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PRELIMINARY CHEMICAL COMPOSITION STUDY OF PRE-COLONIAL CERAMICS FROM PANTANAL SUL MATO-GROSSENSE BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Trace element concentration of potsherds from two archaeological sites was measured by neutron activation analysis. The archaeological sites are located in the flood plains of Paraguai River in the heart of South America in a singular area of natural preservation called Pantanal. Archaeological studies in this region began in 1990, with the classification of *c.a.* 200 sites. These archaeological sites present a large amount of ceramic material not only on the surface but also along a depth profile, where the most antique dating is 2.640 B.P. Discriminant Analysis was applied in the data treatment in order to obtain more conclusive information. The measured elements were Na, Lu, U, Yb, La, Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf, and Tb. The composition analysis results enable to attribute a significant distinction to potsherds coming from the archaeological site MS-CP-71 and MS-CP-61. Both sites were characterized as long term settlements of great importance to the study of the ancient population that inhabited this area.

Keywords: Neutron Activation Analysis; Archaeometry; Pantanal; Pottery; Clay; Discriminant Analysis.

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1. INTRODUCTION

The present work is part of a study that aims shedding light in the technology applied by pre-colonial Indians who lived near the west border of Mato Grosso do Sul Pantanal, in the fabrication of their ceramic artifacts. This research aims providing information on the procedures applied by the ancient artisan in the pottery fabrication and to enable the recognition of an identity of the ceramics by means of chemical and physical analysis of the archaeological material. In the part herein presented we have as a main objective the characterization of the pottery coming from two different archaeological sites regarding its elemental composition. Archaeological studies in this region began in 1990, with the classification of *c.a.* 200 sites. These archaeological sites present a large amount of ceramic material not only on the surface but also along a depth profile, where the most antique dating is 2.640 B. P.

The study of archaeological remains from sites of Pantanal, a nature preservation area located in the heart of South America, can contribute in a large extent to a better understanding of pre-colonial Indian populations that inhabited this region, since they seem not to be related to the Indian communities that lived in the area along the *luso-hispanic* colonization period.[1] The pottery fabricated by these populations often has yellow, red and sometimes black surfaces very often with a dark grey bulk, which has been demonstrated to be a result of the drying and firing procedure of the pieces occasioned by "black heart" formation.[2] The pottery under study present different types of additives such as shells, sponge spicules and burnt bone.[3] A detailed investigation of the technology attained by pre-colonial civilizations, about which there is no historical report, can be achieved through the characterization of the ceramic remains. Therefore an extensive work involving the study of this kind of archaeological material by means of physic and chemical analyses techniques that enables to enlighten questions regarding the age, fabrication process and the identity of the components present in the ceramic mass is been performed. In order to attain information about the methodology and the condition used in the fabrication process of these objects, morphological and mechanical analyses were applied. The obtained results enabled to establish a domain of certain procedures by the artisans regarding the use of several kinds of additives, as well as the assembling technique of the vessels and their firing procedure.[4] The ceramics compositional analysis by Neutron Activation Analysis will be presented in the present work. The results indicate potsherds from the archaeological sites MS-CP-71 and MS-CP-61 form two distinct groups regarding their elemental composition.

Different analytical techniques may be applied to determine trace elements concentration, such as the various forms of ICP, [5] EDXRF,[6, 7, 8] and INAA, [9, 10, 11] among others. Within these techniques, INAA associated with the spectrometric gamma rays of high resolution have been preferentially used for the determination of the chemical composition in ceramic samples, because it presents several advantages such as better sensitivity, precision and accuracy. [12] In this type of study, analytical parameters have an extreme importance, since there are small differences in the concentration of elements in the samples.

Thirty one pottery samples from the archaeological site MS-CP-71 and fourteen from archaeological site MS-CP-61 were analyzed. The analysis by means of INAA enabled the concentration determination of fifteen elements. The data treatment was performed by means discriminant analysis and for elemental analysis result of one clay source was added to the data set in order to be able to observe the corresponding grouping. Based on the obtained results it was possible to verify the existence of two pottery groups.

2. EXPERIMENTAL

2.1 Sample preparation and standard

Ceramic powder samples were obtained by cleaning the outer surface of the sherds and drilling to a depth of 2-3 mm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the sherd as possible without drilling through the walls.[11] Forty five ceramic samples were analyzed. Finally, these materials were dried in an oven 105°C for 24h and stored in desiccators.

The Standard Reference Material NIST-SRM 1663b (Constituent Elements in Coal Fly Ash) was used as standard, and Brick Clay (NIST-SRM 679) and IAEA –Soil 7 (Trace Elements in Soil) were used as check samples in all analysis. These materials were dried in an oven at 105°C, for 24 h the samples and 2 h the standards, and stored in desiccator until weighing. [10]

2.2 Description of the method

Generally speaking, NAA method is based on the properties of nucleuses, in which a neutron incident interacts with a nucleus of the target element. During the sample bombardment with neutrons a small fraction of the nucleus from each one of the sample constituent elements will be transformed into unstable radioactive isotope, which decays with a characteristic half-life. During the decay, these isotopes emit gamma rays with energies that are characteristic for each element. The measure of these gamma rays permits the qualitative and quantitative determination of the sample elements.

About 100 mg of ceramic or clay samples, NIST-SRM 1663b, Brick Clay and IAEA – Soil 7 were weighed in polyethylene bags and involved in aluminum foil. Groups of eight samples and one of each reference material were packed in aluminum foil and irradiated in the pool research reactor, IEA-R1m, from the IPEN-CNEN/SP at a thermal neutron flux of about 5×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8h.

Two measurement series 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. Na, Lu, U, Yb and, La were measured after 7 days cooling time and Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf and Tb after 25-30 days. Gamma ray spectra analysis and the concentrations were performed using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra.

3. RESULTS AND DISCUSSION

NAA is a highly sensitive technique and it can determine the elements which are found in very low concentrations, such as ppm (parts per million) or ppb (parts per billion). One of the basic premises for the use of a chemical composition analysis on clay deposits and archaeological ceramics samples is that the samples can be better differentiated if the analytical technique has a good sensitivity, precision and accuracy. If an element is not measured with good precision it may hinder the observation of real differences in concentration and, the discriminating effect of other well-measured elements tends to be reduced. These small differences can enable the observation of groups with similar composition, since artifacts manufactured with the same or geologically similar raw material source will be more chemically similar than other ones, which were manufactured with a raw material collected in a different geological environment. [10] Thus, the determination of the concentration of various elements in the trace level, will tend to produce a highly specific "fingerprinter" for a source of clay as raw material.

Other parameters related to the properties of analytical methods, are accuracy and precision. Accuracy is related to the real concentration of the sample element, a value that does not depend on the applied method. The analytical methods accuracy is determined by means of the reference materials, which concentration was determined by various analytical methods. In this case NAA has great accuracy for various elements. [9-11] The determination of the analytic precision is also of great importance and must be determined. Precision regards the reproducibility of the obtained results and its limitations can result from sample inadequate preparation, either due to contamination with the same element that is being determined, or due to a non homogeneous sample.

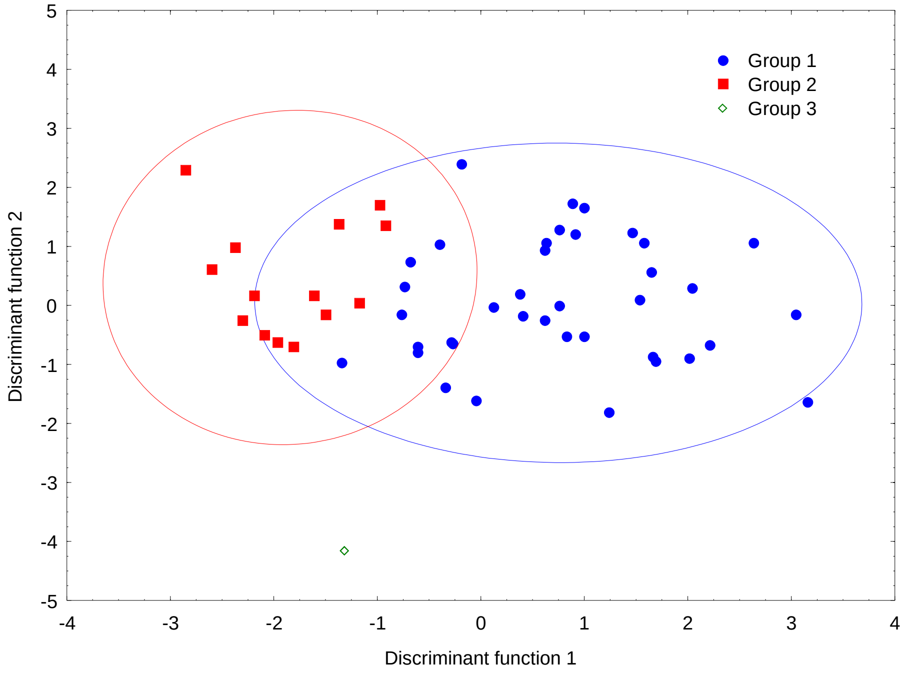

Figure 1: **Discriminat functions for pottery samples from the archaeological sites MS-CP-71 and MS-CP-61. Ellipses represent a confidence level of 95%. Group 1 encloses the ceramics from the archaeological site MS-CP-71, Group 2 the ceramics from site MS-CP-61 and Group 3 is represented by a single clay sample, included in the analysis in order to get a better view of the ceramic grouping.**

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***Table 1.* Results for the elemental composition of pottery from the archaeological sites MS-CP-71 and MS-CP-61 in μg g^{-1}, unless otherwise indicated**

Sample	Na(%)	Lu	U	Yb	La	Th	Cr	Cs	Sc	Rb	Fe(%)	Eu	Ce	Hf	Tb
A01	0,125	0,430	1,48	3,05	41,34	11,85	53,63	3,86	13,29	84,9	2,48	1,42	80,11	7,04	0,66
A04	0,188	0,476	2,82	3,20	43,86	13,51	79,12	5,91	15,69	128,63	5,81	1,49	85,1	6,41	0,83
A05	0,133	0,523	2,99	3,41	44,57	12,82	56,58	3,69	14,8	88,74	3,85	1,59	90,3	8,24	0,68
A07	0,139	0,446	3,57	2,95	34,19	12,02	57,68	4,25	11,52	103,27	2,76	1,15	70,85	6,43	0,57
A09	0,072	0,473	2,49	2,98	39,25	12,69	45,58	2,99	10,16	111,02	2,84	1,31	79,6	6,33	0,55
A12	0,174	0,495	3,63	3,17	39,25	14,07	63,15	5,55	12,2	198,52	3,97	1,45	82,21	7,64	0,95
A13	0,12	0,237	1,25	1,24	20,51	9,19	60,57	5,27	12,2	100,09	1,87	0,713	37,36	3,47	0,32
A18	0,129	0,607	3,32	4,18	53,72	16,89	79,94	6,07	16,7	142,97	3,11	1,78	107,47	7,79	1,02
A03	0,095	0,392	2,59	2,72	39,32	13,20	77,20	7,20	16,10	173,20	6,70	1,30	75,10	3,90	0,90
A06	0,087	0,393	2,01	2,41	38,44	13,00	75,50	7,80	16,00	164,70	6,70	1,20	74,70	3,80	0,60
A11	0,102	0,331	3,13	2,11	27,73	10,60	43,40	3,30	9,00	107,20	2,50	0,90	58,90	4,40	0,50
A14	0,088	0,396	1,99	2,79	39,43	9,70	33,20	2,20	12,80	39,70	2,80	1,60	77,70	5,60	0,60
A15	0,067	0,421	1,73	2,97	46,56	11,80	45,70	2,80	15,40	62,00	3,30	1,50	82,90	6,70	0,60
A16	0,162	0,584	0,81	3,66	37,34	13,80	65,80	5,00	13,00	124,40	3,30	1,20	76,20	10,70	0,90
A17	0,116	0,620	2,82	3,65	36,72	12,90	49,90	4,10	11,30	111,40	2,50	1,20	70,50	13,50	1,40
A18	0,108	0,560	3,56	3,90	50,48	15,10	72,60	5,70	15,20	120,00	2,80	1,60	97,00	8,30	1,50
A20	0,137	0,609	2,29	4,04	50,39	13,27	77,90	7,90	15,70	197,80	4,40	1,80	100,20	7,00	1,50
A22	0,125	0,336	2,78	2,84	41,65	11,30	35,80	1,90	14,80	106,60	3,50	1,60	76,50	4,90	1,02
A23	0,112	0,438	2,12	2,89	42,15	11,00	37,30	2,60	13,40	99,40	2,90	1,40	76,70	5,70	0,90
A25	0,165	0,450	3,33	3,08	30,87	10,90	43,50	4,40	9,90	94,60	3,50	0,99	57,70	8,00	1,00
A26	0,095	0,630	2,78	4,40	59,69	16,70	64,50	5,00	14,80	167,70	4,10	1,90	98,90	8,30	0,60
A28	0,152	0,629	1,26	4,02	41,95	14,00	48,80	4,30	12,20	211,90	3,30	1,40	94,00	8,50	0,95
A29	0,215	0,607	1,65	4,24	48,77	14,90	62,50	6,40	13,50	243,40	3,50	1,70	95,20	8,60	1,10
A30	0,057	0,532	2,02	3,22	48,81	13,20	43,90	3,30	15,30	65,20	3,40	1,60	83,60	7,40	0,30
A32	0,07	0,60	2,78	4,20	50,40	16,10	67,60	3,00	12,90	34,40	4,20	1,70	106,00	8,00	1,30
A33	0,14	0,40	1,60	2,80	34,20	11,40	58,40	4,70	12,40	110,40	3,40	0,80	61,60	9,90	1,02
A34	0,23	0,40	2,80	3,20	36,50	12,60	66,30	3,50	13,40	164,80	2,70	1,10	70,60	6,90	0,96
A35	0,17	0,60	1,60	4,20	45,00	14,50	49,70	7,00	13,00	298,90	3,40	1,50	94,60	9,70	1,50
A36	0,11	0,70	2,50	4,70	62,30	16,80	61,90	10,40	14,90	111,40	5,50	1,90	130,10	9,20	1,60
A37	0,16	0,40	2,20	2,90	36,30	11,50	63,30	3,70	10,90	120,90	2,10	1,20	70,80	6,60	1,70
A38	0,11	0,50	2,80	2,50	31,50	10,90	53,90	5,70	11,40	116,40	3,30	0,93	64,70	6,70	0,50
A39	0,11	0,60	4,20	3,70	47,20	15,70	83,40	8,00	17,60	42,50	5,40	1,30	90,10	7,70	1,70
A40	0,08	0,60	4,40	3,90	55,80	16,80	91,00	10,80	20,20	50,80	4,50	1,60	106,10	7,90	1,50
A41	0,13	0,40	2,50	2,70	36,70	10,00	54,70	4,80	11,70	93,70	2,40	1,10	63,00	3,60	1,40
A44	0,11	0,50	6,10	3,90	41,30	14,80	68,40	6,10	13,30	57,10	5,30	1,20	81,60	9,40	2,40
A45	0,01	0,50	3,70	3,10	34,20	13,00	73,20	7,00	14,80	44,80	5,00	1,20	59,90	9,10	1,10
A53	0,11	0,50	4,30	3,60	47,40	15,10	87,90	5,70	16,80	54,70	6,40	1,50	146,60	7,60	1,00

B01	0,07	0,70	4,40	4,40	62,10	16,50	69,90	6,90	15,50	72,00	2,60	2,10	118,80	7,70	1,20
B02	0,07	0,60	4,20	4,10	43,60	17,00	78,10	6,20	15,30	112,50	5,20	1,50	90,70	8,80	1,30
B03	0,07	0,70	6,10	4,40	55,60	17,10	75,80	6,90	15,00	87,70	4,40	1,70	108,20	10,40	1,20
B05	0,09	0,70	4,40	4,30	49,50	15,60	74,00	6,10	14,50	92,50	3,80	1,60	100,90	9,40	0,60
B06	0,07	0,60	4,00	3,60	42,00	13,60	63,20	4,90	14,40	90,10	3,20	1,40	87,30	7,70	0,90
B09	0,09	0,60	4,60	3,60	36,50	14,10	60,40	5,80	11,70	143,00	3,10	1,30	71,50	11,00	0,90
B10	0,09	0,70	6,80	4,30	53,30	17,50	74,30	5,60	15,80	105,20	5,40	1,70	101,80	9,60	0,80
B11	0,1	0,60	3,10	3,70	39,20	12,80	53,10	6,80	11,60	126,90	3,80	1,20	78,70	9,00	0,40
B07	0,067	0,798	2,83	5,11	68,37	15,69	79,53	6,57	15,42	105,75	6,47	2,53	147,16	6,96	1,36
B12	0,088	0,854	3,03	5,40	70,71	16,91	83,38	7,23	16,16	129,61	6,64	2,7	147,46	7,40	1,36
B13	0,088	0,546	2,46	3,77	43,80	15,37	78,91	7,87	15,69	123,16	3,74	1,54	79,14	7,30	0,71
B14	0,062	0,692	3,87	4,24	44,23	16,75	81,39	8,19	16,19	147,11	4,41	1,74	95,37	8,26	0,86
B15	0,094	0,813	4,10	4,74	56,26	16,17	76,01	7,32	15,17	126,54	4,62	1,99	110,05	9,19	1,57
B17	0,115	0,579	2,81	3,82	41,99	14,08	72,19	5,23	13,76	94,23	3,31	1,4	79,43	9,46	0,72
B18	0,087	0,675	5,73	4,26	52,17	15,65	75,42	5,64	14,75	89,17	4,13	1,83	109,43	8,74	1,51
R01	0,078	0,605	2,76	3,61	39,72	11,7	49,51	4,28	10,56	65,01	3,8	1,36	79,15	11,95	0,815
R02	0,046	0,805	3,48	4,46	66,18	18,03	74,21	9,37	16,24	60,09	2,03	2,24	121,29	7,71	1,27
R03	0,041	0,664	3,77	3,79	44,94	15,19	65,5	5,97	14,55	20,52	4,93	1,45	83,4	10,78	1,06
R05	0,018	0,504	2,74	2,68	29,43	14,59	64,32	5,57	12,88	33,24	3,00	0,93	51,70	9,65	1,02
R06	0,070	0,673	2,60	3,72	38,02	12,92	55,08	4,53	10,89	43,54	3,28	1,30	71,68	14,93	1,21
R07	0,124	0,741	5,32	4,46	57,55	18,16	73,56	8,40	15,94	79,31	3,72	1,53	99,85	8,24	0,99
R08	0,042	0,843	4,45	4,13	59,98	21,73	88,72	8,86	18,66	144,36	3,76	1,67	110,93	10,16	1,02
R04	0,039	0,627	6,03	3,83	44,88	15,60	68,00	5,70	13,20	47,10	2,80	1,40	85,70	11,50	1,00

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The results obtained by INAA analyses of potsherds for the archaeological sites MS-CP-71 and MS-CP-61 are presented in table 1. Discriminant analysis was applied in order to obtain more conclusive information from the data set. Therefore, the results were initially transformed to log base10 aiming to compensate for the large differences of magnitudes between the measured elements. [13] The log base 10 transformation of data before a multivariate statistical method is a usual procedure. One reason for that is that within the raw material elements have a natural log-normal distribution and thus 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 unstandardized multivariate statistical analysis. The multivariate statistical method of data analysis chosen was the discriminant analysis based on its property to maximize the difference between two or more groups which is based on the fact that principal variance-covariance matrix is an accurate representation of the total variance and covariance.

In the Figure 1 a graph of the discriminant function 2 *versus* the discriminant function 1 for all the studied ceramic samples is presented. The obtained ellipses represent a confidence level of 95%. Based on this result it is possible to conclude that the pottery coming from the archaeological sites MS-CP-71 and MS-CP-61 can be distinguished based on their elemental composition.

4. CONCLUSION

The analyses by INAA enabled characterizing the potsherds from the archaeological sites MS-CP-71 and MS-CP-61 concerning some major and most important, trace element composition. The data treatment by Discriminant Analysis indicates that it is possible to observe two distinct groups of samples. The elements responsible for the discrimination of the two groups are Na, Lu, U, Yb, La, Th, Cr, Cs, Sc, Rb, Fe, Eu, Ce, Hf, and Tb. These evidences indicate that the potters from the pre-colonial population of the two settlements under study made use of different clay sources, most probably collected in the surrounding of each archaeological site.

5. ABBREVIATIONS

INAA Instrumental neutron activation analysis
AAS Atomic absorption spectrometry
ICP Inductively coupled plasma
IAEA International Atomic Energy Agency

6. ACKNOWLEDGEMENTS

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