# Second Research Co-Ordination Meeting of the Co-Ordinated Research Programme on Nuclear Analytical Techniques in Archaeological Investigations

## Characterization of Brazilian Prehistoric Ceramics

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**Radiochemistry Division**

**Instituto de Pesquisas Energéticas e Nucleares**

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**Dr. Casimiro S. Munita**

**Dra. Márcia A. Alves**

**MSc. Rosemeire P. Paiva**

**Érika F. Momose**

## INTRODUCTION

Ceramic chemical composition characteristics play an important role in the study of ceramic (1,2). It is well established that pottery can be grouped based on similarities or dissimilarities derived from chemical data (2,3). A more ambitious goal is the chemical "fingerprinting" of pottery representating a long period of time (e.g. 5000 BC to AD 1000) and a wide geographical area (e.g. Mediterranean) allowing potential sources for "unknowns" or "foreingnware" to be identified (3,4). This goal requires not only a large chemical data base but also that elements useful for identification purposes be recognized and that statistically robust methods of discriminating pottery be developed.

Several authors used Instrumental Neutron Activation Analysis, INAA, as the technique convenient for ceramics materials, because it combines great analytical sensitivity with relatively small sample, allowing the simultaneous determination of several elements in a large range of concentration, without any chemical treatment (5-7). Nevertheless, as for other analytical methods, error risk are present at each step of the analytical process, from the sampling up to the interpretation of results. Moreover, for provenance studies, it is necessary to increase both sensitivity and accuracy to obtain the largest possible number of determinations with an analytical dispersion lower than the dispersion due to the differences of ceramic provenance.

The aim of this research is to characterize by means of inorganic elements, the Brazilian pre-historical ceramic origin as potential indicators of the indian culture. The data obtained will help archaeological studies already made in the region with the objective of making spatial, temporal and cultural reconstruction of this time.

Samples of two sites, Água Limpa and Prado, were collected. The ceramic found were associated to food preparation, funeral urns and decorative uses. The

funeral ceramics were associated to primary buring (in foetal position) into covered ceramic urns. Both sites are superficial with an unique stratigraphic level (litho-ceramic) located in the intermediary part of an hill with a water course in its inferior part. More details about the archaeological studies already accomplished in the sites and sampling procedure were given in the First Progress Report (8).

As agreed in the first research co-ordination meeting (CRP) in Washington, USA, from 23-26 June 1997, the results of the intercomparison exercise using Brick Clay, NIST-SRM-679, Ohio Red Clay and Blind sample are presented in this report. The results obtained for 90 ceramics fragments from Água Limpa site are also included.

## EXPERIMENTAL

### Sample Preparation

Sample for NAA were obtained from ceramic fragments by cleaning an area with tungsten carbide rotatory file attached to the end of a flexible shaft, variable speed drill. Depending on thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls. Finally, the powered samples were dried in an oven at 105°C for 24 h and stored in a dissecator.

### Standard and Check Sample Preparation

Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1) were used as standards, and Brick Clay and Ohio Red Clay were used as check samples in all analysis.

These materials were dried an oven at 105°C for 24 hours and stored in dissecator until weighed.

**Method**

The INAA procedure described in the previous Report (8) consists of four stages:

1.-About 100 mg of ceramic samples, Brick Clay, Ohio Red Clay, Buffalo River Sediment and Coal Fly Ash were weighed in polyethylene bags and involved in aluminium foil.

2. Groups of 6 ceramic samples and one of each reference material were packed and irradiated in the swimming pool research reactor, IEA-R1m at a thermal neutron flux of about $5 \times 10^{12}$ n $cm^{-2}$ $s^{-1}$ for 8h.

3. As, Ba, K, La, Lu, Na, Nd, Sm and Yb were measured after 7 days cooling time and Ce, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Tb, Th, Zn and U after 15 days.

4.- Computer data processing and calculation of the elemental concentrations.

**Equipment**

The measurement were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of $^{60}Co$, with S-100 MCA of Canberra with 8192 channels.

The analysis of gamma ray spectra are made by means of the Vispect II software, developed by Dr. D. Piccot, Saclay, France.

## RESULTS AND DISCUSSION

### Intercomparison and Quality Control

During the last meeting in Washington, all participants received three different materials: Brick Clay (NIST-SRM-769), Ohio Red Clay and a Blind sample. In Tables 1, 2 and 3 the results and their estimated lower detection limit are presented.

INAA procedure was controlled by means of the analysis of Brick Clay and Ohio Red Clay irradiated in each group of six samples for quality control purposes. Standard Reference Materials, SRMs, are indispensable tools for verifying the validation of analytical procedures in quality assurance programs.

The results of twenty four elements are presented in Tables 4 and 5. In these Tables mean, standard deviation (SD) and relative standard deviation (RSD %) are also presented. The results were compared with values obtained from literature (9-12). For both materials the precision for most elements was around 5% (As, Ce, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sb, Sc, Th) and only for Ba, Nd, Sm, Ta, Tb, U, Yb and Zn was around 10%. The interference of $^{235}U$ fission in the determination of La and Ce was negligible. The determination of Zn is not reliable by the strong gamma ray interferences of $^{46}Sc$ and $^{182}Ta$. For most elements observed values agree with certified or published ones.

The method was also applied to 90 ceramic fragments from Agua Limpa site. The result are presented in Table 6.

## CONCLUSION

As mentioned in the First Progress Report (last year plan), during the second year of the project the analytical procedure was applied in 90 ceramic fragments of Água Limpa site. The data obtained are being studied and submitted to cluster and principal component analysis. Cluster analysis expresses the similarity of samples without previous knowledge of their provenance. The principal component analysis brings out the correlations between different samples and identifies the most important elements to characterize each provenance.

For quality control the analytical method was validated by the analysis of Brick Clay and Ohio Red Clay carried out with each group of six samples. The results showed that the systematic error in determining 24 certified elements was lower than 10%.

## Future Plan Work

Next year the analysis of the ceramic samples from Prado site and repetition of whole validation procedure with standard reference materials will be carried out. Ceramic fragments from Rezende site will also be analyzed with the purpose to compare the chemical composition from three sites (Água Limpa, Prado and Rezende).

## Papers Presented at Congress

1. Potencialidades da Análise por Ativação com Nêutrons Instrumental em Estudos de Cerâmicas Arqueológicas, which will be presented at the VII General Conference on Nuclear Energy, Belo Horizonte, Minas Gerais, Brazil, October 27-30, 1998

2. Chemical Characterization of Brazilian Ceramics using INAA and their Cultural Implications, presented at X International Conference on Modern Trends in Activation Analysis, NIST, USA, April 19-23, 1999

3. Caça, Coleta e Pesca entre Horticultores-Ceramistas de Água Limpa, Monte Alto, São Paulo. IX Reunião Científica da Sociedade de Arqueologia Brasileira, Rio de Janeiro, Brasil, 23-29, 1997

**Paper Published**

1. Estudo de Cerâmica Pré-Histórica no Brasil: das Fontes de Matéria-Prima ao Emprego de Microscopia Petrográgica, Difratometria de Raios X e Microscopia Eletrônica, CLIO 1(12), 27-86, 1997.

2. Metodologia e Técnicas de Campo Aplicáveis em Sítios de Horticultores Ceramistas.MAE/FAPESP, Suplemento I, 49-52,1997.

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Table 1. Results obtained for Brick Clay in the intercomparison exercise, in μg $g^{-1}$, unless indicate.

| Element | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | DL |
|---|---|---|---|---|---|---|---|
| As | 8.6 ± 0.2 | 9.0 ± 0.1 | 8.8 ± 0.1 | 7.9 ± 0.2 | 8.7 ± 0.1 | 7.7 ± 0.2 | 0.15 |
| Ba | 492 ± 156 | 524 ± 112 | 420 ± 85 | 425 ± 78 | | | 74 |
| Ce | 108.1 ± 0.6 | 101.4 ± 0.9 | 90.8 ± 0.8 | 103.9 ± 0.5 | 101.2 ± 0.9 | 97.7 ± 0.6 | 0.8 |
| Co | 24.2 ± 0.2 | 25.7 ± 0.2 | 24.7 ± 0.2 | 24 ± 0.2 | 25.5 ± 0.2 | 22.4 ± 0.1 | 0.1 |
| Cr | 102 ± 1 | 104 ± 2 | 95 ± 2 | 100 ± 1 | 102 ± 2 | 93.0 ± 0.9 | 2 |
| Cs | 9.7 ± 0.2 | 9.7 ± 0.2 | 9.4 ± 0.2 | 9.2 ± 0.2 | 9.8 ± 0.2 | 8.6 ± 0.2 | 0.3 |
| Dy | 6.2 ± 0.5 | 5.4 ± 0.3 | 5.4 ± 0.3 | 6.1 ± 0.2 | 5.2 ± 0.2 | 5.7 ± 0.2 | 0.34 |
| Eu | 1.74 ± 0.04 | 1.65 ± 0.04 | 1.57 ± 0.04 | 1.75 ± 0.03 | 1.61 ± 0.05 | 1.62 ± 0.03 | 0.03 |
| Fe, % | 10.5 ± 0.1 | 9.1 ± 0.1 | 9.0 ± 0.1 | 10.4 ± 0.1 | 9.0 ± 0.1 | 9.8 ± 0.1 | 0.02 |
| Hf | 4.4 ± 0.1 | 4.3 ± 0.2 | 4.4 ± 0.2 | 4.4 ± 0.1 | 4.3 ± 0.2 | 4.0 ± 0.1 | 0.2 |
| K, % | 2.2 ± 0.2 | 2.32 ± 0 06 | 2.33 ± 0.06 | 1.9 ± 0.1 | 2.27 ± 0.06 | 2.1 ± 0.2 | 0.02 |
| La | 44.7 ± 0.5 | 44.0 ± 0.5 | 44.5 ± 0.5 | 43.0 ± 0.5 | 42.8 ± 0.5 | 41.5 ± 0.5 | 0.05 |
| Lu | 0.51 ± 0.01 | 0.51 ± 0.01 | 0.49 ± 0.01 | 0.49 ± 0.01 | 0.52 ± 0.01 | 0.46 ± 0.01 | 0.02 |
| Mn | 1650 ± 47 | 1633 ± 38 | 1587 ± 37 | 1566 ± 37 | 1645 ± 38 | 1613 ± 36 | 1 |
| Na | 1214 ± 23 | 1154 ± 8 | 1142 ± 9 | 1130 ± 21 | 1131 ± 9 | 1137 ± 23 | 2 |
| Nd | 43 ± 4 | 36 ± 5 | 45 ± 6 | 37 ± 3 | 35 ± 3 | | 6 |
| Rb | 192 ± 5 | 188 ± 8 | 178 ± 8 | 188 ± 4 | 196 ± 8 | 180 ± 4 | 9 |
| Sb | 0.99 ± 0.03 | 0.87 ± 0.03 | 0.96 ± 0.04 | 0.91 ± 0.02 | 0.87 ± 0.03 | | 0.3 |
| Sc | 21.0 ± 0.1 | 22.0 ± 0.2 | 21.6 ± 0.2 | 20.7 ± 0.1 | 21.9 ± 0.2 | 19.4 ± 0.1 | 0 03 |
| Sm | 8.36 ± 0.02 | 8.07 ± 0 02 | 8.11 ± 0 02 | 8 03 ± 0.02 | 7 89 ± 0 02 | 7.56 ± 0.02 | 0.006 |
| Tb | 0.88 ± 0 07 | 1 05 ± 0 09 | 0.85 ± 0 07 | 0 91 ± 0 05 | 1 09 ± 0 08 | 1.01 ± 0.06 | 0 2 |
| Th | 13.3 ± 0 1 | 13.5 ± 0 2 | 13.6 ± 0 2 | 13 0 ± 0 1 | 13 8 ± 0 2 | 12.0 ± 0.1 | 0 2 |
| Ti | 5426 ± 441 | 5675 ± 431 | 4989 ± 518 | 5664 ± 533 | | | 573 |
| U | 2.5 ± 0 2 | 2.2 ± 0 2 | 2.1 ± 0.2 | 2 5 ± 0.1 | 2.4 ± 0.2 | 2.2 ± 0.1 | 0.25 |
| V | 142 ± 19 | 159 ± 5 | 167 ± 6 | 133 ± 8 | 138 ± 8 | 148 ± 10 | 11 |
| Yb | 3.76 ± 0 05 | 3.76 ± 0.05 | 3 68 ± 0 06 | 3 74 ± 0.02 | 3.68 ± 0 05 | 3.07 ± 0.04 | 0.08 |
| Zn | 139 ± 3 | 146 ± 4 | 152 ± 3 | 144 ± 4 | 130 ± 3 | | 7 |

Table 2. Results obtained for Ohio Red Clay in the intercomparison exercise, in μg $g^{-1}$, unless indicate.

| Element | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | DL |
|---|---|---|---|---|---|---|---|
| As | 12.5 ± 0.2 | 13.2 ± 0.2 | 13.5 ± 0.1 | 12.8 ± 0.2 | 13.7 ± 0.2 | 14.1 ± 0.1 | 0.1 |
| Ba | 565 ± 117 | 570 ± 73 | 514 ± 79 | 549 ± 67 | | | 58 |
| Ce | 112.4 ± 0.5 | 113 4 ± 0.6 | 115.3 ± 0.9 | 112.2 ± 0.9 | 116.8 ± 0.9 | | 0.6 |
| Co | 21.0 ± 0.1 | 21.2 ± 0.1 | 23.3 ± 0.2 | 21.5 ± 0.1 | 23.0 ± 0.2 | | 0.08 |
| Cr | 82.3 ± 0.7 | 83.9 ± 0.8 | 90 ± 1 | 85.8 ± 0.9 | 90 ± 2 | 93 ± 1 | 1.4 |
| Cs | 9.5 ± 0.1 | 9.7 ± 0.1 | 10.1 ± 0.1 | 10 ± 0.2 | 9.9 ± 0.2 | 10.3 ± 0.2 | 0.2 |
| Dy | 6.0 ± 0.3 | 5.9 ± 0.1 | 6.2 ± 0.2 | 5.6 ± 0.2 | 6.4 ± 0.2 | | 0.25 |
| Eu | 1.64 ± 0.03 | 1.67 ± 0.03 | 1.59 ± 0.04 | 1 75 ± 0.03 | 1.55 ± 0.04 | 1.6 ± 0.04 | 0.02 |
| Fe, % | 5.82 ± 0.05 | 5.86 ± 0.06 | 5.29 ± 0.09 | 5.98 ± 0.06 | 5.14 ± 0.08 | 5.33 ± 0.09 | 0.01 |
| Hf | 6.6 ± 0.1 | 7.0 ± 0.1 | 6.9 ± 0.2 | 7.1 ± 0.1 | 6.8 ± 0.2 | 6.7 ± 0.1 | 0.14 |
| K, % | 2.9 ± 0.2 | 3.0 ± 0.2 | 3.3 ± 0.1 | 2.8 ± 0.2 | 3.3 ± 0.1 | 3.3 ± 0.1 | 0.02 |
| La | 43.0 ± 0.5 | 44.2 ± 0.5 | 43.5 ± 0.5 | 43.8 ± 0.5 | 44.1 ± 0.5 | 45.0 ± 0.6 | 0.04 |
| Lu | 0.54 ± 0.01 | 0.55 ± 0 01 | 0.56 ± 0.01 | 0 57 ± 0.01 | 0 57 ± 0.01 | 0.58 ± 0.01 | 0.01 |
| Mn | 266 ± 12 | 246 ± 6 | 250 ± 6 | 256 ± 6 | 250 ± 6 | 236 ± 5 | 0.7 |
| Na | 1248 ± 23 | 1294 ± 24 | 1229 ± 9 | 1209 ± 22 | 1247 ± 9 | 1269 ± 9 | 2 |
| Nd | 37 ± 3 | 38 ± 3 | 37 ± 4 | 39 ± 2 | 38 ± 5 | 35 ± 4 | 5 |
| Rb | 174 ± 4 | 170 ± 4 | 176 ± 7 | 178 ± 4 | 183 ± 8 | 196 ± 7 | 6 |
| Sb | 1.27 ± 0.03 | 1.30 ± 0.03 | 1 24 ± 0.03 | 1.37 ± 0 02 | 1.23 ± 0.03 | 1.35 ± 0 03 | 0 04 |
| Sc | 16.4 ± 0.1 | 16.5 ± 0.1 | 18 0 ± 0.1 | 16.8 ± 0.1 | 17.6 ± 0.1 | 18.3 ± 0.1 | 0.02 |
| Sm | 7.78 ± 0 02 | 7.99 ± 0 02 | 7 7 ± 0 02 | 8.18 ± 0 02 | 7 74 ± 0.02 | 8.16 ± 0 02 | 0 004 |
| Tb | 0.97 ± 0 04 | 1.02 ± 0 05 | 1 10 ± 0 06 | 1 02 ± 0 05 | 1.04 ± 0 07 | 1.05 ± 0.06 | 0 12 |
| Th | 14.1 ± 0 1 | 14.2 ± 0 1 | 15 5 ± 0.2 | 14 4 ± 0.1 | 14 7 ± 0 2 | 15.5 ± 0.2 | 0.13 |
| Ti | 5845 ± 374 | 6034 ± 362 | 6193 ± 353 | 5631 ± 300 | 6112 ± 346 | | 253 |
| U | 2.6 ± 0.1 | 2.8 ± 0.1 | 2 6 ± 0.1 | 2.7 ± 0.1 | 3 ± 0.2 | 2.8 ± 0 1 | 0.17 |
| V | 193 ± 4 | 203 ± 10 | 213 ± 6 | 216 ± 5 | 190 ± 4 | 195 ± 5 | 3.8 |
| Yb | 4.04 ± 0.03 | 4.27 ± 0 03 | 3 95 ± 0.04 | 4.22 ± 0.02 | 3.98 ± 0 04 | 4.21 ± 0 04 | 1.5 |
| Zn | 113 ± 2 | 105 ± 3 | 107 ± 3 | 108 ± 4 | 110 ± 3 | | 4 |

Table 3. Results obtained for Blind sample in the intercomparison exercise, in μg $g^{-1}$, unless indicate.

| Element | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | LD |
|---|---|---|---|---|---|---|
| As | 22.0 ± 0.4 | 24.7 ± 0.2 | 26.2 ± 0.3 | 23.2 ± 0.4 | 24.5 ± 0.4 | 0.2 |
| Ba | 665 ± 111 | 697 ± 135 | 604 ± 127 | 655 ± 93 | 587 ± 92 | 84 |
| Ce | 105.2 ± 0.5 | 109 ± 1 | 111 ± 1 | 108.3 ± 0.5 | 109.6 ± 0.6 | 0.9 |
| Co | 32.5 ± 0.2 | 36.7 ± 0.3 | 38.4 ± 0.4 | 33.9 ± 0.2 | 35.4 ± 0.2 | 0.1 |
| Cr | 87.4 ± 0.8 | 98 ± 2 | 99 ± 2 | 91.3 ± 0.9 | 91.6 ± 0.8 | 2 |
| Cs | 11.6 ± 0.2 | 12.7 ± 0.3 | 12.7 ± 0.3 | 12.0 ± 0.2 | 12.5 ± 0.2 | 0.3 |
| Dy | 5.7 ± 0.5 | 5.7 ± 0.3 | 5.7 ± 0.3 | 5.2 ± 0.3 | 5.5 ± 0.3 | 0.35 |
| Eu | 1.83 ± 0.03 | 1.77 ± 0.05 | 1.89 ± 0.05 | 1.86 ± 0.03 | 1.85 ± 0.03 | 0.03 |
| Fe, % | 6.13 ± 0.06 | 5.62 ± 0.09 | 5.73 ± 0.09 | 6.20 ± 0.06 | 6.28 ± 0.06 | 0.015 |
| Hf | 7.5 ± 0.1 | 8 ± 0.2 | 7.9 ± 0.2 | 7.9 ± 0.1 | 7.9 ± 0.1 | 0.2 |
| K, % | 2.9 ± 0.2 | 3.2 ± 0.1 | 3.5 ± 0.1 | 2.8 ± 0.2 | 2.8 ± 0.2 | 0.03 |
| La | 44.1 ± 0.5 | 45.9 ± 0.6 | 48.8 ± 0.6 | 45.5 ± 0.6 | 47.6 ± 0.6 | 0.06 |
| Lu | 0.47 ± 0.01 | 0.48 ± 0.01 | 0.55 ± 0.01 | 0.46 ± 0.01 | 0.49 ± 0.01 | 0.015 |
| Mn | 1205 ± 33 | 1214 ± 28 | 1200 ± 28 | 1239 ± 29 | 1164 ± 26 | 1 |
| Na | 4877 ± 88 | 4907 ± 35 | 5150 ± 36 | 4905 ± 89 | 5221 ± 96 | 3 |
| Nd | 38 ± 3 | 39 ± 5 | 36 ± 3 | 36 ± 3 | 38 ± 3 | 6 |
| Rb | 176 ± 4 | 181 ± 8 | 194 ± 8 | 180 ± 4 | | 9 |
| Sb | 2.7 ± 0.04 | 2.73 ± 0.04 | 2.86 ± 0.04 | 2.85 ± 0.04 | 2.92 ± 0.05 | 0.05 |
| Sc | 16.6 ± 0.1 | 18.5 ± 0.1 | 18.9 ± 0.1 | 16.9 ± 0.1 | 17.1 ± 0.1 | 0.02 |
| Sm | 6.89 ± 0.02 | 7.98 ± 0.02 | 6.19 ± 0.01 | 7.53 ± 0.02 | 8.45 ± 0.02 | 0.007 |
| Tb | 1.01 ± 0.05 | 0.82 ± 0.08 | 1.09 ± 0.08 | 0.98 ± 0.05 | 1.07 ± 0.05 | 0.2 |
| Th | 15.5 ± 0.1 | 16.8 ± 0.2 | 17.2 ± 0.2 | 15.6 ± 0.1 | 15.9 ± 0.1 | 0.2 |
| Ti | 6360 ± 751 | 6852 ± 598 | 5794 ± 355 | 5890 ± 430 | 5318 ± 332 | 265 |
| U | 3.7 ± 0.1 | 3.9 ± 0.2 | 4.0 ± 0.2 | 3.9 ± 0.1 | 4.4 ± 0.2 | 0.3 |
| V | 144 ± 10 | 136 ± 7 | 144 ± 4 | 131 ± 5 | 133 ± 4 | 3 |
| Yb | 3.56 ± 0.04 | 3.48 ± 0.06 | 3.56 ± 0.05 | 3.11 ± 0.02 | 3.33 ± 0.03 | 0.08 |
| Zn | 180 ± 3 | 174 ± 4 | 209 ± 5 | 203 ± 3 | 210 ± 3 | 6 |

Table 4. Results obtained for Brick Clay used as check sample, in μg $g^{-1}$, unless indicate.

| Determination | As | Ba | Ce | Co | Cr | Cs | Eu | Fe, % | Hf | K, % | La | Lu | Na | Nd | Rb | Sb | Sc | Sm | Ta | Tb | Th | U | Yb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BC1 | 9.0 | 404 | 97.3 | 24.0 | 96.2 | 9.3 | 1.72 | 8.28 | 4.03 | 2.2 | 48.9 | 0.49 | 1144 | 52 | 164 | 0.8 | 21.60 | 8.51 | 1.25 | 1.19 | 12.83 | 2.6 | 4.49 | 113 |
| BC2 | 9.9 | 578 | 106.4 | 26.3 | 107 | 9.9 | 1.76 | 9.29 | 4.6 | 2.2 | 53.4 | 0.58 | 1235 | 61 | 183 | 0.88 | 23.87 | 9.46 | 1.43 | 1.07 | 14.6 | 3 | 3.71 | 134 |
| BC3 | 10.0 | 467 | 106.9 | 26.6 | 110 | 10.3 | 1.75 | 9.22 | 4.35 | 2.4 | 54.7 | 0.55 | 1248 | 61 | 200 |  | 23.77 | 9.86 | 1.33 | 1.2 | 14.6 | 2.8 | 5.12 | 123 |
| BC4 | 10.6 | 559 | 103.9 | 26.0 | 111 | 9.4 | 1.74 | 9.5 | 4.5 | 2.4 | 56.9 | 0.55 | 1275 | 48 | 196 | 1.03 | 24.37 | 10.23 | 1.48 | 1.3 | 15 | 3 | 4.57 | 138 |
| BC5 | 10.2 | 440 | 105.7 | 26.5 | 106 | 9.8 | 1.8 | 9.1 | 4.6 | 2.44 | 58.4 | 0.56 | 1262 | 44 | 179 | 0.97 | 23.61 | 10.3 | 1.54 | 1.3 | 14.2 | 2.9 | 4.42 | 121 |
| BC6 | 10.3 | 440 | 98.4 | 24.6 | 106 | 9.4 | 1.8 | 8.99 | 4.3 | 2.27 | 51.9 | 0.52 | 1272 | 56 | 175 | 0.88 | 23.66 | 9.26 | 1.38 | 1.2 | 14.4 | 2.8 | 3.60 | 133 |
| BC7 | 9.8 | 373 | 100.3 | 24.9 | 105 | 9.8 | 1.74 | 8.96 | 4.1 | 2.29 | 50.8 | 0.51 | 1207 | 54 | 182 | 0.86 | 23.16 | 7.11 | 1.35 | 1.4 | 14.6 | 2.4 | 3.95 | 125 |
| BC8 | 10.1 | 453 | 105.4 | 25.9 | 107 | 9.5 | 1.8 | 8.97 | 4.4 | 2.51 | 52.5 | 0.54 | 1203 | 42 | 186 | 0.9 | 23.16 | 9.09 | 1.3 | 1.2 | 14.6 | 2.9 | 4.24 | 136 |
| BC9 | 10.8 | 482 | 100.5 | 25.0 | 112 | 10 | 1.87 | 9.11 | 4.1 | 2.43 | 49.9 | 0.52 | 1257 | 48 | 188 | 0.89 | 23.79 | 8.63 | 1.4 | 1.1 | 14.1 | 2.4 | 3 47 | 144 |
| BC10 | 10.2 | 426 | 101.2 | 25.2 | 103 | 9.8 | 1.79 | 9.06 | 4.6 | 2.5 | 49.6 | 0.53 | 1290 | 46 | 181 | 0.92 | 23.48 | 9.1 | 1.31 | 1.1 | 13.4 | 2.3 | 4 14 | 129 |
| BC11 | 10.0 | 468 | 102.6 | 25.1 | 105 | 9.9 | 1.78 | 9.07 | 4.3 | 2.39 | 51.4 | 0.52 | 1203 | 48 | 178 | 0.95 | 23.13 | 9.12 | 1.6 | 1.2 | 14.1 | 2.7 | 4.06 | 195 |
| BC12 | 9.0 | 447 | 94.9 | 23.7 | 103 | 9.5 | 1.7 | 8.6 | 3.9 | 2.2 | 48.9 | 0.52 | 1231 | 42 | 161 | 0.87 | 22.28 | 8.51 | 1.25 |  | 13 | 2.7 | 4.60 | 199 |
| BC13 | 9.5 | 464 | 101.4 | 25.6 | 104 | 9.6 | 1.76 | 8.85 | 4.3 | 2 4 | 53.7 | 0.52 | 1205 | 53 | 171 | 0.95 | 22.84 | 9.43 | 1.7 | 1.2 | 13 8 | 2.8 | 4 19 | 209 |
| BC14 | 10.5 | 423 | 102.8 | 24.9 | 102 | 9 4 | 1.72 | 8.68 | 4.16 | 2.52 | 53.4 | 0.51 | 1265 | 48 | 188 | 0.95 | 22.43 | 9.81 | 1.52 | 1.6 | 13.5 | 2.8 | 3.78 | 120 |
| BC15 | 10.1 | 357 | 101.1 | 25.0 | 104 | 10.1 | 1.73 | 9.34 | 4.3 | 2.2 | 51.0 | 0.49 | 1266 | 57 | 193 | 0.81 | 24.19 | 9.03 | 1.29 | 1.1 | 14.5 | 2.5 | 4.22 | 135 |
| Mean | 10.0 | 452 | 102 | 25.3 | 105 | 9.7 | 1.76 | 9.0 | 4.3 | 2 4 | 52 | 0.53 | 1238 | 51 | 182 | 0.9 | 23.3 | 9.2 | 1.4 | 1.2 | 14.1 | 2.7 | 4.2 | 144 |
| SD | 0.5 | 59 | 3 | 0.9 | 4 | 0.3 | 0.04 | 0.3 | 0.2 | 0.1 | 3 | 0.02 | 39 | 6 | 11 | 0.1 | 0 8 | 0.8 | 0.1 | 0.1 | 0.6 | 0.2 | 0 4 | 31 |
| RSD, % | 5.0 | 13.0 | 2.9 | 3.6 | 3.8 | 3 1 | 2.3 | 3.3 | 4 6 | 4.2 | 5.8 | 3.8 | 3.1 | 11.8 | 6.0 | 11.0 | 3.4 | 8.7 | 7.1 | 8.3 | 4.2 | 7.4 | 9.5 | 21.5 |
| Comparison with literature values |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Bishop(9) | 10 | 473 | 103 | 26.8 | 108 | 9 67 | 1 69 | 9 02 | 4 59 | 2 3 | 56 6 | 0 614 | 1360 | 47 | 218 3 | 0 981 | 23 | 9 17 | 1 24 | 1.22 | 14 4 | 2 4 | 4 12 | 130 |
| RE, % | 0.0 | 4.4 | 1 0 | 5.6 | 2.8 | 0 3 | 4 1 | 0.2 | 6 3 | 4 3 | 8 1 | 13.7 | 9 0 | 8.5 | 16.6 | 8.2 | 1 3 | 0.3 | 12 9 | 1 6 | 2 1 | 12.5 | 1 9 | 10.7 |
| Certificate(10) |  | 432 2 | 105 | 26 | 109 7 | 9 6 | 1 9 | 9 05 | 4 6 | 2 433 |  |  | 1304 |  | 190 |  | 22 5 |  |  |  | 14 |  |  | 150 |
| RE, % |  | 4 6 | 2 9 | 2 7 | 4 2 | 1 2 | 7 4 | 0 6 | 6 5 | 1 3 |  |  | 5 1 |  | 4 2 |  | 3 6 |  |  |  | 0 7 |  |  | 4 0 |

Table 5. Results obtained for Ohio Red Clay, used as check sample, in μg $g^{-1}$, unless indicate.

| Determination | As | Ba | Ce | Co | Cr | Cs | Eu | Fe, % | Hf | K, % | La | Lu | Na | Nd | Rb | Sb | Sc | Sm | Ta | Tb | Th | U | Yb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| OC1 | 15.1 | 617 | 113.7 | 22.7 | 87.5 | 10.0 | 1.72 | 5.00 | 6.82 | 3.2 | 51.9 | 0.56 | 1333 | 65 | 169 | 1.34 | 18.41 | 8.98 | 1.77 | 1.25 | 14.9 | 3.3 | 3.81 | 93 |
| OC2 | 15.7 | 649 | 111.9 | 22.7 | 87.7 | 10.0 | 1.74 | 5.06 | 7.1 | 3.7 | 54 | 0.63 | 1423 | 59 | 176 | 1.48 | 18.57 | 9.07 | 1.78 | 1.23 | 15.2 | 3.2 | 3.29 | 96 |
| OC3 | 15.7 | 681 | 117.3 | 23.1 | 92.2 | 10.6 | 1.72 | 5.18 | 7.18 | 3.4 | 55.7 | 0.63 | 1375 | 53 | 165 | 1.37 | 18.96 | 9.74 | 1.68 | 1.28 | 15.9 | 3.3 | 3.84 | 90 |
| OC4 | 15.9 | 705 | 112.5 | 23.4 | 91.6 | 10.1 | 1.69 | 5.28 | 7.2 | 3.6 | 56.1 | 0.62 | 1380 | 52 | 171 | 1.39 | 19.33 | 9.66 | 1.76 | 1.3 | 16.1 | 3.3 | 3.78 | 112 |
| OC5 | 15.0 | 616 | 109.4 | 22.1 | 87.2 | 9.8 | 1.71 | 4.88 | 6.7 | 3.31 | 55.8 | 0.61 | 1350 | 42 | 164 | 1.26 | 18.14 | 7.23 | 1.8 | 1.2 | 14.9 | 3.2 | 3.33 | 94 |
| OC6 | 16 2 | 655 | 110.7 | 22.6 | 95 | 10.4 | 1.82 | 5.25 | 6.7 | 3.6 | 53.8 | 0.59 | 1401 | 49 | 175 | 1.26 | 19.53 | 9.33 | 1.72 | 1.2 | 16.3 | 3.1 | 3.83 | 106 |
| OC7 | 16.2 | 573 | 111.6 | 23 | 92 | 10.9 | 1.73 | 5.21 | 6.6 | 3.0 | 52.1 | 0.58 | 1323 | 48 | 177 | 1.32 | 19.03 | 8.88 | 1.7 | 1.3 | 16.3 | 3.6 | 4.52 | 101 |
| OC8 | 16.3 | 629 | 116.8 | 23.1 | 92.1 | 9.8 | 1.82 | 5.12 | 7.2 | 3.56 | 54.5 | 0.65 | 1359 | 51 | 166 | 1.37 | 18.91 | 9.57 | 1.65 | 1.2 | 16.2 | 3.3 | 4.45 | 112 |
| OC9 | 16 7 | 682 | 114.8 | 23.2 | 96 | 11.5 | 1.83 | 5.35 | 6 9 | 3.5 | 51.5 | 0.61 | 1419 | 44 | 186 | 1.32 | 19.86 | 8.9 | 2.2 | 1.3 | 15.7 | 3.1 | 4.61 | 111 |
| OC10 | 16 9 | 598 | 114.6 | 22.2 | 90 | 10.4 | 1.78 | 5 17 | 7.6 | 3.7 | 51.4 | 0.65 | 1496 | 54 | 172 | 1.30 | 19 07 | 9.07 | 1.6 | 1.3 | 15.0 | 3.0 | 4.73 | 95 |
| OC11 | 15 5 | 482 | 109.4 | 21.6 | 89 | 9.8 | 1.69 | 4.98 | 6.8 | 3.5 | 51.6 | 0.6 | 1327 | 45 | 170 | 1.22 | 18.15 | 7.2 | 1.5 | 1.0 | 15 3 | 3.1 | 4.06 | 137 |
| OC12 | 15 7 | 584 | 109.9 | 21.7 | 90 | 10.0 | 1.86 | 4.96 | 6.7 | 3.8 | 51.0 | 0.59 | 1341 | 46 | 154 | 1.26 | 18.27 | 9.26 | 1.52 | 1.1 | 14.9 | 3.2 | 4.40 | |
| OC13 | 16.3 | 608 | 114 | 24.0 | 89 8 | 10.1 | 1.82 | 5 16 | 7.2 | 3.3 | 55.9 | 0.30 | 1376 | 52 | 172 | 1.43 | 18.87 | 9.78 | 2.0 | 1 18 | 15 3 | 3.4 | 4.25 | 129 |
| OC14 | 17.0 | 603 | 121 | 22.2 | 88 2 | 10.5 | 1.98 | 5 07 | 6.8 | 3.7 | 56.5 | 0.61 | 1458 | 51 | 184 | 1.40 | 18.57 | 11.58 | 1.8 | 1.3 | 15.4 | 3.0 | 4.54 | 98 |
| OC15 | 15.8 | 638 | 112 | 21.5 | 90 | 10.4 | 1.8 | 5.31 | 7.0 | 3.8 | 53.0 | 0.62 | 1436 | 61 | 200 | 1.22 | 19.52 | 9.5 | 1.44 | 1.1 | 16 4 | 3 2 | 4.73 | 107 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Média | 16.0 | 621 | 113 | 22.6 | 91 | 10.3 | 1.8 | 5.1 | 7.0 | 3.5 | 54 | 0 6 | 1386 | 52 | 173 | 1 3 | 18.9 | 9 | 1.7 | 1.2 | 15.6 | 3 2 | 4.1 | 106 |
| SD | 0.6 | 54 | 3 | 0.7 | 3 | 0.5 | 0.1 | 0.1 | 0 3 | 0.2 | 2 | 0.1 | 51 | 6 | 11 | 0.1 | 0.5 | 1 | 0.2 | 0.1 | 0.6 | 0.2 | 0.5 | 14 |
| RSD, % | 3.7 | 8 7 | 2.9 | 3.2 | 2 9 | 4.5 | 4.4 | 2.7 | 3.9 | 6.6 | 3.7 | 14.2 | 3 7 | 12.5 | 6 2 | 5.8 | 2.8 | 11.2 | 11.1 | 7.5 | 3.7 | 4 9 | 11.5 | 13.0 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Comparison with literature values | | | | | | | | | | | | | | | | | | | | | | | | |
| Glascock (11) | 13 | 614 | 106.1 | 20 2 | 89 2 | 10 3 | 1.54 | 5 19 | 7.11 | 3 31 | 48 | 0.552 | 1290 | 40.1 | 176 | 1 34 | 17 8 | 7 99 | 1 48 | 1 02 | 14 4 | 2 98 | 3 94 | 97 |
| RE. % | 23.1 | 1.2 | 6.8 | 11 9 | 1 5 | 0 1 | 15.6 | 1.1 | 2 0 | 6.1 | 11 8 | 6.9 | 7 5 | 28.3 | 1 5 | 0 8 | 6 1 | 14 9 | 16 8 | 19 2 | 8.2 | 8.1 | 5.2 | 9.1 |
| Harbottle (12) | | 703 | 110 7 | 19 94 | 91 | 10 2 | 1 76 | 5 31 | 6 3 | 3 41 | 50 | 0 77 | 1370 | | 175 | 1 24 | 20 | 8 3 | 1 79 | | 15 5 | | 4 31 | 96 4 |
| RE. % | | 11 6 | 2 4 | 13 4 | 0 5 | 0 8 | 1 2 | 3 4 | 10 6 | 3 0 | 7 3 | 23 4 | 1 2 | | 0 9 | 7 2 | 5 6 | 10 6 | 3 5 | | 0 6 | | 3 8 | 9 7 |
| Blackman (12) | 13.5 | 626 | 106.4 | 20.65 | 90 3 | 10.29 | 1.45 | 5 16 | 7 61 | 3.67 | 54 7 | 0.639 | 1410 | 40 | 203 | 1 5 | 17.87 | 8 16 | 1 47 | | 15.38 | 2.98 | 4.33 | |
| RE. % | 18.5 | 0.7 | 6.5 | 9.5 | 0 3 | 0.0 | 22.8 | 0 5 | 8 5 | 4.3 | 1.9 | 7.7 | 1.7 | 28.7 | 14.6 | 11.4 | 5 6 | 12 5 | 17.6 | | 1.3 | 8 1 | 4.3 | |
| Kuleff (12) | 13.7 | 729 | 119 | 19.1 | 78 | 10 | 1.5 | 5 33 | 6 3 | 3 74 | 50.4 | 0.58 | 1330 | 42 | 171 | 1 4 | 20 8 | 8.1 | 1.6 | | 19.5 | 2.8 | 4.2 | |
| RE. % | 16.8 | 14.8 | 4.8 | 18 4 | 16 1 | 2 9 | 18 7 | 3 7 | 10 6 | 6 1 | 6.5 | 1 7 | 4 2 | 22 5 | 1 4 | 5 0 | 9 2 | 13 4 | 8.0 | | 20 1 | 15.0 | 1 3 | |
| Brissaud (12) | 15.4 | 677 | 113.8 | 20.83 | 104 | 10.97 | 1.614 | 5 42 | 7 38 | 3.81 | 49.57 | 0.522 | 1420 | 44.1 | 165 | 1.37 | 19 69 | 8.13 | 2.09 | 0 197 | 16.46 | 3.33 | 5.73 | |
| RE. % | 3.9 | 8.2 | 0.4 | 8 5 | 12.9 | 6 2 | 10.3 | 5 3 | 5 6 | 7 8 | 8.2 | 13.0 | 2.4 | 16.7 | 5 1 | 3.0 | 4 1 | 13.0 | 17.3 | 517.3 | 5.3 | 3 3 | 27.7 | |

Table 6. Mean, standard deviation and range of results obtained from 90 ceramic fragments of Água Limpa Site, State of São Paulo, Brasil.

| Element | Mean ± SD | Range |
|---|---|---|
| As | 2.2 ± 1.1 | 0.2 - 7.2 |
| Ba | 1308 ± 341 | 671 - 2350 |
| Ce | 126 ± 34 | 84.9 - 356 |
| Co | 22.0 ± 7.5 | 11.2 - 52.4 |
| Cr | 159 ± 35 | 82 - 275 |
| Cs | 1.8 ± 0.5 | 0.3 - 3 |
| Eu | 2.6 ± 0.7 | 1.78 - 7.1 |
| Fe, % | 3.4 ± 1.0 | 1.81 - 9.67 |
| Hf | 8.7 ± 2.1 | 5.4 - 23.7 |
| K, % | 1.8 ± 0.4 | 0.24 - 2.7 |
| La | 72.9 ± 16.6 | 43.6 - 178.9 |
| Lu | 0.4 ± 0.1 | 0.24 - 0.67 |
| Na | 1843 ± 690 | 217 - 4068 |
| Nd | 60 ± 14 | 37 - 137 |
| Rb | 71 ± 17 | 3 - 120 |
| Sb | 0.2 ± 0.1 | 0.08 - 0.65 |
| Sc | 16.2 ± 4.0 | 10.16 - 44.9 |
| Sm | 9.8 ± 2.1 | 6.33 - 23.76 |
| Ta | 3.7 ± 1.6 | 1.2 - 16.4 |
| Tb | 1.1 ± 0.3 | 0.67 - 2.6 |
| Th | 12.9 ± 2.5 | 9.06 - 27.7 |
| U | 1.4 ± 0.5 | 0.8 - 4.7 |
| Yb | 3.6 ± 3.6 | 2.07 - 37 |
| Zn | 65 ± 30 | 16 - 229 |