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Preliminary chemical studies at the Jericho archaeological site

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ABSTRACT

This study measured the chemical composition of 45 ceramic samples from the Jericho archaeological site, Palestine, by means of instrumental neutron activation analysis (INAA). The mass fraction of Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sc, Sm, Th, U, Yb and Zn was determined with the purpose to detect the presence of ceramic groupings based on their composition. The analytical method is appropriate for this type of study because it is a non-destructive technique with high sensitivity, accuracy and precision, and determines chemical elements in trace and ultra-trace levels. These characteristics are essential to study small concentration variations. Initially the mass fractions were normalized to compensate for the large difference in magnitude among elements determined in percentage and trace level. Subsequently, the dataset was interpreted through cluster and discriminant analysis. The results showed the existence of three different chemical groups.

Keywords: **archaeometry, INAA, pottery, tell es-Sultan, Jericho archaeological site**

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1. INTRODUCTION

Archaeological artifacts are objects produced by humans in ancestral societies and are products of daily activities and their social and technological use. Basing on these remains that archaeologists can interpret the behavior of ancient societies and study cultural processes, thus reconstructing the human past [1]. Such reconstructions may focus on any aspect of the societies way of life, such as their spatial organization.

Archaeological remains compose a range of objects that can include constructions, works of art, earthworks, cave engravings, ceramic vessels and various other materials [1]. Due to their abundance and durability, ceramic objects are among the artefacts most studied by archaeologists. The technological process of ceramic manufacture can often be specific to the ethnic groups that produced them. Such studies can be considered interdisciplinary, since they arouse the interest of several areas of science [2].

The exact sciences assist archaeology in the characterization of archaeological remains. From this cooperation arises archaeometry, a science that uses physical-chemical analytical techniques to study these objects [2]. Interdisciplinarity is important here, since an object can be characterized from numerous aspects that include its typology (shape, color, texture, decoration) [3], to the determination of its chemical composition. Typological analysis is very useful when applied to whole or reconstructed objects, but of little useful for ceramic fragments.

Ceramics have a specific chemical composition, with complex and varied raw materials. Assuming that ceramics made with clay from the same source have a similar chemical composition [4], it is possible to study the relationship between the composition of ancient artefacts and the geographic location of the raw materials from which these artifacts were made. This allows models to be created of the distribution of ceramic production, which often says something about the degree of cultural integration among the society(ies) that made them. Such studies emerge from attempts to sort and group artifacts in function of their chemical composition.

There are several analytical techniques that can be applied to ceramics to determine their chemical composition, including atomic absorption spectrometry, AAS [5], inductively coupled plasma emission spectrometry [6], X-Ray Fluorescence Spectrometry (XRF) [7], and instrumental neutron activation analysis, INAA [8-10].

Most of the chemical elements that are of interest for chemical characterization are present in the parts per million (ppm) range and some in the parts per billion (ppb) range. Therefore, the analysis chosen for the determination of these elements needs to be sufficiently sensitive and accurate [11]. INAA, associated with high resolution gamma ray spectrometry, is convenient for these analyses, since it is a non-destructive analytical technique, requires a small sample that is easily and quickly prepared, and allows the simultaneous determination of several elements [12]. In relation to other analytical techniques, INAA presents high sensitivity, precision and accuracy [13].

This work presents the preliminary results of the analysis of 45 ceramic fragments from Jericho archaeological site in which the mass fractions of chemical elements Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sc, Sm, Th, U, Yb and Zn were determined by means of INAA. In order to interpret these results, it is essential to apply appropriate multivariate statistical techniques such as cluster analysis and discriminant analysis [12].

2. MATERIALS AND METHODS

2.1 Archaeological background

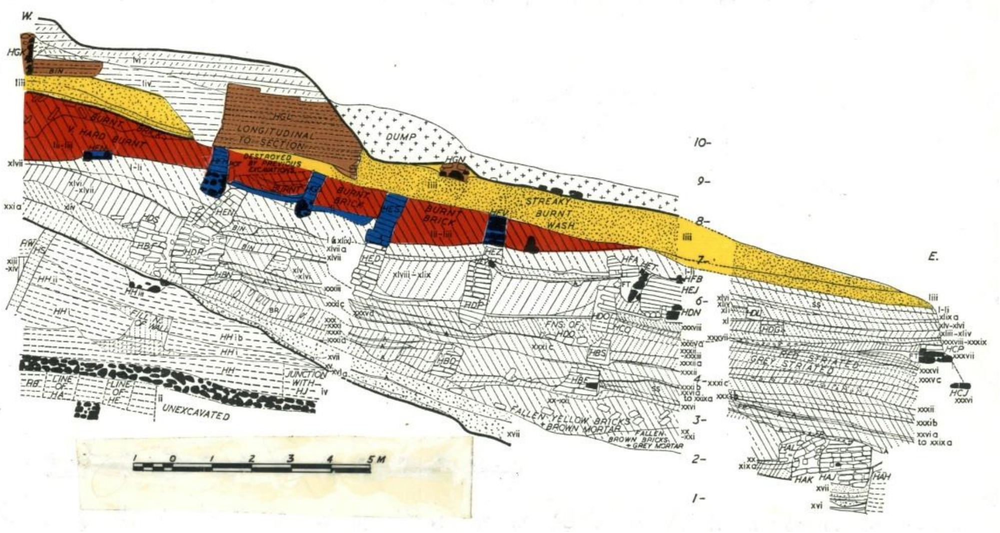
The ceramics used in this study were collected from the Jericho archaeological site. The site it is strategically located in the modern Tell es-Sultan in the Jordan Valley, Palestine, just north of the Dead Sea. It is one of the best-known site in the Middle East because of its ancient evidence of human occupation (for some scholars, the most ancient in the world) [14, 15]. The site has been excavated several times and revealed a sequence of multiple occupation layers (stratum) [14, 15]. The first excavations of the site were made by Charles Warren in 1868. Ernst Sellin and Carl Watzinger excavated between 1907 and 1909, and in 1911. John Garstang excavated between 1930 and 1936. Extensive investigations using more modern techniques were made by Kathleen Kenyon between 1952 and 1958. Lorenzo Nigro and Nicolò Marchetti conducted excavations in 1997–2000. Since 2009, the Italian-Palestinian archaeological project of excavation and restoration was resumed by Rome La Sapienza University and Palestinian MOTA-DACH, under the direction of Lorenzo Nigro and Hamdan Taha, and Jehad Yasine, since 2015 [14, 15].

The stratigraphic correlation between excavations is based upon similarities in material culture, mainly pottery, and on the relative stratigraphic position of the strata in relation to architectural features encompassing different areas.

2.2 Samples Collection

The 45 samples were collected in March 2017 at the Jericho archaeological site, located in the modern Tell es-Sultan, in the Jordan River valley, Palestine. The excavation was performed north of the excavated portion by K. Kenyon on the HII and III blocks that correspond to late Bronze Age stratum. The location of sample collection is shown in red in Figure 1.

Figure 1: *Stratigraphy of sample collection location.*



Source: R.P. Silva.

2.3 Samples preparation

The ceramic fragments were initially washed with Milli-Q water. The external surface was then removed with a fine bristle brush and holes were made in the fragment with a tungsten carbide rotary file, attached to a variable speed drill [16]. Around 400 mg of powdered sample was obtained from four to six holes on the surface of the ceramic fragment, preventing the drill from crossing over the walls. This powder was dried for 24 h in an oven at 104 ^{o}C and stored in a desiccator. Around 100 mg of each sample were weighed in polyethylene involucres and sealed with a sealing iron. Each involucre was wrapped in Al foil. Groups of up to 8 powdered ceramic samples and two reference materials (Standard Reference Material, NIST- SRM 1633b, Constituent elements in Coal Fly Ash) were subject to analysis and the Sediment candidate certified reference material, named RM in this work, was used for analytical quality control. Both reference materials were irradiated in the swimming pool of reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, at a thermal neutron flux of around 10^{12} cm $^{-2}$ × cm^{-1} [16].

2.4 Equipment

Gamma-ray spectrometry was carried out with a hyperpure Ge detector (model GX 2519) from Canberra, with a resolution of 1.9 keV at the 1332 keV gamma peak of 60Co. The spectra were collected by a Canberra S-100 MCA with 8192 channels. The software Genie2000 NAA Processing Procedure, developed in Canberra, was used to analyze the gamma-ray spectra [17]. Two measurement series were carried out. The elements K, La, Lu, Na, Sm, U and Yb were measured after 7 days of decay, and elements Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Th and Zn were measured after 25-30 days of decay [17].

2.5 Statistical treatment

To elucidate the major variations in the compositional data set obtained by INAA, one must use multivariate statistics that consider the correlation between elemental concentrations and absolute concentrations during analysis. The basis for all multivariate analyses is that all the elements included are independent variables. The data set were studied by cluster analysis and discriminant analysis.

Cluster analysis is a general term that applies to a variety of specific techniques. It essentially works by measuring and grouping samples based on their similarity/dissimilarity (i.e. distance), on the basis of the defined measure. The interpretation of cluster analysis is highly subjective; thus, it is normally only used to identify possible groupings, after which other techniques are employed for group refinement and classification. Here, was used discriminant analysis [18].

Discriminant analysis is a multivariate technique based on the assumption that the pooled variance-covariance matrix is an accurate representation of the total variance and covariance of the data set. Bivariate plots of discriminant functions are useful for visually displaying groups. Confidence ellipses, i.e. probability intervals, are usually drawn around groups to emphasize the differences between groups or to show the associations between individual samples and known groups [18].

3. RESULTS AND DISCUSSION

In this work, the Sediment candidate of reference material was used to study the precision of the technique, since all sources of error for this candidate are already known (calculation made by the Department of Environmental Sciences, Wageningen University, Netherlands), and have been analyzed by 41 NAA laboratories [19]. The results of this study were statistically compared with the data of these 41 laboratories in order to evaluate the analytical process and to establish the chemical elements which can be used in data interpretation. The analyzed elements are shown in Table 1, as well as the energy of the radioisotope used in the analysis, the measured value (mean of six determinations), the relative standard deviation (RSD), and the recommended value.

The analyses with RSD less than 10% were used [20]. All potential interference occurring in gamma-ray spectrometry were considered and checked. A possible source of error in the determination of rare earth elements is the presence of significant amounts of fissible nuclides, ^{235}U and ^{233}U. It is well-known that rare earth elements nuclides, especially the light rare elements (La to Sm) are produced both by activation and by fission. In the present work no interferences were expected in the samples because of the very low uranium fission in the determination of La and Ce. This interference is negligible when the U concentration is below 5 ppm [21]. Although Co and Ta had RSD less than 10%, it was not included in the data set because their concentration can be affected by tungsten carbide files [22]. The determination of Zn is not reliable due to strong γ-ray interference by ^{46}Sc. Therefore, the elements Na, K, La, Yb, Sc, Fe, Cs, Ce, Eu, Hf e Th were used in the subsequent data analysis.

Table 1: Results for RM in µg/g unless otherwise indicated.

Elements	**Energy (keV)**	**Experimental Results***	**SD**	**% RSD**	**Recommended Value**	**SD**
Na mg/g	1368.55	4.59	0.22	4.82	4.69	0.34
K mg/g	1524.58	13.31	1.14	8.53	12.67	0.66
La	1596.21	21.23	1.09	5.14	19.46	1.72
Sm	103.18	3.30	0.95	28.78	( )	( )
Yb	396.32	1.69	0.12	7.31	( )	( )
Lu	208.36	0.26	0.05	20.34	( )	( )
Sc	889.28	5.50	0.26	4.78	5.67	0.37
Cr	320.08	63.35	3.06	4.83	70.98	7.31
Fe mg/g	1099.25	25.53	1.97	7.71	25.39	1.42
Co	1332.50	7.77	0.35	4.54	8.14	0.75
Zn	1115.55	360.49	26.57	7.37	( )	( )
Rb	1077.00	68.84	14.32	20.81	61.38	5.02
Sb	1690.98	3.59	1.01	28.06	2.46	0.39
Cs	795.84	4.01	0.37	9.13	3.77	0.36
Ce	145.44	38.72	3.31	8.56	39.99	5.03
Eu	1408.01	0.83	0.07	8.02	( )	( )
Hf	482.18	7.45	0.44	5.87	( )	( )
Th	312.17	5.38	0.26	4.80	5.69	0.63

*means with n=6 ; ( ) = no recommended values.

In total, 45 samples were analyzed, and none of the considered elements presented missing values. Initially the results were transformed in log10 to compensate for the large differences of magnitudes between the large and trace-level measured elements. Table 2 shows the range and the mean of the samples analyzed.

The results were submitted to cluster and discriminant analysis with the purpose of studying the similarities or dissimilarities between ceramic fragments. The intention was to group similar samples according to their characteristics, which in turn can be considered as several simultaneously related variables, all of the having equal importance in the beginning of the analysis. Another consideration is that the data must follow a normal distribution.

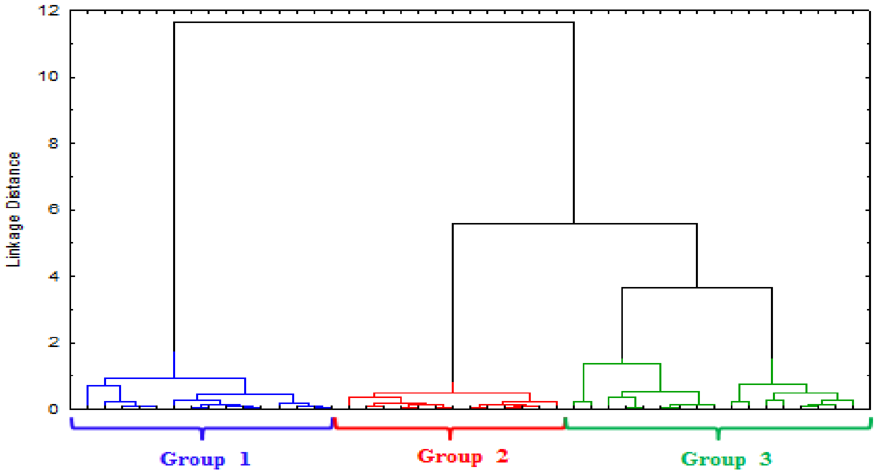
Next, the results were submitted to a cluster analysis with a matrix of 45 × 11, whose purpose is to identify groups of chemically similar samples and, thus, samples from the same clay source. The squared Euclidean distance was adopted as the criterion of appearance and Ward's method as the clustering algorithm, since it tends to form groups with high internal homogeneity and takes into account the cluster structure [23]. StatSoft's Statistica software [24] was used to perform all the statistical studies.

Table 2: Mean Standard Deviation and Range for ceramic samples from Jericho archaeological site, in µg/g) unless indicated, n = 45.

Element	Range	Mean ±SD*
Na mg/g	2.49-13.34	7.59 ±2.75
K mg/g	10.45-52.44	29.25±10.72
La	12.37-72.45	25.52±12.11
Yb	0.69-4.78	2.06±0.94
Sc	7.83-21.43	12.37±3.05
Fe mg/g	18.83-85.79	33.63±10.68
Cs	0.62-6.98	3.34±1.45
Ce	24.43-136.67	49.70±23.38
Eu	0.61-2.71	1.15±0.46
Hf	1.41-12.08	4.30±2.93
Th	3.61-14.44	6.29±2.36

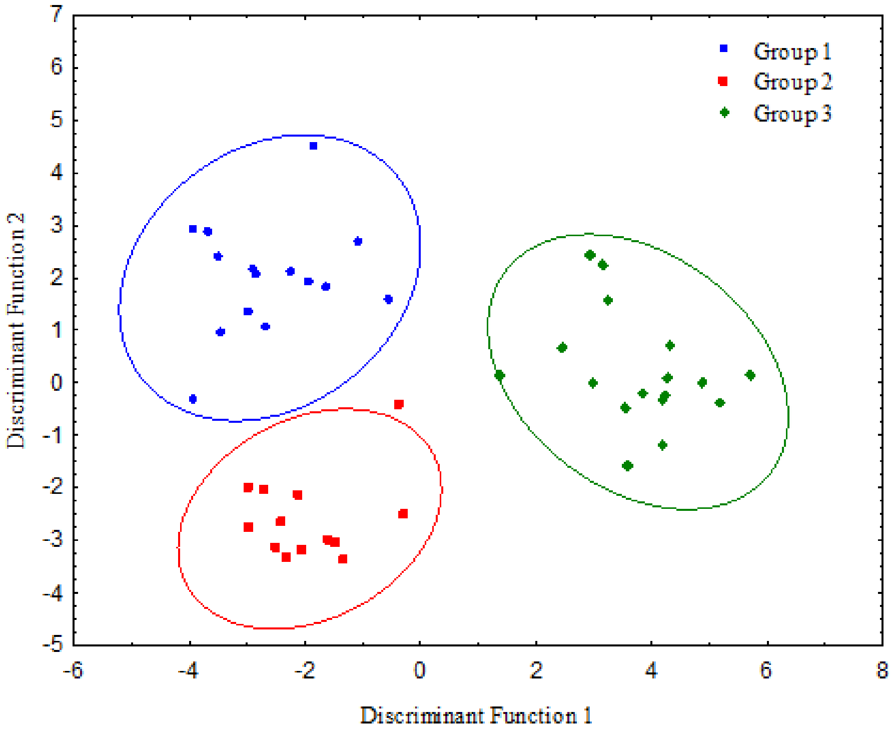
Figure 2 is a dendrogram showing that the samples were pre-classified into three groups with very similar in chemical composition, allowing us to infer that the ceramics from this site come from three different sources of clay.

Figure 2: Dendrogram of matrix data using Euclidean squared distance and Ward's Method.



Source: Author

Figure 3: Discriminant Analysis of Jericho site samples.



Source: Author

4. CONCLUSION

The results of this preliminary study of the chemical composition in ceramics at the Jericho archaeological site provided evidence indicating that the raw material used in the manufacture of these objects is from three distinct sources of clay.

The compositional groups found corroborate archaeological studies of the area, which revealed a sequence of multiple layers of occupation, based on the similarities of material culture. Further studies may contribute additional information to determine whether the clays are of local origin or not. Future studies using dating techniques will also be able to establish the temporal space in which these different ceramics groups are inserted.

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