RADIATION IN ARCHAEOMETRY APPLIED TO TAQUARY VALLEY

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ABSTRACT

In the present work, soil and archaeological ceramic samples from one archaeological site located in Taquari Valley, (Lajeado, RS), were investigated. Ceramics pottery fragments were dated using thermoluminescence method and analyzed by mass spectrometry. The samples were grounded, sieved, and then divided in two: a) the fraction with lower grain size diameters was used in the chemical analysis, b). the portion with intermediate size grain diameter was chemically leached, submitted to different doses and then finally the thermoluminescence was measured. The ages obtained varied from 385 up to 926 years BP. The chemical analysis of soil and ceramics was made using ICP-MS (Plasma Mass Spectrometry) analytical technique. The ICP-MS determination was performed in the solubilized samples. For solubilization of each sample it was used a microwave-assisted digestion technique. Mn ,Fe, Al, Ca, K, Ti, Mg, Na, Cr, V, Ni, Zn, Pb, Li, Cu, La, Ce, Th, U, Sr and Ba have been determined in the studied samples. To guarantee the analytical performance a series of certified reference materials were used (IAEA-Soil 7, and GSJ- JG1a, JA-3, JB2 and JB-3). The ICP-MS data treatment using hierarchical cluster analysis with the squared Euclidean distances was used to calculate dissimilarities between samples. In the resulting dendrogram, the distinct groups of samples were evidenced.

1. INTRODUCTION

In archaeometry the radiations play an important role in two aspects: (1) first they are used in dating archaeological substances, (2) second to assess chemical elements in ceramics and soil. Of course, the natural radiation is also very important since it induces point defects to be used in Thermoluminescence as well as Electron Paramagnetic Resonance dating.

The research in archaeometry appeared around 1960, with extensive use of analytical methods for the characterization of objects of art, archaeological and cultural heritage. In theory, every vessel carries a chemical compositional pattern identical to the clay from which

it was made and this relationship is the basic of the provenance studies, also known as archaeometry. The reasoning behind provenance or sourcing studies is to probe into the past and attempt to re-create prehistory by obtaining information on exchange and social interaction [1]. However, in Brazil until the early 1990s, the archaeological studies were related only to archaeological dating using physical methods [2]. Due to the potential of the area, the wide range of applications and their characteristics involving multidisciplinary art and science, this area has, in recent years, gaining prominence in the surveys conducted by various Brazilian researchers groups.

The basic premise for using chemical composition analysis, on ceramics or in any other sample, is that the samples can be differentiated if the analytical technique, with a good sensitivity, precision and accuracy is used. If an element is not measured with good precision, it may obscure real differences in concentration and, the discriminating effect of other well-measured elements tends to be reduced. These small differences can be used to form groups of similar composition.

The determination of the analytic precision is of great importance and must be quantified. Precision is related to the capacity that the method has to reproduce the same result. The precision limitations can result from the sample inadequate preparation, either due to contamination with the same element that we want to determine, or due to in-homogeneities problems.

The determination of all analytical parameters must be measured and quantified to make corrections before applying the method in real samples, because these small variations may affect the power capacity to distinguish between the sample groups.

There are several robust analytical techniques that can be used to assess chemical elements in ceramics and soil, such as the X-ray fluorescence spectrometry (XRF) [3], the atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICPOES) [4], the plasma mass spectrometry (ICP-MS) [5] and instrumental neutron activation analysis (NAA) [6], and so on. Each one of these techniques presents its potential and limitations in current analysis [7]. For instance, only some of them have no restrictions related to the number of elements that can be determined simultaneously or to the linear dynamic range of response. It means it is possible to perform in a single sequence analysis, determination of elements present in very low levels (µg/kg) and in higher levels (% mass). Regarding to the archaeometry investigations, it is highly important that the chemical analysis must be rigorously done. In this work, ICP-MS was chosen as the analytical technique once it fulfills completely the analytical performance need for archaeometry purposes.

The plasma mass spectrometry is an analytical tool which gaseous ions generated in the source of ions are introduced into the mass spectrometer and separated according to the ratio mass/charge, during transport, under action of electric and magnetic fields that alter their trajectories. Several ions sources are used in mass spectrometry, including inductive coupled plasma (ICP). The plasma mass spectrometry (ICP-MS) offers a number of advantages: high frequency analysis, the possibility of determination of a wide range of elements, including elements with high ionization potential, feasibility of isotopic determination ratios and the broad linear dynamic range.

In order to have additional information about the material analyzed, the samples were also dated using the Thermoluminescene (TL) method [8]. In order to have the age of sample using TL method as dating technique it is necessary to determine the annual dose (D_{an}) and the accumulated dose (D_{ac}). For dating the ceramic the following expression is used:

$$Age(yrs) = \frac{D_{ac}}{D_{an}} \qquad (1)$$

The extrapolation of the curve (straight) of TL intensity versus dose determines the intersection with the axis of doses, i.e. the dose that sample had received while was underground. This dose is called the accumulated dose, Dac, or equivalent dose, Deq. The method used for determining Dac was the additive method [9].

In practice, normally it is also collected at least one soil sample, where the pottery was withdrawn. Once there are two main sources of ration in the pottery: a) the radiation resulting from the disintegration of radioactive elements (uranium, thorium and potassium) contained in the pottery, and b) irradiation from the soil, which surrounds the ceramic. The α, β and γ rays from radionuclide present in the ceramic undoubtedly contribute to Dan. In terms of the external radiation only γ rays are significant once α rays have a low penetration, and therefore it is not strong enough to achieve the quartz grains inside the ceramic. The knowledge of the annual dose, or rate of the natural radiation with the ceramics was irradiated, for obvious reasons, it is crucial. There are several methods to calculate Dan, in this study the Ikeya [9] tables 4.3 and 4.4 of (1993, pp 109 e110) were used. For using these tables, it is necessary to have uranium, thorium and potassium concentrations. This information was obtained through the ICP-MS analysis.

2. OBJECTIVE

The main purpose of this work of archaeometry research is, like all others archeometry studies, through chemical elements pattern, to establish a correlation between samples and later one to "define" a fingerprint to the Taquari Valley archaeological site, i.e. to discover the original provenance of each artifact found. This information is helpful to the archaeologists to understanding the past traditions of the ancient cultures.

3. EXPERIMENTAL

2.1. Materials and Methods

Soil samples and ceramics fragments from four archaeological sites located in Taquari Valley, (Lajeado, RS), were collected. The site location is in the figure 1. The samples were identified by numbers (1558, 1559, 2439, 2364, 3751) and these numbers refers to the soil layers, once each sample was buried on different depths, they were also found on the different distances from the river course despite, all samples having been collected on the same sampling site and near each other.

Figure 1. Location of the Lajeado on Taquari Valley (Brazil-RS)

3.1.1. Sample preparation and analysis

3.1.1.1. Thermoluminesce analysis

Each ceramic fragment was cleaned, broken and sprayed, in a dark room, very careful to avoid to triboluminescence effect, and then sieved to retain only the desired grain size. Samples with grain size lower than 0.08mm were separated for chemical analysis by plasma mass spectrometry (Elan Perkin Elmer 6100). In this fraction potassium, uranium and thorium levels were determined for the subsequent determination of the annual dose rate.

Around 700 mg of sample with size diameter between 0.088 mm and 0180 mm was chemically treating with HCl solution (37% v/v) for forty minutes. Then, it was treated with a HF solution (10% v/v). It is important to note that between the chemical treatments the sample was leached with purified water (Ω 18MOhm) to eliminate up completely all the acidity of the medium. The residue was on standby for about 48 hours to dry completely. Then, each sample was split into several parts, and each portion was irradiated with doses of 10, 20, 30 and 40 Gy, in a type irradiator GAMACELL with dose rate of 2.98 kGy/h (Jan 2007), installed in CTR-Centro de Tecnologia of Radiação - IPEN/SP. The thermoluminescence measurements were performed using a TL reader (model 110 Daybreak Automatic System), with heating rate of 10^{0}C/s, in order to obtain the curve of TL intensity versus dose, with the objective to know the cumulative dose.

3.1.1.2. ICP-MS analysis

All sub-samples, with grain size diameter lower than 0.080mm, were once more homogenized (grounded and ultrasonic sieved) and digested in acid mixture solution (nitric acid and fluoridric acid – 5:2) with a closed microwave-assisted furnace (DGT 100 plus – Provecto Analitica) and analyzed using a quadrupole ICP-MS system (ELAN Perkin Elmer 6100). The elements determined quantitatively were Mn, Fe, Al, Ca, K, Ti, Mg, Na, Cr, V, Ni, Zn, Pb, Li, Cu, La, Ce, Th, U, Sr and Ba. The element selection was based on the fact Brazil soil is rich on silicates and these elements are the silicates main and micro components. Once it was not expected the chemical composition of the samples to be the

same then, a robust ICP-MS analytical program was developed and for that gravimetric reference solutions, prepared from the dilution of each mono-element Spex® stock solution, were used to obtain the individual analytical curves. It was also prepared synthetic matrix solutions to evaluate the matrix effect. A series of four GSJ geological certified reference materials (JG1a, JA-3, JB2 and JB-3) and one soil certified reference material (IAEA Soil 7) were also analyzed to performance the analytical method developed.

To evaluate the analytical process and establish which chemical elements could be used in the data interpretation, a statistics comparison between the real and theoretical elemental concentrations of the certified reference material IAEA-Soil-7 Trace Elements in Soil was done. Mn, Fe, Al, Ca, K, Ti, Mg, Na, Cr, V, Ni, Zn, Pb, Li, Cu, La, Ce, Th, U, Sr and Ba data presented good precision and were used in subsequent studies.

3. RESULTS AND DISCUSSION

3.1. Thermoluminescence results

In the table 1 the ages of each sample analyzed is presented. It is important to mention this data were obtained after the determination of annual and accumulated dose as previously mentioned.

Table 1. Ages (years) of Ceramics Fragments Studied

Sample	1558	1559	2439	2364	3751
Age (years BP)	630 ± 68	926 ± 89	606 ± 45	558 ± 78	385 ± 46

3.2. ICP-MS results

The ICP-MS results are presented in the table 2 and in the table 3. These data are average of three replicates of each sample. The standard deviation of each measurement is around 15% for higher concentrations (%) and around 5% for lower concentrations (µg/g).

In order to check the accuracy and also precision of the data F test and also Anova test were applied and these tests had shown the samples are not statically different once there is no any discrepancy. For further details about F test and Anova test consult Levine at all [10]

Table 2. Chemical Composition (% mass) obtained by ICP-MS analysis

Sample Element	1558	1559	2439	2364	3751
Mn (%)	0.11	0.03	0.44	0.26	0.32
Fe (%)	8.62	3.35	11.69	7.54	9.36
Al (%)	1.42	0.86	15.54	10.69	10.70
Ca (%)	4.49	1.41	7.39	4.00	3.50
K (%)	1.15	1.44	1.19	1.24	0.91
Ti (%)	1.45	1.81	2.85	1.04	1.49
Mg (%)	4.82	5.77	5.85	0.08	3.78
Na (%)	0.30	0.31	0.08	0.22	0.53

Table 3. Chemical Composition (µg/g) obtained by ICP-MS analysis

Sample Element	1558	1559	2439	2364	3751
Cr	57.48	93.49	89.49	86.23	61.76
V	10.78	27.13	9.20	17.30	26.59
Ni	7.06	14.71	34.01	14.32	31.55
Zn	78.73	59.90	114.97	56.33	50.90
Pb	150.95	303.63	82.33	69.52	108.71
Li	44.54	114.92	56.41	146.39	83.44
Cu	79.07	131.06	7.40	111.39	150.73
La	7.10	15.80	17.92	19.19	12.41
Ce	35.07	14.11	46.61	21.87	63.53
Th	9.90	14.73	25.02	6.83	3.66
U	11.99	17.28	9.39	5.93	17.50
Sr	21.97	12.09	34.24	16.06	15.49
Zr	126.42	296.66	68.64	409.11	184.20

Initially, the results were transformed to log base to compensate the differences between the trace elements and the macro elements. The log base transformation of data before a multivariate statistical method is common. One reason for this is a belief that, within the raw

materials of manufacture, elements have a natural log-normal distribution, and that normality of the data is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variables and would thus give them approximately equal weight in an un-standardized multivariate statistical analysis.

After that, the data set were studied by cluster analysis because is an efficient statistical method for examining the relations between samples by means of the similarity or dissimilarity among the samples. Figure 2 shows the dendrogram of the samples using Ward linkage and squared-mean Euclidean distance.
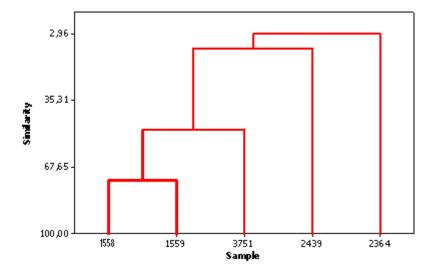

Figure 2. Dendrogram with Ward linkage and squared Euclidean distance for the samples 1558, 1559, 3751, 2439 and 2364.

Preliminary studies of the samples showed clearly that the soil samples 1558 and 1559 have similar chemical composition pattern, indicating probably both samples were made from soil arriving from the same location. Moreover is possible to see also that the samples 2439, 2364 and 3751 have different chemical composition pattern indicating the soil used to make the ceramic was collected from a different place from those of 1558 and 1559,.

4. CONCLUSIONS

The data treatment by hierarchical cluster analysis the squared Euclidean distances was used to calculate dissimilarities between samples. In the resulting dendrogram were evidenced the distinct groups of samples that have different chemical composition pattern indicating different raw materials were used for making the ceramics, once the sample 2364 has very little similarity with some other samples as 1558 and 1559, indicating maybe the site where it was found it is not the its original provenance site.

ACKNOWLEDGMENTS

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