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Application of physical–chemical analytical techniques in the study of ancient ceramics

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Abstract

The results of the study of 53 ceramic fragments from several archaeological deposits, supposedly Tartessian, are shown in this manuscript. Visible spectroscopy, X-ray diffractometry and energy dispersive X-ray spectroscopy combined with scanning electron microscopy have been used for determining the color, the chemical and mineralogical composition, and interesting microstructures like microorganisms, tempers, vitrifications, and crystal formation.

Inductively coupled plasma-atomic emission spectrometry has been used in order to determine the percentage of the eight major chemical elements (Na, Mg, Al, Si, K, Ca, Ti, Fe). They are always present in ceramic pastes and tempers. Statistical processing, including cluster analysis, is made using the obtained results.

Given these data, some aspects of ceramic production can be deduced and the pieces can be compared. The correlation of these results with archaeological data, about if sites belongs to Tartessian times, has validated this methodology. In addition, it has supported the archaeological methodology.

Keywords: Ancient ceramics; Inductively coupled plasma-atomic emission spectrometry; Chromatic measurements (CIE64); Scanning electron microscopy; X-ray diffractometry; Cluster analysis

1. Introduction

Ceramic fragments, found in many archaeological deposits, are one of the references in archaeological research. Ceramic production is one of the older and extended human activities in all civilizations. The detailed analysis of technological aspects (firing, tempers, finish, etc.), of attributes (shape, size, decoration, etc.), and the marks of use of ceramic remains, allows the functionality, complexity of the productive process, degree of specialization and social complexity of the groups that made and/or used them to be deduced.

As aforementioned, the chemical and mineralogical composition of ceramic paste (mass, tempers and inclusions), is one of the parameters that contributes to characterize a certain production and, therefore, to identify a certain society or civilization. There are many published papers referred to these aspects of ceramics. In these, several study techniques have been used [1–9].

This article is focussed on the physical–chemical characterization of ceramics, supposedly Tartessian, belonging to the Archaeological Museum of El Puerto de Santa María (Cádiz), with the aim of comparing different population groups sited in the same Tartessian zone. Thus, ceramic fragments from *Pocito Chico*, *Campín Bajo*, *Arroyo Chaparral*, *Cantarranas*, *Beatillas*, *Venta Alta*, and *Vaina sites*, have been studied using several spectroscopic techniques. These techniques have allowed the chromatic characterization, the characterization of the paste and tempers, and the identification and quantification of elements present in ceramic paste.

2. Experimental methodology

2.1. Samples

The archaeologists of Puerto de Santa María Museum have selected the archaeological deposits and the 53 ceramic

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Table 1
General identifying data of ceramic fragments studied

Key	Archaeological key[a]
T1	PCH/97/1/4/4.300
T2	PCH/3/96
T3	PCH97/1/41/4.297
T4	PCH/96/51/30
T5	PCH/97/1/...
T6	PCH/97/1/41/4.297
T7	PCH/97/1/41/4.298
T8	PCH/97/1/34/4.299
T9	PCH
T10	PCH
T11	PCH
T12	PCH/.../37
T13	PCH/97/1/2/4.303
T14	PCH
M1	PCH/96...60
M2	PCH/971 VI V 787
M3	PCH/97/I/41/3144
M4	PCH/97/1/39/2073
M5	
M6	PCH/96/1.../57
M7	PCH/97/1/2/221
M8	PCH/97/1/28/4296
M9	PCH/96/.../24
CTR1	Cantarranas, edge 59
CTR2	Cantarranas, body 179
CTR3	Cantarranas, body 193
CTR4	Cantarranas, edge 424
CMB1	Campín Bajo, edge
CMB2	Campín Bajo, body 23
CMB3	Campín Bajo, body 88
CMB4	Campín Bajo, body 12
CMB5	Campín Bajo, body 48
CMB6	Campín Bajo, body 10
CMB7	Campín Bajo, body 11
VA1	Venta Alta, edge 42
VA2	Venta Alta, edge 444
ACH1	Arroyo Chaparral, edge 1
ACH2	Arroyo Chaparral, edge 7
ACH3	Arroyo Chaparral, edge 5
ACH4	Arroyo Chaparral, body 6
ACH5	Arroyo Chaparral, body 8
V1	Vaina, tripod edge 32
V2	Vaina, patera edge 140
B1	Beatillas, urn 27
B2	Beatillas, cup 34
CMP1	Campillo, bottom1, cup 1
CMP2	Campillo, bottom1, plate 6
CMP3	Campillo, bottom1, patera 7
CMP4	Campillo, bottom1, Oinochoe 8
CMP5	Campillo, bottom1, Samaria foot 5
CMP6	Campillo, bottom1, decorated body 4
CMP7	Campillo, bottom1, bottom 9
CMP8	Campillo, bottom1, cup 36

[a] PCH: Pocito Chico site; other sites as specified.

samples. The identification key and archaeological key of each sample, as well as its place of origin, are given in Table 1. The samples correspond to small pieces of several utensils (plates, vessels, etc.). They are from nine archaeological deposits, supposedly Tartessian, and some of them show external decoration.

2.2. Chromatic characterization

Normally, the pictorial layer chromatic characterization is made using subjective methods based on the visual comparison between the sample and a table of pre-established colors such as, for example, the Munsell Code [10,11]. This method can lead to serious errors because it is very much influenced by external factors such as the illumination used during the comparison, the subjective observational abilities of the researcher, and the chromatic stability of the patterns used for the comparison.

In this work, an objectively reproducible chromaticity characterization has been carried out using electronic spectroscopy. The method consists of the determination of the optical reflectance within the visible frequency range using an Otsuka MCPD 1100 visible ultraviolet spectrophotometer. The system is equipped with optical fiber light conducting elements that enable the direct study of the pictorial surface of the material to be made without perturbing it.

Using the normalized CIE64 system [10–12], the chromaticity coordinates x_{10}, y_{10} deduced from the tristimulus values X_{10}, Y_{10}, Z_{10} have been calculated. These variables, that define the tonality and the color saturation, have been represented in the color space diagram. An incandescent tungsten lamp with a filtered emission was used as an illumination system and the CIE illuminant was a D_{65} standard source.

As a white pattern, a polymeric tablet supplied for Top Sensor Systems (model WS-2), was used. The sample chamber has a normalized geometry of $0°/45°$ for the illumination/observation process, in order to minimize the specular/diffuse reflectance ratio of the captured radiation and for obtaining a realistic chromaticity value.

2.3. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy

Scanning electron microscopy (SEM), in secondary electron and backscattering mode, has been used for observing interesting microstructures like microorganisms, tempers, vitrifications, crystallizations or particles of composed with heavy elements that cannot be detected in general analysis. In addition, energy dispersive X-ray spectroscopy (EDX) has been used for qualitative elementary chemical analysis of the zone that is visualized in the monitor. A LINK AN10000 energy dispersive X-ray detector system, joined to a JEOL JSM820 scanning electron microscope, was used. To prevent surface charging, the samples were gold-coated, so that a constant gold signal appears in all EDS output.

2.4. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

We take the hypothesis as a starting point that several ceramic pastes are similar when they contain similar proportions of chemical elements because they come from similar clays and tempers. This composition is related to the place where they were made and the artisan technique. With this supposition, eight major chemical elements in the ceramic paste have been selected that are always present in common pastes and tempers (calcite, quartz, and common silicates); these are Na, Mg, Al, Si, K, Ca, Ti, Fe, and are found in the main publications consulted [1–9]. In the selection of these elements, those for which the proportion may vary during the heating time, are eliminated. Only the concentration of the selected elements is considered, not the compound present, the oxidation state and whether it makes up the mass or temper.

With this aim, a quantitative analysis technique that is suitable regarding availability/cost has been selected. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is the technique. A Philips ICP PU 7000 spectrometer was used. The Milestone Ethos 1600 was the digestion system used.

Fragments of ceramic paste from inside the sample were obtained for the analysis, after removing the surface layer of decorative painting. Then, they were pulverized and homogenized. Calibration of the system was made using the GXR-3 reference sample, supplied by the US Geological Survey. The results for each sample are expressed as the median value of eight instrumental measurements and its standard deviation.

From the mass percentages obtained using quantitative analysis of eight chemical elements that are mainly present in antique ceramics, a statistical treatment was carried out, including cluster analysis, using the SPSS computer program. The centroid method for grouping and a matrix of squared Euclidean distances have been utilized, establishing a hierarchical diagram or dendogram that links the more similar samples.

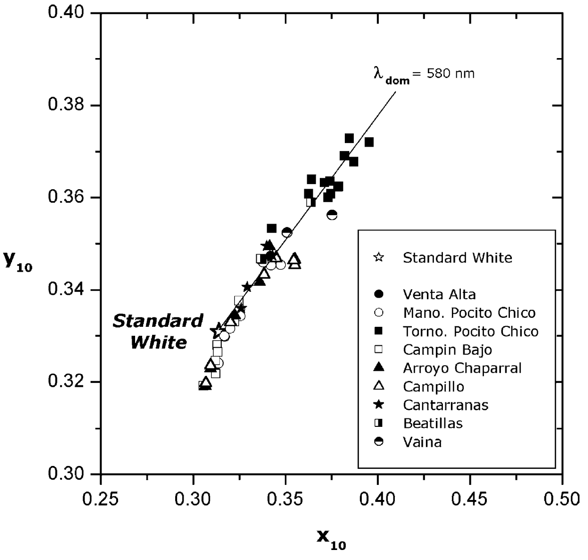

Fig. 1. CIE64 colorimetric diagram enlargement for the ceramic samples. It can be observed how the samples studied are grouped.

2.5. X-ray diffractometry (XRD)

This technique allows the crystalline substances present in ceramic mass to be determined. The equipment used was a Phillips PW1830 diffractometer, provided with

Table 2
CIE64 chromatic coordinates values of the ceramic samples studied

Sample	Chromatic characterization		
	x_{10}	y_{10}	Y_{10}
T1	0.3821	0.3690	65.824
T2	0.3955	0.3720	63.454
T3	0.3871	0.3677	60.954
T4	0.3644	0.3639	70.646
T5	0.3713	0.3632	61.939
T6	0.3847	0.3728	62.069
T7	0.3372	0.3466	39.322
T8	0.3627	0.3608	73.085
T9	0.3741	0.3635	68.570
T10	0.3788	0.3624	62.829
T11	0.3785	0.3623	68.610
T12	0.3425	0.3533	86.497
T13	0.3731	0.3600	65.552
T14	0.3746	0.3608	64.068
CTR1	0.3398	0.3495	38.178
CTR2	0.3294	0.3406	39.709
CTR3	0.3430	0.3474	61.363
CTR4	0.3260	0.3360	47.311
M1	0.3476	0.3454	36.362
M2	0.3172	0.3298	40.789
M3	0.3254	0.3358	43.722
M4	0.3170	0.3300	38.329
M5	0.3202	0.3316	45.363
M6	0.3256	0.3343	47.640
M7	0.3422	0.3453	57.374
M8	0.3136	0.3241	39.294
M9	0.3380	0.3460	71.000
CMB1	0.3123	0.3218	17.837
CMB2	0.313	0.3280	40.868
CMB3	0.3133	0.3265	23.073
CMB4	0.3223	0.3331	28.643
CMB5	0.3056	0.3192	23.472
CMB6	0.3122	0.3246	26.260
CMB7	0.3248	0.3376	40.828
VA1	0.3119	0.3229	28.646
VA2	0.3419	0.3473	36.206
ACH1	0.3362	0.3416	60.400
ACH2	0.3067	0.3191	39.087
ACH3	0.3095	0.3229	44.912
ACH4	0.3226	0.3344	26.329
ACH5	0.3415	0.3493	42.649
V1	0.3754	0.3562	54.852
V2	0.3511	0.3524	65.724
B1	0.3641	0.3589	58.919
B2	0.3367	0.3467	42.784
CMP1	0.3069	0.3198	35.562
CMP2	0.3551	0.3454	54.339
CMP3	0.3551	0.3465	59.520
CMP4	0.3545	0.3464	62.393
CMP5	0.3385	0.3433	67.974
CMP6	0.3203	0.3330	67.237
CMP7	0.3450	0.3469	65.312
CMP8	0.3094	0.3236	48.527

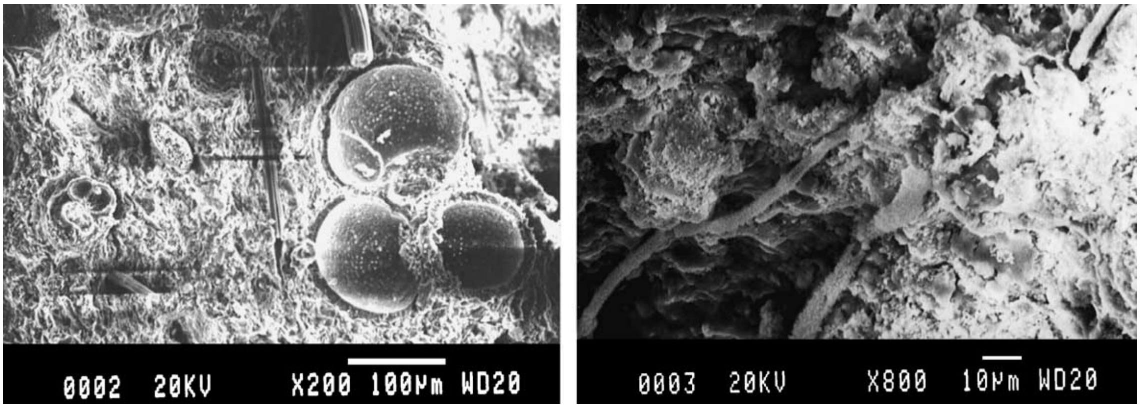

Fig. 2. Microorganisms localized in (a) CTR2; (b) CTR3 samples, and observed using SEM in secondary electron mode.

automated software for PC-APD powder diffraction and PC-IDENTIFY software for crystalline phase identification.

In all cases, the Cu Kα radiation has been used, applying 40 kV to the tube and 40 mA for the filament.

3. Results and discussion

3.1. Chromatic characterization

The chromatic study of the ceramic mass was carried out in two ways. Initially, a colorimetric study of the exposed surface, both interior and exterior, was made. However, in the majority of samples, great variations of the color between the internal and external surfaces was observed. Generally this is due to several decorations on the external surface. For that reason, the average color of the ceramic powder, pressed in tablets, has been measured. This powder has been obtained using the joint pulverization of several fragments from different ceramic zones, until particles <40 mm diameter were obtained. The decorations on these fragments had been scraped off because they do not belong to the color of the ceramic mass.

The results of the chromatic characterization of these tablets are shown in Table 2. The CIE64 colorimetric diagram is obtained when the x_{10}, y_{10} colorimetric coordinates are represented. In Fig. 1, an enlargement of that diagram is shown. How the samples are adjusted to a line that begins from the white theoretical point to the orange ochre color ($\lambda_{\text{dom}} = 580$ nm) is observed in that diagram. Within this line, three groups can be differentiated according to their distance from the achromatic stimulus or white.

The first group is made up of samples that have chromatic coordinates very near to the theoretical white. They are samples whose appearance is greyish, more or less clear, depending on the value of the Y_{10} luminosity coordinate. The samples from Campín Bajo (CMB), Arroyo Chaparral (ACH), most of the “handmade” samples from Pocito Chico (M), some from Campillo (CMP1, CMP6, CMP8), one from Cantarranas (CTR4) and one from Venta Alta (VA1) are in this group.

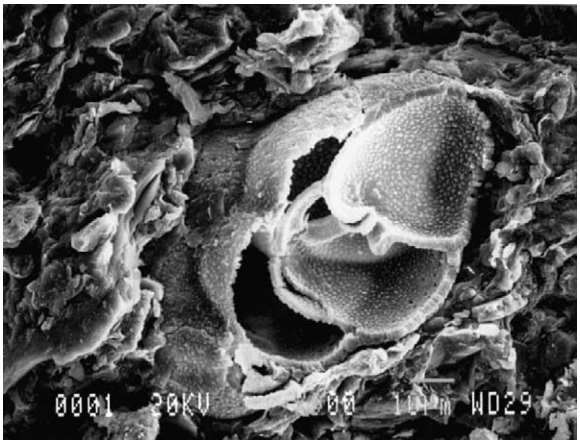

Fig. 3. Microorganisms localized in a T6 sample and observed using SEM in secondary electron mode. Usually, they are found in ceramics from the Basin of the Gualdalquivir River.

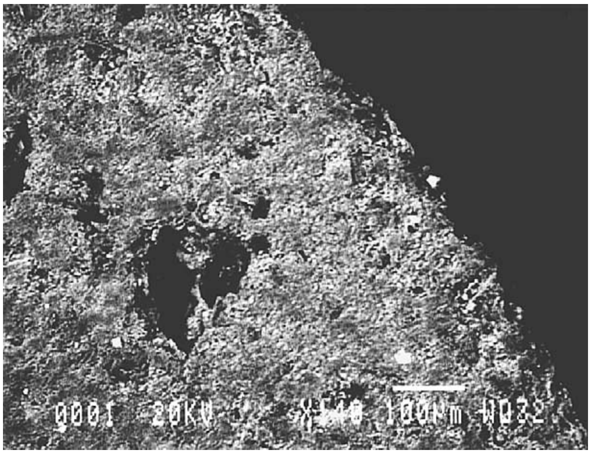

Fig. 4. T9 sample (Pocito Chico) microphotograph using BSE, in which particles that are more brilliant than the rest are observed that correspond to P, La and Ce.

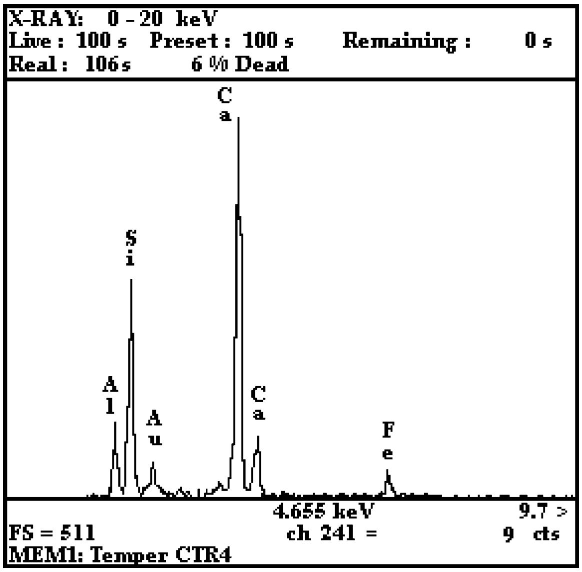

Fig. 5. EDS spectrum of black temper found in sample CTR4, where the presence of a great amount of calcium, silicon, aluminum and iron are observed.

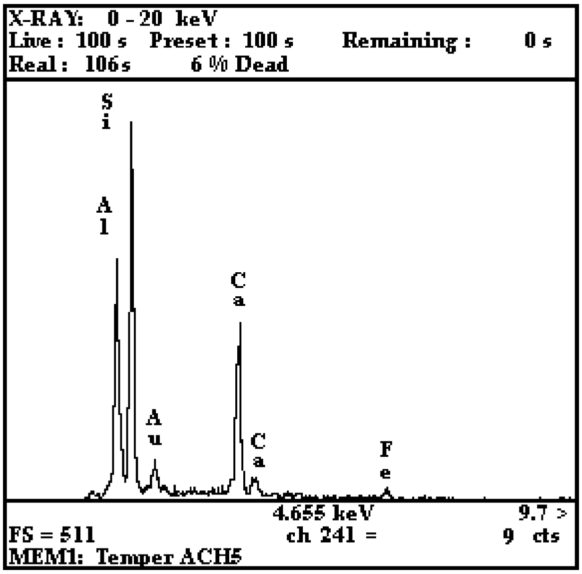

Fig. 6. EDS spectrum of black temper found in sample ACH5, in which a great amount of silicon and aluminum with respect to the amount of calcium, is observed.

The following group is made up of the samples that are between the other two groups, and show a medium saturation. They are characterized by being of a greyish ochre color. In this group most of the samples are from Cantarranas (CTR), Campillo (CMP), some from Arroyo Chaparral (ACH1, ACH5), some “handmade” samples from Pocito Chico (M1, M7, M9), some “potter’s wheel” samples from Pocito Chico (T7, T12), one from Vaina (V2), one from Venta Alta (VA2) and one from Beatillas (B2).

The last group is made up of samples that have chromatic coordinates that are into the orange or yellowish ochre color zone, corresponding to a dominant wavelength between 575 and 585 nm. They all show high luminosity values. Most of the “potter’s wheel” samples from Pocito Chico (T), one from Vaina (V1), and one from Beatillas (B1) appear in this group.

As it is observed, the color parameters determination of the ceramic paste characterizes the sample but does not provide any cluster criterion regarding the archaeological

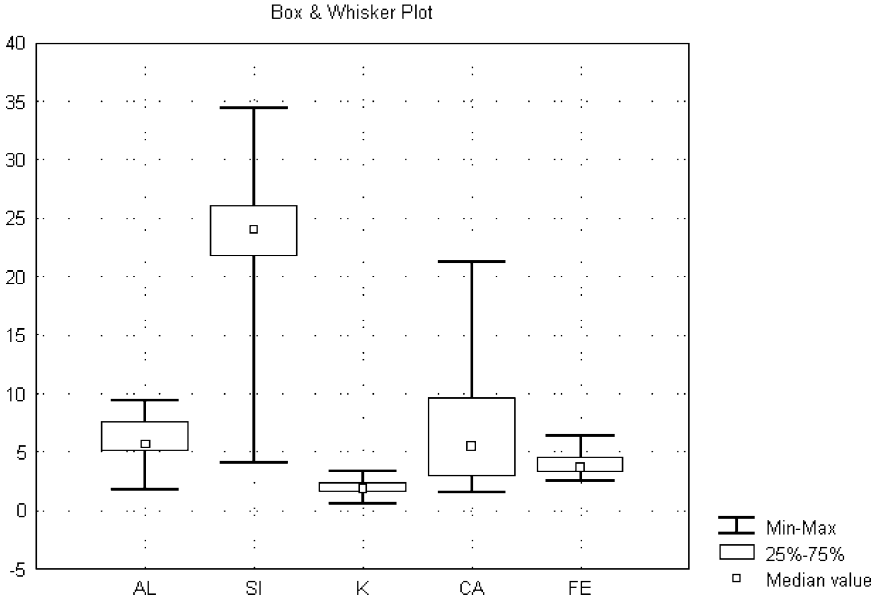

Fig. 7. Representation of means and standard deviation of the five chemical elements that show greater variations in the values obtained in this sample group.

deposit or the origin. It is necessary to indicate that the color of any object is not due to the presence of certain chemical elements, but to the presence of certain compounds. Thus, for example, the reddish color of ceramics usually is associated with a great amount of iron. However, the black color can be due to the presence of iron if the piece has been heated in a depleted oxygen atmosphere and this does not reach its maximum oxidation state. In addition, the black color may be due to the presence of carbon that has been incorporated during the heating because of the combustion smoke. Also,

Table 3
Mass percentages of eight chemical elements that are considered as major in ancient ceramic studies

Key	Na	Mg	Al	Si	K	Ca	Ti	Fe
T1	0.53 ± 0.01	0.99 ± 0.02	5.62 ± 0.10	25.60 ± 0.5	2.75 ± 0.05	7.86 ± 0.14	0.35 ± 0.01	3.59 ± 0.07
T2	0.60 ± 0.01	1.02 ± 0.02	5.54 ± 0.10	27.70 ± 0.5	3.12 ± 0.06	4.97 ± 0.09	0.37 ± 0.01	3.98 ± 0.07
T3	0.50 ± 0.01	0.99 ± 0.02	5.52 ± 0.10	27.30 ± 0.5	3.28 ± 0.06	5.36 ± 0.10	0.31 ± 0.01	4.04 ± 0.07
T4	0.52 ± 0.01	0.90 ± 0.02	5.33 ± 0.10	24.60 ± 0.5	2.64 ± 0.05	8.82 ± 0.16	0.35 ± 0.01	3.47 ± 0.06
T5	0.74 ± 0.01	1.17 ± 0.02	6.71 ± 0.13	27.70 ± 0.5	2.92 ± 0.06	9.62 ± 0.19	0.45 ± 0.01	4.31 ± 0.08
T6	0.44 ± 0.01	1.03 ± 0.02	3.79 ± 0.07	24.80 ± 0.5	2.30 ± 0.04	6.27 ± 0.12	0.37 ± 0.01	2.89 ± 0.05
T7	0.44 ± 0.01	0.88 ± 0.02	5.58 ± 0.10	24.00 ± 0.4	2.79 ± 0.05	7.85 ± 0.14	0.40 ± 0.01	3.16 ± 0.06
T8	0.66 ± 0.01	1.21 ± 0.02	5.38 ± 0.09	26.00 ± 0.5	2.82 ± 0.05	4.65 ± 0.08	0.50 ± 0.01	3.58 ± 0.06
T9	0.43 ± 0.01	0.89 ± 0.02	5.20 ± 0.10	24.00 ± 0.5	2.57 ± 0.05	7.11 ± 0.13	0.42 ± 0.01	3.12 ± 0.06
T10	0.52 ± 0.01	0.90 ± 0.02	5.66 ± 0.10	26.50 ± 0.5	3.40 ± 0.06	3.92 ± 0.07	0.49 ± 0.01	3.38 ± 0.06
T11	0.45 ± 0.01	1.16 ± 0.02	3.40 ± 0.06	24.50 ± 0.5	2.37 ± 0.04	2.54 ± 0.05	0.40 ± 0.01	3.21 ± 0.06
T12	0.86 ± 0.01	1.01 ± 0.02	3.20 ± 0.06	25.30 ± 0.5	2.45 ± 0.05	4.34 ± 0.08	0.39 ± 0.01	3.22 ± 0.06
T13	0.46 ± 0.01	0.96 ± 0.02	4.79 ± 0.10	23.90 ± 0.5	2.98 ± 0.06	6.13 ± 0.12	0.38 ± 0.01	3.29 ± 0.07
T14	0.47 ± 0.01	0.92 ± 0.02	4.77 ± 0.09	23.90 ± 0.5	2.73 ± 0.05	5.66 ± 0.11	0.41 ± 0.01	3.01 ± 0.06
M1	0.66 ± 0.01	1.31 ± 0.03	8.24 ± 0.11	24.80 ± 0.5	2.18 ± 0.04	2.42 ± 0.05	0.66 ± 0.01	5.96 ± 0.12
M2	0.32 ± 0.01	0.80 ± 0.02	5.02 ± 0.10	25.40 ± 0.5	1.98 ± 0.04	5.46 ± 0.11	0.43 ± 0.01	4.01 ± 0.08
M3	0.44 ± 0.01	1.33 ± 0.03	8.44 ± 0.17	24.80 ± 0.5	2.40 ± 0.05	1.92 ± 0.04	0.52 ± 0.01	5.46 ± 0.11
M4	0.29 ± 0.01	1.04 ± 0.02	7.52 ± 0.15	24.00 ± 0.5	2.18 ± 0.04	5.20 ± 0.10	0.45 ± 0.01	4.40 ± 0.09
M5	0.47 ± 0.01	1.27 ± 0.03	4.89 ± 0.10	22.80 ± 0.4	1.52 ± 0.03	5.11 ± 0.10	0.46 ± 0.01	4.81 ± 0.09
M6	0.30 ± 0.01	0.87 ± 0.02	3.74 ± 0.07	21.70 ± 0.4	1.68 ± 0.03	6.20 ± 0.12	0.37 ± 0.01	3.64 ± 0.07
M7	0.28 ± 0.01	0.81 ± 0.02	5.37 ± 0.11	25.20 ± 0.5	2.05 ± 0.04	4.85 ± 0.09	0.39 ± 0.01	4.06 ± 0.08
M8	0.23 ± 0.01	0.92 ± 0.02	7.41 ± 0.15	27.10 ± 0.5	2.46 ± 0.05	3.33 ± 0.06	0.46 ± 0.01	4.79 ± 0.09
M9	0.20 ± 0.01	0.87 ± 0.02	1.75 ± 0.04	20.10 ± 0.4	1.83 ± 0.04	5.48 ± 0.10	0.30 ± 0.01	3.45 ± 0.07
CTR1	0.23 ± 0.01	0.64 ± 0.01	4.57 ± 0.04	9.54 ± 0.19	0.77 ± 0.02	21.25 ± 0.4	0.26 ± 0.01	2.52 ± 0.05
CTR2	0.19 ± 0.01	0.72 ± 0.01	4.23 ± 0.08	11.95 ± 0.2	0.61 ± 0.01	20.87 ± 0.4	0.25 ± 0.01	2.56 ± 0.05
CTR3	0.32 ± 0.01	0.85 ± 0.03	5.03 ± 0.10	4.93 ± 0.10	1.13 ± 0.02	17.99 ± 0.4	0.25 ± 0.01	2.78 ± 0.06
CTR4	0.16 ± 0.01	0.58 ± 0.01	4.27 ± 0.08	10.52 ± 0.2	0.50 ± 0.01	18.68 ± 0.4	0.24 ± 0.01	2.63 ± 0.05
CMB1	0.48 ± 0.01	1.12 ± 0.02	8.07 ± 0.16	18.40 ± 0.4	1.93 ± 0.04	2.25 ± 0.05	0.50 ± 0.01	4.56 ± 0.09
CMB2	0.59 ± 0.01	1.60 ± 0.03	9.41 ± 0.19	20.53 ± 0.4	1.69 ± 0.03	2.01 ± 0.04	0.61 ± 0.01	5.71 ± 0.11
CMB3	0.36 ± 0.01	1.24 ± 0.02	7.07 ± 0.14	23.87 ± 0.5	1.47 ± 0.03	2.67 ± 0.05	0.48 ± 0.01	4.34 ± 0.09
CMB4	0.40 ± 0.01	0.87 ± 0.02	6.45 ± 0.13	24.48 ± 0.5	2.27 ± 0.05	1.69 ± 0.03	0.43 ± 0.01	3.31 ± 0.07
CMB5	0.45 ± 0.01	1.12 ± 0.02	8.26 ± 0.16	23.02 ± 0.5	1.71 ± 0.03	2.25 ± 0.05	0.53 ± 0.01	4.83 ± 0.10
CMB6	0.55 ± 0.01	1.33 ± 0.03	7.82 ± 0.15	23.65 ± 0.5	2.26 ± 0.04	8.49 ± 0.17	0.48 ± 0.01	4.27 ± 0.08
CMB7	0.43 ± 0.01	1.16 ± 0.02	8.60 ± 0.17	21.47 ± 0.4	2.35 ± 0.05	1.57 ± 0.03	0.42 ± 0.01	4.95 ± 0.10
VA1	0.39 ± 0.01	1.20 ± 0.02	8.37 ± 0.17	23.61 ± 0.5	1.37 ± 0.03	1.86 ± 0.04	0.48 ± 0.01	4.71 ± 0.09
VA2	0.40 ± 0.01	1.23 ± 0.02	8.81 ± 0.18	23.05 ± 0.5	1.79 ± 0.04	2.95 ± 0.06	0.51 ± 0.01	5.34 ± 0.11
ACH1	0.28 ± 0.01	0.96 ± 0.02	7.25 ± 0.14	31.48 ± 0.6	1.16 ± 0.02	2.90 ± 0.06	0.44 ± 0.01	4.14 ± 0.08
ACH2	0.16 ± 0.01	0.73 ± 0.01	8.63 ± 0.17	29.38 ± 0.6	1.26 ± 0.03	1.47 ± 0.03	0.51 ± 0.01	4.65 ± 0.09
ACH3	0.28 ± 0.01	0.79 ± 0.02	7.32 ± 0.15	30.12 ± 0.6	1.36 ± 0.03	2.20 ± 0.04	0.44 ± 0.01	4.50 ± 0.09
ACH4	0.31 ± 0.01	0.93 ± 0.02	8.61 ± 0.17	29.47 ± 0.6	1.85 ± 0.04	1.76 ± 0.03	0.51 ± 0.01	5.06 ± 0.10
ACH5	0.91 ± 0.01	1.94 ± 0.04	7.55 ± 0.15	21.25 ± 0.4	1.23 ± 0.02	12.51 ± 0.3	0.58 ± 0.01	6.39 ± 0.13
V1	0.57 ± 0.01	1.37 ± 0.03	8.07 ± 0.16	23.55 ± 0.5	2.26 ± 0.05	5.28 ± 0.11	0.47 ± 0.01	4.42 ± 0.09
V2	0.34 ± 0.01	1.14 ± 0.02	5.34 ± 0.11	20.58 ± 0.4	1.17 ± 0.02	10.80 ± 0.2	0.31 ± 0.01	3.17 ± 0.06
B1	0.68 ± 0.01	1.41 ± 0.03	6.39 ± 0.13	26.63 ± 0.5	1.44 ± 0.03	9.50 ± 0.19	0.37 ± 0.01	3.97 ± 0.08
B2	0.27 ± 0.01	0.84 ± 0.02	5.08 ± 0.10	21.90 ± 0.4	0.83 ± 0.02	13.47 ± 0.3	0.31 ± 0.01	3.65 ± 0.07
CMP1	0.64 ± 0.01	0.97 ± 0.02	4.89 ± 0.10	13.95 ± 0.3	1.68 ± 0.03	10.79 ± 0.2	0.33 ± 0.01	2.45 ± 0.05
CMP2	0.55 ± 0.01	1.12 ± 0.02	5.56 ± 0.11	10.82 ± 0.2	1.81 ± 0.04	9.88 ± 0.20	0.33 ± 0.01	2.81 ± 0.06
CMP3	0.56 ± 0.01	1.06 ± 0.02	6.01 ± 0.12	18.62 ± 0.4	1.74 ± 0.03	10.06 ± 0.2	0.33 ± 0.01	3.09 ± 0.06
CMP4	0.59 ± 0.01	0.99 ± 0.02	5.67 ± 0.11	4.07 ± 0.08	1.83 ± 0.04	10.28 ± 0.2	0.35 ± 0.01	3.00 ± 0.06
CMP5	0.63 ± 0.01	1.12 ± 0.02	5.86 ± 0.12	26.20 ± 0.5	1.96 ± 0.04	10.43 ± 0.2	0.40 ± 0.01	3.09 ± 0.06
CMP6	0.49 ± 0.01	1.29 ± 0.03	8.03 ± 0.16	34.34 ± 0.7	2.58 ± 0.05	5.42 ± 0.11	0.51 ± 0.01	3.99 ± 0.08
CMP7	0.39 ± 0.01	0.65 ± 0.01	5.07 ± 0.10	22.45 ± 0.5	0.90 ± 0.02	14.61 ± 0.3	0.36 ± 0.01	3.23 ± 0.07
CMP8	0.55 ± 0.01	1.21 ± 0.02	8.36 ± 0.17	27.43 ± 0.5	1.48 ± 0.03	5.50 ± 0.11	0.49 ± 0.01	4.74 ± 0.09
GRX	0.11 ± 0.01	0.79 ± 0.02	4.04 ± 0.10	30.56 ± 0.06	0.57 ± 0.01	2.48 ± 0.04	0.42 ± 0.01	3.64 ± 0.06

it can have been introduced in the mass after the heating due to culinary use or due to storage remains or burials.

3.2. SEM and EDS analysis

The initial study using these techniques allowed knowledge of what major (EDS) and minor (BSE–EDS) elements are present in the ceramic paste. Thus, the major presence of these elements: Na, Mg, Al, Si, K, Ca, Ti, C and Fe, was detected in all the samples.

Later, the work has been mainly centered in the samples that have been demonstrated to have a chemical composition different from the majority. Thus, microorganisms found in CTR2 and CTR3 samples are shown in Fig. 2. As is observed, two different microorganisms appear. One of them coincides with the microorganisms that usually are found in ceramics from the Basin of the Guadalquivir River [13,14], that are shown in Fig. 3 and localized in sample T6. The other microorganisms are different in size and shape.

The use of SEM in backscattering mode (BSE) has allowed it, in addition, to detect minor chemical elements with greater atomic mass, and to observe their localization. That is, if they belong to the temper or to ceramic paste. The kind and frequency of these particles could differentiate certain ceramics from others.

In work carried out on ceramics from the Basin of Guadalquivir River, particles corresponding to phosphorus, lanthanum and cerium have always been detected by EDS.

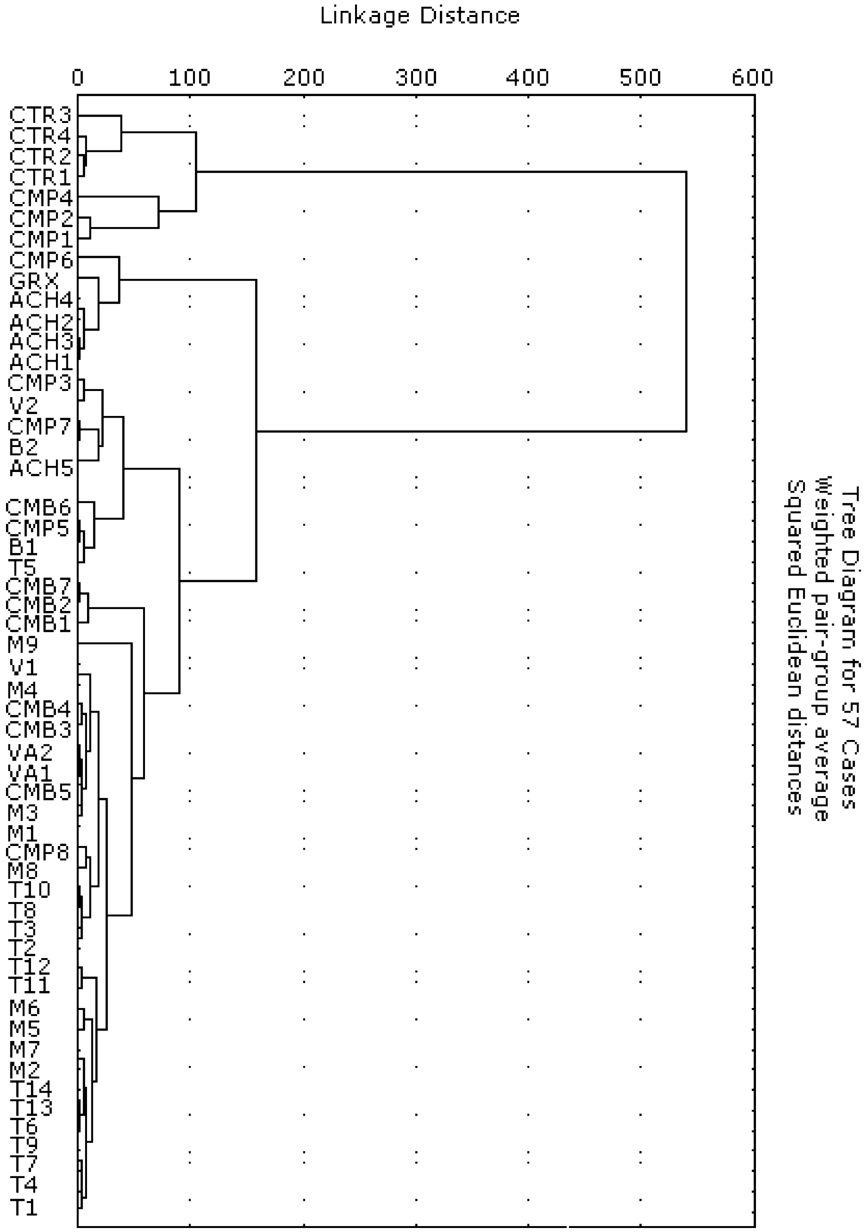

Fig. 8. Resulting dendogram of cluster analysis from the ICP-AES data, using the centroid method and the matrix of squared Euclidean distances.

These particles have never been detected in ceramics that do not belong to this hydrographic basin [6].

The presence of these particles has been observed in all the samples studied, except in the samples from the Cantarranas site. This is further data that supports the hypothesis that these ceramics are different from the rest. A microphotograph of a T9 sample using BSE is shown in Fig. 4, where particles that are more brilliant than the rest of the ceramic mass are observed. They correspond to these chemical elements identified above.

On the other hand, differences in the temper works are also observed. The tempers of most of the ceramics in this study are made up of calcite or quartz. However, in ceramics from the Cantarranas site, a black temper is observed using optical microscopy. Its EDS analysis reveals the presence of a remarkable amount of silicon, aluminum and iron, besides a great amount of calcium. This can be observed in the EDS spectrum of CTR4 sample (Fig. 5) as an example.

In the same way, some differences in sample ACH5 are observed. Thus, in the EDS spectrum of this sample (Fig. 6) it is observed that the temper has a great amount of silicon and aluminum with respect to the amount of calcium.

3.3. ICP-AES results and cluster analysis

The results obtained using ICP-AES for determination of eight major elements in the ceramics studied are shown in Table 3. From the values obtained, a statistical analysis of the eight variables per sample was carried out.

The intervals where the values of percentage of five elements that have greater variations in this set of samples is shown in Fig. 7. In the figure, it is clearly observed that the two elements that show greatest variations are silicon and calcium. Therefore, these two elements can influence the discrimination of pieces regarding their composition. Precisely, they are found in tempers. In addition, it is observed that the presence of iron is not related to the color of the samples. Thus, for example, sample ACH5 that has the highest iron content, is made up of the greyish ochre group.

The statistical processing using cluster analysis, carried out on these results, are shown in the dendogram in Fig. 8. Observing this diagram, it is deduced that:

- One group has the majority of the site samples.
- No samples corresponding to CTR key that are from Cantarranas site are similar to any other samples. These samples are characterized by higher percentages of calcium, and together with some from Campillo, lower percentages of silicon and iron.
- The CMP1, CMP2 and CMP4 samples are different from others of the group and of the same site. Specially CMP4 shows, together with the samples from Cantarranas, a lower percentage of silicon and iron. The percentage that corresponds to calcium for these samples is within the average value of the set of samples.
- The ACH samples (Arroyo Chaparral) are all grouped except ACH5. This is justified because ACH1, ACH2, ACH3 and ACH4 samples have higher values, together with CMP6, for the percentage of silicon, high values for iron and lower values for calcium. However, sample ACH5 has a higher content of iron of all the samples, a high percentage of calcium and a medium value for the percentage of silicon.
- All the other samples can be considered very similar to each other, especially the VA1 and VA2 samples from Vaina, and the samples with T (potter's wheel) and M (handmade) that belong to the Pocito Chico site. From these last ones, the similarity in its composition must be stressed and only porosity differences have been found [15].

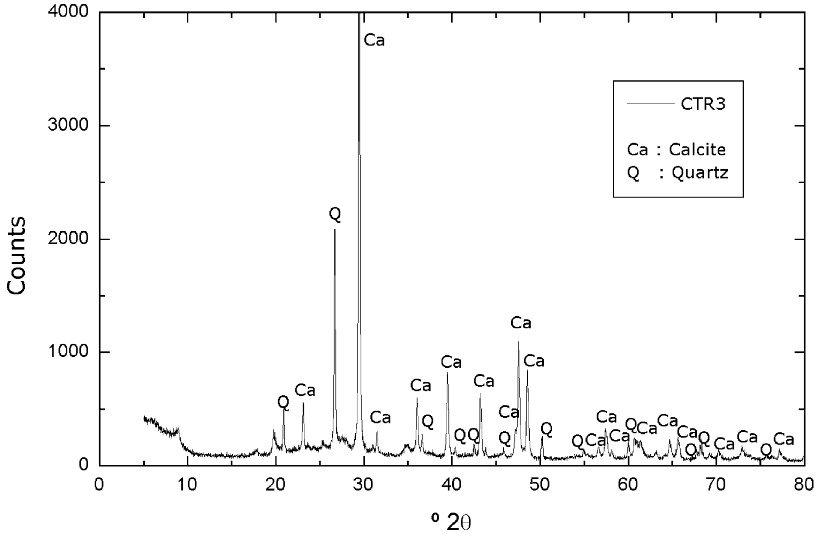

Fig. 9. Diffractogram of sample CTR3, in which a large amount of calcite with respect to quartz and several silicates is observed.

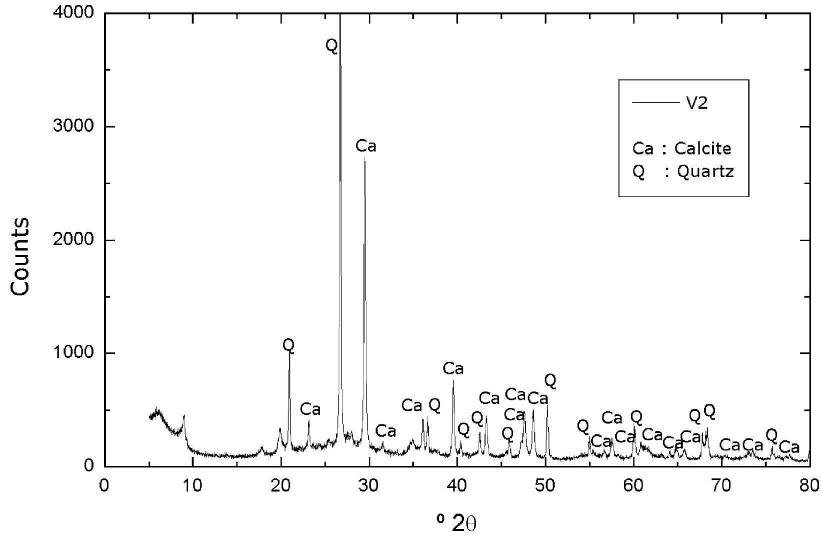

Fig. 10. Diffractogram of ceramic sample V2, in which a large amount of quartz with respect to calcite and several silicates is observed.

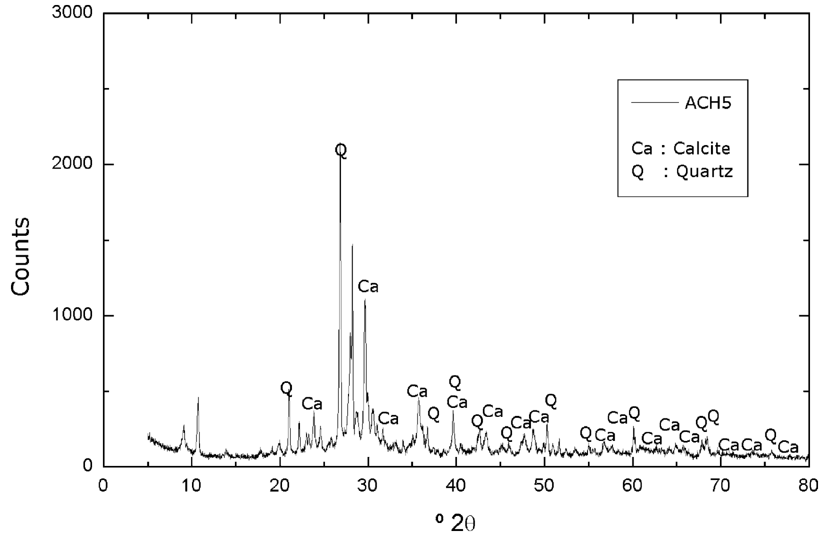

Fig. 11. Diffractogram of ceramic sample ACH5, in which a large amount of several silicates with respect to calcite and quartz is observed.

3.4. XRD analysis

In all the samples, calcite, quartz and several silicates have been found and the only difference is the relation of the peak height. In addition, it is observed that this difference among the peak heights is independent of the colorimetric group in which the samples are classified. Thus, the diffractogram of three samples that belong to the second colorimetric group is shown below.

The diffractogram of sample CTR3 is shown in Fig. 9. A large amount of calcite with respect to the amount of quartz and silicates is found. This coincides with the fact that it is a sample from the Cantarranas site, characterized because it has a higher percentage of calcium and a lower percentage of silicon.

The diffractogram of sample V2 is represented in Fig. 10 in which the proportion of quartz than that of calcite and silicates. This sample corresponds to the major group that is characterized for medium values of quartz and silicon.

Finally, the diffractogram of sample ACH5 is shown in Fig. 11 where the presence of a great amount of silicates is very remarkable. This coincides with data obtained for this sample using EDS, in which a great amount of silicon with respect to calcium is observed.

4. Conclusions

The physical–chemical techniques used for studying ceramics provide information about texture, inclusions and chemical and mineralogical composition of the paste and temper. From these data, some aspects of ceramic production can be deduced and the sample pieces can be compared.

The determination of color parameters of the homogenized paste characterizes the sample but does not give any grouping criterion as to archaeological deposit or origin. On the other hand, a relation with the presence of a certain chemical element that unequivocally identifies the reason of its coloration has been observed.

The archaeological data that are available from the Cantarranas site indicate that although this site is in the same geographical zone as the other ceramics, the context seems to indicate a time before Tartessian time. On the other hand, the results obtained in this work indicate that this site is dissimilar from the rest of the group because the differences seem to indicate that although the clay can be similar, the temper is not the same. All this has caused the Cantarranas site to be studied to establish if the differences found are due to a chronological factor or they are imported ceramics.

To a lesser extent, this difference on the tempers can be the reason for the other grouping, where the clay can be the same in all the samples of this zone but the deliberate addition of one or other temper can differentiate the production.

For making deductions with greater reliability, it is necessary to increase the database. In addition, it is basic to get ceramics from other zones for comparing the samples. Thus, it is necessary to compare samples of ceramics from Eastern countries in order to determine if the samples that do not seem to have been produced locally, have been imported.

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