11	0.15	0.16	0.19

Source: The authors.

Table 3: Coefficients of variation (%) – * stand for lowest variations.

Oxides	Content in basalt (%)				Content sandstone (%)			
	0 t	5 t	10 t	15 t	0 t	5 t	10 t	15 t
SiO ₂	0,0002	4,63	0,59*	2,9	0,0001	3,27	3,40	0,04*
Al ₂ O ₃	0,6933	8,22	2,29*	4	0,0149	6,02	5,00	0,66*
Fe ₂ O ₃	0,0003	7,05	0,77*	4,38	0,0002	7,82	8,81	0,76*
TiO ₂	0,0004	0,9	0,22*	0,47	0,0089	5,79	8,19	1,74*
MgO	0,0003	0,27	0,26	310E-17*	0,0007	12,5	6,66	3,09*
K ₂ O	7,77E-06	0,22	0,04*	0,1182	0,0115	5,51	4,90	0,17*
SO ₃	0,0018	0,12	0,28	0,1175*	0,0028	3,70	5,97	1,42*
P ₂ O ₅	0,0025	0,09	0,17	0,0556*	0,5792	3,76	5,88	1,49*
MNO	0	0,07	0,02*	0,0310	0,0071	0*	8,66	4,89

Source: The authors.

Table 4: ANOVA analysis (p values).

Oxides	Basalt pellets		Sandstone pellets	
	ANOVA	ANOVA	ANOVA	ANOVA
	(0, 5, 10 and 15 t)	(5, 10 and 15 t)	(0, 5, 10 and 15 t)	(5, 10 and 15 t)
SiO ₂	0.693331	0.6852	0.014993	0.0944
Al ₂ O ₃	0.000345	0.6335	0.000297	0.1121
Fe ₂ O ₃	0.00044	0.8804	0.008935	0.3171
TiO ₂	0.000387	0.7121	0.000786	0.5034
MgO	7.78E-06	0.3732	0.011509	0.5817
K ₂ O	0.001858	0.4920	0.002877	0.1976
SO ₃	0.002587	0.2007	0.579236	0.2544
P ₂ O ₅	0	0.4249	0.007187	0.1644
MNO	4.16E-07	0.7702	0.586718	0.0552

Source: The authors.

soil. Because it is considered a thinner soil, it was necessary to increase the compression of the samples to ensure results with low coefficients of variation, concentrated on the compression of 15 t. The basaltic soil, due to its higher degree of complexation given by the presence of clay minerals, presented lower coefficients of variation concentrated in the compression of 10 t. However, considering that soil

in powder form presented more satisfactory results in statistical analyzes, the factors that influence the results in the compressions become insignificant. These results allow to verify the potential of the XRF technique combined with chemometrics to simultaneously and rapidly determine the levels of several essential elements in soil (table 5).

The technique also denoted low cost compared to the traditional method (extraction by $H_2SO_{4(conc)}$ or $HF_{(conc)}$), lower risks to the analyst due to less exposure to high concentration chemical reagents, optimization of time and does not destroy the sample. The technique has its recognized potential for soil and sediment analysis and is adapted for environmental studies (USEPA, 2006).

Table 5: Chemical properties of the soil of Passo Fundo according to previous studies, in the form of powder and in the form of pellet (10 t), with XRF.

Oxides	Content in basalt (%)		
	SACHETTI, et al.(2014)	0 t	10 t
SiO ₂	70.52	61.26	62.74
Al ₂ O ₃	13.28	16.75	20.69
Fe ₂ O ₃	6.49	14.93	10.98
TiO ₂	0.97	3.11	2.65
MgO	0.84	0.0	0.97
K ₂ O	3.99	0.66	0.61
P ₂ O ₅	0.21	0.88	0.18
MNO	0.10	0.14	0.11

Source: The authors.

Conclusions

XFR can be considered as a low cost technique for determining major oxides in soil, in short time frames compared to other analytical techniques. The experiments demonstrated that the use of soil powder is the most appropriate form of sample introduction, meeting several statistical criteria (low standard deviation, low coefficient of variation, no significant difference between mediums), given that the incidence of X rays must comprise the highest amount of analyte in the sample. Still, it is always recommended to use adequate chemometric studies, that vary according to the amount of variables in each study, in conjunction with the XRF technique, to verify the reliability of the data obtained.

Acknowledgments

The authors would like to thank the Universidade de Passo Fundo for the support and professor Clóvia Marozzin Mistura.

References

ALLEONI, L. R. F.; IGLESIAS, C. S. M.; MELLO, S. C.; CAMARGO, O. A.; CASAGRANDE, J. C.; LAVORENTI, N. A. Atributos do solo relacionados à ad-

sorção de cádmio e cobre em solos tropicais. *Acta Scientiarum: Agronomy*, Maringá, v. 27, n. 4, p. 729-737, out./dez. 2005.

BARTH, J. A. C. et al. Mobility, turnover and storage of pollutants in soils, sediments and waters: achievements and results of the EU project AquaTerra. A review. *Agronomy for Sustainable Development*, Berlin, v. 29, n. 1, p. 161-173, 2009.

BRISOLA, D. F.; FERNANDES, T. L. A. P. Otimização no preparo de amostras para análise em espectrofotômetro de fluorescência de raios X. In: JORNADA DE INICIAÇÃO CIENTÍFICA, 16., 2008, Rio de Janeiro. *Anais...* Rio de Janeiro: CETEM, 2008. p. 202-208.

EMBRAPA - EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA. *Sistema brasileiro de classificação de solos*. 3. ed. Rio de Janeiro: Embrapa, 2013.

EPA - UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. Choosing the right procedure. In: _____. *SW-846: test methods for evaluating solid waste*. Washington, DC: Office of Solid Waste and Emergency Response, 2014. p. 46-87

GIASSON, E. Introdução ao estudo do solo. In: MEURER, E. G. *Fundamentos da química do solo*. Porto Alegre: Evangraf, 2012. p. in-fin.

IUPAC - INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY. Nomenclature system for X-ray spectroscopy: recommendations 1991. *Pure and Applied Chemistry*, Great Britain, v. 63, n. 5, p. 35-740, 1991.

JENKINS, R. X-ray techniques: overview. In: MEYERS, R. A. (Ed.). *Encyclopedia of analytical chemistry*. Chichester: Wiley, 2006. p. 13269-13288.

SACHETTI, A. S.; JIMÉNEZ ROJAS, J. W.; HEINECK, K. S. Caracterização geotécnica dos solos de Passo Fundo e Erechim, e geológica da rocha de Passo Fundo. *Revista de Engenharia Civil IMED*, Passo Fundo, v. 1, n. 1, p. 11-17, ago. 2014.

SBCS - SOCIEDADE BRASILEIRA DE CIÊNCIA DO SOLO. Comissão de Química e Fertilidade do Solo. *Manual de adubação e de calagem para os Estados do Rio Grande do Sul e de Santa Catarina*. Porto Alegre, 2012.

STRECK, E. V.; KÄMPF, N.; DALMOLIN, R. S. D.; KLAMT, E.; NASCIMENTO, P. C.; SCHNEIDER, P.; GIASSON, E.; PINTO, L. F. S. *Solos do Rio Grande do Sul*. 2. ed. Porto Alegre: Emater, 2008

TTERRA, J.; SANCHES, R. O.; BUENO, M. I. M. S.; MELQUIADES, F. B. Análise multielementar de solos: uma proposta envolvendo equipamento portátil de fluorescência de raios X. *Semina: Ciências Exatas e Tecnológicas*, Londrina, v. 35, n. 2, p. 207-214, jul./dez. 2014.

U. S. ENVIROMENTAL PROTECTION AGENCY. Chapter two: Choosing the right procedure. In: SW-846: Test Methods for Evaluating Solid Waste. Estados Unidos: órgão governamental, 2014, p. 46-87.

Received: July 26, 2018
Accepted: Nov. 18, 2018