

# Chemical characterization of clay SRM by X-ray fluorescence – results comparison from different laboratories

## Caracterização química de SRM de argilas por fluorescência de raios X – comparação de resultados de diferentes laboratórios

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### Abstract

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Two Energy Dispersive X-ray Fluorescence equipments have been compared in order to verify its performance for clay characterization and potential application to the study in archaeometric field and industry. Two clay standard reference materials (SRM), IPT-42 and IPT-51 and one IAEA intercomparison sample were analyzed by two different methodologies and equipments. Asentamiento Universitario Zapala laboratory has a Shimadzu EDX-800HS bench top equipment and 13 elements from S to Zr were quantified in the standards. Applied Nuclear Physics Laboratory has a portable EDXRF system. It was possible to quantify K, Ti and Fe and qualitatively to identify Mn, Rb, Zn and Zr.

**Key words:** X-ray fluorescence. Portable. Clay. Soil.

### Resumo

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Foram comparados dois equipamentos de Fluorescência de Raios X por Dispersão em Energia (EDXRF) de modo a verificar sua performance na caracterização de argilas e potenciais aplicações em estudos nos campos de arqueometria e na indústria. Dois materiais de referência padrão (standard reference materials – SRM) de argilas, IPT-42 e IPT-51 e uma amostra de intercomparação da IAEA foram analisados por duas metodologias e equipamentos diferentes. O laboratório do Asentamiento Universitario Zapala possui um equipamento de bancada Shimadzu EDX-800HS e quantificou 13 elementos nos padrões, do S ao Zr. O Laboratório de Física Nuclear Aplicada tem um sistema portátil de EDXRF, possibilitando quantificar K, Ti e Fe e identificar qualitativamente Mn, Rb, Zn e Zr.

**Palavras-chave:** Fluorescência de raios X. Portátil. Argila. Solo.

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## Introduction

Clays are rocks formed by very fine particles, smaller than 2  $\mu\text{m}$ , composed by minerals as montmorillonite, beidellite, nontronite, among others. It is frequent to find them in the nature associated to other minerals like feldspars, quartz, carbonates and micas.

These minerals are aluminosilicate that can be formed by two castrate tetrahedral and a central octahedral to which denominates: T-O-T (2:1) or T-O (1:1) (NEWMAN, 1987). Characteristic physicochemical properties of those sands turn them

thoroughly used in pharmaceutical industry, metallurgical, cosmetic and construction. They are also used for the discoloration and clarification of vegetables oils, as catalysts in different chemical processes, selectivity of heavy metals in contaminated fluids, in the production of paintings, grease, lubricant, plastics and in the oil refinement industry (BATEMAN, 1986).

Clays were also thoroughly used by ancient cultures for production of several pieces and decorations. The composition determination of ancient ceramic samples has a special relevance to the construction of models concerning the production and distribution of these materials in the past. Energy Dispersive X-Ray Fluorescence (EDXRF) is widely used for clay and ceramic measurement due to its non-destructive and multi-element analysis (ROLDÁN et al., 2004), (BONA et al., 2007), (AKYUZ et al., 2002). Therefore, the use of this methodology as analytical techniques in analyses of samples archaeological is frequent. So, the aim of this study was to verify the performance of two EDXRF equipments for clay characterization and to assure the validity of the analytical results.

Another objective was to promote the integration and experiences changes of two laboratories: Asentamiento Universitario Zapala, Facultad de Ingeniería at Zapala-Neuquén, Argentina and Applied Nuclear Physics Laboratory at Londrina, Brazil.

Two clay standard reference materials (SRM), IPT-42, IPT-51 and one IAEA intercomparison sample were analysed by two different methodologies and equipments.

## Experimental

### *Samples*

Were analyzed two Standard Reference Materials: São Simão clay, code IPT-42; Si-Al refractory, code IPT-51 and one IAEA intercomparison clay sample. The samples were prepared in the form of pressed powder pellets with 15 mm of diameter at 15 T consisting of 500 mg of  $\text{H}_3\text{BO}_3$  as binder and 500 mg of sample, which were homogenized for 15 minutes and 1g were obtained for measurements. Three pellets of each sample were obtained. The moisture of each sample was determined at 40°C for 60 h and all the concentration values are presented for dry mass.

Due to the work methodology of fundamental parameters for the bench top equipment, it was necessary to accomplish a conventional technique for  $\text{CO}_2$  quantification.

### *Instrumentation and Quantification Methodology*

Asentamiento Universitario Zapala laboratory has a Shimadzu EDX-800HS bench top equipment with a Rh anode X-ray tube and a Si(Li) detector. The measurements were performed in vacuum atmosphere. It was used fundamental parameters methodology for quali-quantification. The measurements were performed in two channels, Ti/U at 50kV, 13 $\mu\text{A}$  with excitation time of 98 seconds and Na/Sc at 15 kV, 202 $\mu\text{A}$  for 99 seconds. The incident beam had 10mm collimation.

Applied Nuclear Physics Laboratory has a portable EDXRF system, although all the measurements were performed in laboratory. The measurement system comprises a Si-PIN detector (221 eV FWHM at 5.9 keV and 25  $\mu\text{m}$  Be window),

coupled to a pre-amplifier, both thermoelectrically cooled, a high voltage source with amplifier, MCA Pocket multichannel analyzer and a notebook for data acquisition and evaluation (AMPTEK, 1998). The samples excitation were done with a mini X-ray tube (Ag target, 4 W) (MOXTEK, 2003) and the analysis were carried out with the tube working at 28kV and 10 $\mu$ A. Additionally, on the tube, a silver filter with 50 $\mu$ m was used. The beam was collimated with a silver cylinder with 3.0 millimeters of diameter aperture on detector and the irradiation time was 500 seconds. Four multi-elements Standard Reference Materials of soil and

clay were used for system calibration (Soil 7, Sarm 69, Plastic clay IPT-32 and Pará clay IPT-28). They were measured in pellet form, prepared just as the samples.

## Results

For the portable system it was constructed calibration curves from the intensity results of each standard. It was possible to quantify K, Ti and Fe with accuracy. The detection limits were 0.099%, 0.007% and 0.002% respectively. The calibration equations are presented at Table 1. Qualitatively was verified the presence of Mn, Rb, Zn and Zr.

**Table 1.** Calibration equations with its respective determination coefficient (R<sup>2</sup>). I is the net intensity(cps) and C the concentration (%).Número de operações

Element	Equation	R <sup>2</sup>
K	$I = 4.54 C + 0.72$	0.974
Ti	$I = 51.23 C - 6.63$	0.879
Fe	$I = 206.79 C + 12.75$	1.000

Table 2 presents the results for the IAEA intercomparison sample. 13 elements were quantified with the conventional equipment, although the relative deviation was bigger than 6%, with the majority of the elements around 20%. For the portable equipment, it was possible to identify Zn, Rb e Zr and to quantify Fe, K e Ti with relative deviation smaller than 10%.

For IPT-42 sample 10 elements were evaluated, according to Table 3. Vanadium and Zr were quantified by the bench top system and identified in the portable one. Therefore they were not listed in the standard certificate.

Table 4 shows IPT-51 results, with quantification of 9 elements. Again, V was quantified but not listed in the standard certificate.

In general, the obtained results of the Shimadzu EDX-800HS bench top equipment, showed in the Table 2, 3 and 4, present relative deviations from -10% to 58% for the majority elements (Si, Al, Fe, Ca, K, Mg, Ti), in comparison with the certified values, this deviations could be considered acceptable keeping in mind the work methodology for fundamental parameters. It is necessary to highlight that the biggest deviations are given in the elements presents in less than 1%, so that these deviations neither are very significant. In other hand, trace elements (S, V, Zn, Rb e Zr) were quantified without any inconvenient.

For the portable equipment, K, Fe and Ti were quantified, and discarding one measurement for K, all the other results have relative deviation under  $\pm 20\%$ , what can be considered very good. Zinc, Rb and Zr were identified qualitatively.

**Table 2.** Concentration results for IAEA intercomparison sample.

Element	Certified values	Bench top equipment	Relative deviation*	Portable equipment	Relative deviation*
	[%]	[%]	[%]	[%]	[%]
Si	25.3±0.5	23.30±0.05	8%		
Al	11.09±0.60	12.75±0.05	15%		
Fe	4.99±0.16	4.25±0.01	15%	5.03±0.12	-1%
Ca	0.218±0.016	0.177±0.006	19%		
K	1.960±0.076	1.448±0.013	26%	1.91±0.53	3%
Mg	0.859±0.002	0.908±0.028	-6%		
Ti	0.595±0.020	0.652±0.008	-10%	0.66±0.13	-10%
	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]
S	1504±330	962±41	36%		
Na	4730±687	955±45	80%		
V	167±30	230±6	-38%		
Zn	166.2±5.7	145±5	13%	Identified	
Zr	176.7±9.0	118±7	33%	Identified	
Rb	138.7±5.9	110±9	21%	Identified	

\*related to the certified value.

**Table 3.** Concentration results for IPT-42, Standard Reference Material sample.

Element	Certified values	Bench top equipment	Relative deviation*	Portable equipment	Relative deviation*
	[%]	[%]	[%]	[%]	[%]
Si	23.87±0.05	21.40±0.01	10		
Al	17.03±0.01	19.78±0.02	-16		
Fe	0.76±0.03	0.634±0.010	1	0.76±0.04	-0.3
Ca	0.036±0.007	0.015±0.005	58		
K	0.390±0.004	0.346±0.004	11	0.37±0.11	5
Mg	0.115±0.012	0.339±0.029	-196		
Ti	0.719±0.024	0.616±0.008	14	0.66±0.14	-14
	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]
Na	148±74	29.6±21	80		
V		263.2±24			
Zr		74±26		Identified	

\*related to the certified value.

**Table 4.** Concentration results for IPT-51, Standard Reference Material sample.

Element	Certified values	Bench top equipment	Relative deviation*	Portable equipment	Relative deviation*
	[%]	[%]	[%]	[%]	[%]
Si	25.30±0.05	24.81±0.13	2%		
Al	21.32±0.05	22.01±0.03	-3%		
Fe	0.83±0.02	0.762±0.006	8%	0.706±0.017	15%
Ca	0.0429±0.007	0.034±0.007	22%		
K	0.58±0.03	0.50±0.08	13%	0.176±0.050	69%
Mg	0.121±0.006	0.132±0.02	-9%		
Ti	1.64±0.02	1.62±0.02	1%	1.05±0.22	20%
	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]	[mg Kg-1]
V		521±51			
Zr	518±96	215±10	59%	Identified	

\*related to the certified value.

## Conclusions

Comparing the results obtained for Shimadzu EDX-800HS bench top equipment with the portable one, it can be noted that both equipments present satisfactory results comparatively. To improve the results of the bench top equipment it is necessary the use of calibration curves. For the portable equipment the results can be considered very satisfactory, since relative deviation around 30% can be considered accurate when using portable EDXRF systems (KUMP; NECEMER; RUPNIK, 2005). In other hand, just three elements were quantified.

For the samples IPT-51 and IPT-42, elements were identified that are not presents in the standards certificates, it was the case of V and Zr.

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