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MULTI-TECHNIQUE CHARACTERISATION OF PAINTED ENEOLITHIC CERAMICS ORIGINATING FROM CUCUTENI (ROMANIA)

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Abstract

This paper presents an investigation of Eneolithic painted ceramic artefacts, belonging to the *Cucuteni* culture (phases A and B), focused on the raw materials used for manufacturing the ceramic bodies and the pigments used for the painted decorations. Detailed information on their elemental and molecular composition were obtained by combining Energy Dispersive X-Ray Fluorescence (EDXRF), Energy Dispersive X-ray analysis in the Scanning Electron Microscope (SEM-EDX), and Fourier Transform Infrared (FTIR) spectroscopy for the analysis of the bodies and painting materials used for manufacturing the *Cucuteni* artefacts. X-Ray Diffraction (XRD) was also used to characterize the ceramic bodies.

The Eneolithic ceramic shards were divided into three decorative groups (red, black, and black on red). The major, minor and trace elements found on the decorated surface and in the clay body were determined. The bodies were found to be mainly composed of quartz, K-feldspar, plagioclase, clinopyroxene, hematite, calcite, and micas. The most predominant chemical elements were determined, and a representative ratio (Fe/Mn) was calculated and compared for each samples group. The analysis of the samples revealed a higher content of Fe in the red paint in comparison with the other areas (black and not pigmented) and leads to the conclusion that iron-rich clay was used. The red pigment could be attributed to iron oxide in the form of hematite.

Keywords: multi-technique investigation, painted ceramics, pigments, clay

1. Introduction

The study of archaeological ceramic artefacts may provide information on the subsistence, population, social organization, cultural boundaries, trade networks and alliances of civilizations [1]. However, the interpretation and

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correlation of the data is very complex, due to the heterogeneity of the materials and to the presence of both amorphous and crystalline phases in the ceramic bodies as well as in the pigments used for outer decorations [2]. Therefore, the identification of the composition of painted ceramics requires a comprehensive characterization of bodies and of painting materials, i.e. about the pigments used for the decoration of the pottery surface [3]. The results of an elemental analysis combined with archaeological information can help us in drawing conclusions about the ceramic manufacturing technology, as well as about the trade routes during the Neolithic period [4].

The main phases of the *Cucuteni* culture – A, AB and B – evolved over about 800 years (4300 – 3500 B.C.) [5]. The decorative motifs used by *Cucuteni* potters in painting ceramic objects made this culture famous: spirals and sometimes meanders, egg shapes or other geometric forms stand as a proof of a remarkable aesthetic sense and of a very complex spiritual life [5, 6]. The *Cucuteni* ceramics were traditionally painted in three colours: red, white, and black (dark brown) [5-8]. The technique of painting with red, black and white is a characteristic of the Neolithic period. Generally, the pigments used for decorating ceramics objects in ancient times were based on iron, manganese or calcium compounds [4].

The knowledge of the pigment composition allows its characterization through major or minor components and yields information about the provenance, age and authenticity of the artefact [9]. Important analytical results regarding decorated *Cucuteni* ceramics have been obtained by using XRF [8], synchrotron radiation XRD [7] and Raman spectroscopy [5, 6]. XRF spectroscopy has been recognized as a powerful tool in archaeometry because it provides a fast and nearly complete identification of the most important elements present as main or as trace components in ceramic materials [10, 11]. XRF and XRD analysis indicated that the pigments used to paint *Cucuteni* Eneolithic ceramics contain mainly iron oxides for the red paint and mainly calcite ($CaCO_3$) for the white paint. The black pigments contain a variety of iron and manganese compounds, such as magnetite (Fe_3O_4) and jacobsite (Fe_2MnO_4) [7]. The Raman analysis of the black pigment found on *Cucuteni* pottery shards revealed the presence of Mn-Fe oxides, pyrolusite (MnO_2) and jacobsite [8].

2. Materials and methods

2.1. Samples

The measurements were performed for a number of twenty-one shards of painted ceramic belonging to the Eneolithic period (A and B phases: about 3750 – 3200 BC and 3000 – 2700/2600 BC, respectively [12]), originating from excavations at Cucuteni - Iaşi County (Romania). Also, a number of five painted ceramic pieces (coded GF58, GF61, GF65, GF66, and GF67) obtained by experimental archaeology with raw material originating from the Cucuteni area were investigated for comparison. Most of the shards were analyzed by means of

FTIR spectroscopy and ED-XRF, and some selected fragments by means of XRD and SEM-EDX.

The original painted ceramic shards were separated into three groups based on the visual examination of their decoration technique: i) the group of Black samples includes four shards (phase B) coded GA10, GA19, GA46 and GA56; ii) the group of Black on Red samples includes five shards coded GA02, GA13, GA41 (phase A), GA35, and GA54 (phase B); iii) the group of Red samples includes five shards coded GA03, GA 42 (phase A), GA20, GA33, GA34 (phase B).

EDXRF measurements were performed on the ceramic shards with no surface treatment. Several points were selected both on the painted (red and black) and the unpainted area. The cross sections samples were extracted from the shards coded GA02, GA03, GA13, GA33, GA35, GA41, GA42, GA56 and GF66 and were analyzed with SEM-EDX. In order to elide charging effects, the ceramic samples were coated with a thin layer of graphite. The cross-sections were prepared by including the small ceramic shards in epoxy resin and then the obtained surfaces were polished. Samples of this kind are very useful to study pigments, slips, and the ceramic bodies [13].

The pigment powders were analyzed after scraping them from the outermost layer of the painted ceramic shards in order to carry out infrared analyses. The samples were grounded to form fine particles, and then analyzed by KBr pellets. Thus the T-FTIR spectra (range middle-IR) were obtained from KBr pellets prepared by uniformly mixing about 0.7–1 mg of powdered sample with 120 mg KBr.

2.2. Energy Dispersive X-Ray Fluorescence (ED-XRF)

The measurements were carried out by using an *ARTAX 400* (Bruker AXS, Germany) portable energy dispersive X-ray fluorescence spectrometer. The spectrometer includes an X-ray tube, a semiconductor silicon detector, electronic modules (preamplifier, amplifier, and analog-to-digital converter) and a base tripod. XRF spectra were recorded on the multi-channel analyzer installed on a personal computer. The experimental data collection was performed using the *ArtTAX* software application.

2.3. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

SEM-EDX gives a semi-quantitative mean composition of the ceramic bodies, mineral pigments and chromophores [13]. The images and elemental analyses were acquired with a Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy at different magnifications. Therefore SEM-EDX observations were carried out using a Scanning Electron Microscope Philips 515B fitted with an EDAX DX4 microanalyser with a 15 kV accelerating voltage. The SEM images were taken under high vacuum conditions.

2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR measurement was carried out using a Thermo-Nicolet FTIR Avatar 370 spectrometer (source IR, detector DTGS). To identify the components from the outermost layer of the painted ceramic shards, one FTIR spectroscopy mode, Transmittance-FTIR (T-FTIR) (middle-IR – 4000-400 cm^{-1}) was used. The spectra were corrected by the correction of the *OMNIC*^{TM} software. All the spectra were acquired in the range of 400-4000 cm^{-1} with a spectral resolution of 4 cm^{-1}, and 128 accumulations.

2.5. X-Ray Diffraction (XRD)

The X-Ray Diffraction (XRD) was employed for the semi-quantitative mineral identification of the ceramic bodies. The analysis was performed by using a computer-controlled Philips PW-1710 powder diffractometer with Cu Kα radiation. The instrument was equipped with a diffracted beam curved graphite monochromator. The diffraction data was collected in the ranges of 2θ Bragg angles between 5^o and 50^o, at 0.02^o steps. The mineralogical identification was based on the comparison with a database.

3. Results and discussion

3.1. EDXRF

The most predominant chemical elements were determined, i.e. Fe, Mn and Ca. The representative ratio (Fe/Mn) was calculated for each original ceramic sample. The spectra indicate that the main elements are iron and manganese in the black surfaces [5, 7] and iron and calcium in the red surfaces.

The EDXRF analysis revealed that in the cases of Red, and Black on Red samples groups, the Fe/Mn ratio is higher in the red surfaces (between 33.5 and 63.5) than in the black surfaces (between 4.0 and 7.0) (see Figure 1) or in the paste of the bodies. Therefore, the red pigment used for decorating the Eneolithic ceramic was made with resources based on iron oxides originating from the *Cucuteni* area.

The Fe/Mn ratio calculated for the red surfaces of the fake ceramic samples shows the same variation. The Fe/Mn ratio has been calculated for the black surfaces of fake ceramic samples and it is lower than for the original ceramic samples. Moreover, the Ca/K ratio calculated for the black pigment revealed a variation between 1.3 and 2.5, and a variation between 2.2 and 2.7 for ceramic bodies (areas not pigmented), for the original samples. The Ca/K ratios calculated for the fake samples are also higher than the same ratio calculated for the original samples (see Table 1).

The above mentioned variation of both Fe/Mn and Ca/K ratios for the black surfaces revealed that the pieces of fake *Cucuteni* ceramic were decorated using a different type of black pigment. It seems that the range of these ratios could be used as objective criteria to distinguish original *Cucuteni* painted ceramic from fake ceramic imitations. The results also indicate that local resources were used for the red decorations of both original and fake *Cucuteni* ceramic.

The representative XRF spectra of red and black pigments show that the main elements are iron and manganese in the black pigment, and iron and calcium in the red pigment (see Figure 2).

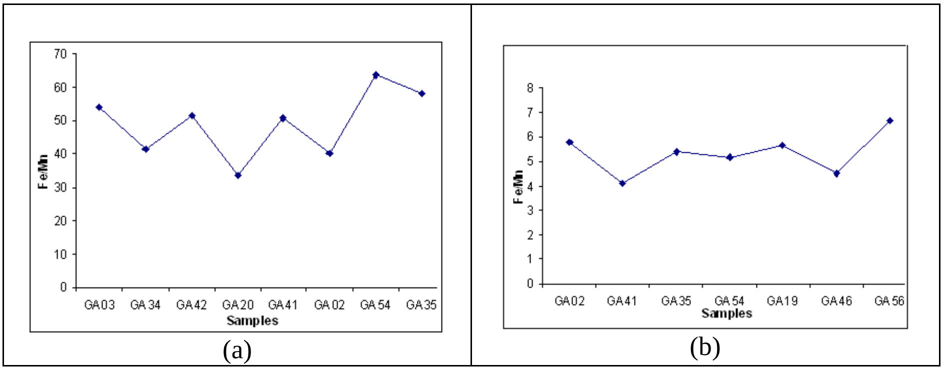


Figure 1. Variation of Fe/Mn elemental ratio for *Cucuteni* ceramic for:
(a) the red surface, (b) the black surface.

Table 1. Variation of elemental ratios: Fe/Mn and Ca/K (*n.p. = not pigmented).

Ratio	Cucuteni ceramic	Fake ceramic
Fe/Mn – Red	33.5 – 63.5	57 – 61
Fe/Mn – Black	4.0 – 7.0	1.5 – 2.0
Ca/K – Body n.p.*	2.2 – 2.7	2.75 – 3.7
Ca/K – Black	1.3 – 2.5	5.5 – 6.0

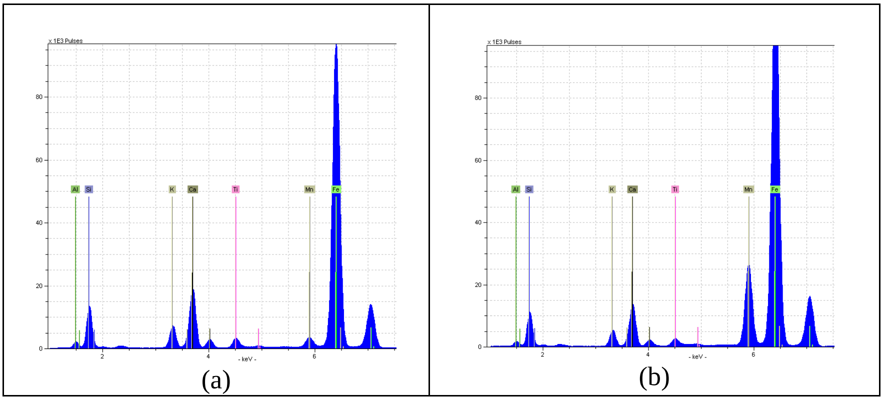
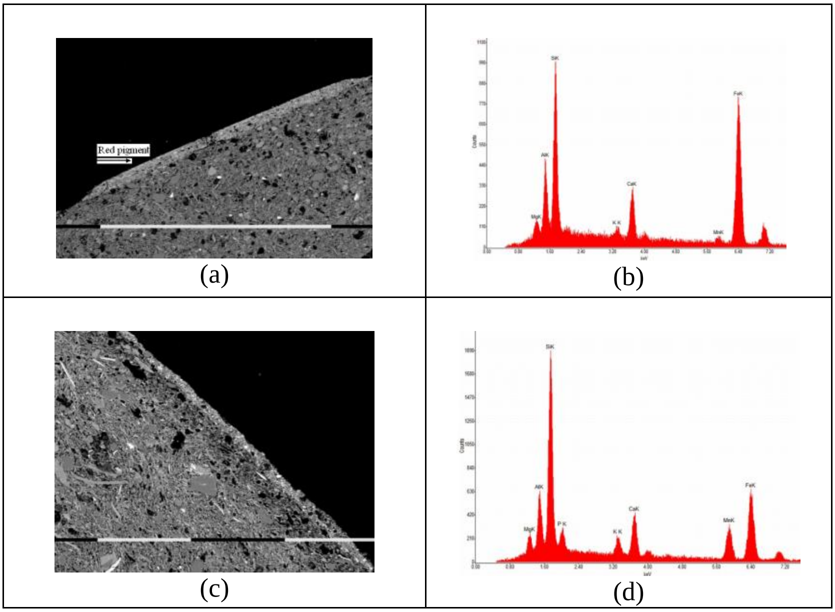


Figure 2. XRF spectra of the pigments of sample GA02:
(a) the red pigment, (b) the black pigment.

3.2. SEM-EDX

The backscattered electron images of the cross-sections from the samples (GA02, GA13) can be seen in the Figures 3a, 3c, and the compositional spectra in the Figures 3b and 3d.



(a) (b) (c) (d)

Figure 3. SEM image for: (a) GA02 sample and (c) GA13 sample; EDS spectrum for: (b) GA02 sample and (d) GA13 sample.

The SEM-EDX analysis of the cross section confirms the data obtained by EDXRF analysis. A high level of Fe (see Figure 3b) is found in the area of the red pigment layer of the GA02 sample in comparison with the other areas (black and not pigmented) and leads to the conclusion that iron-rich clay was used. The levels of Si and Al are also high, confirming the presence of quartz and alumino-silicates in the ceramic bodies. On the other hand, the presence of potassium may be associated to feldspar phases (see Figure 3b and 3d). The EDS spectrum obtained for the GA13 sample indicates the presence of phosphorus [14] (see Figure 3d).

3.3. FTIR analysis

The substances can be accurately identified by using their FTIR spectra [15-20]. The representative FTIR spectra of the samples, recorded from KBr pellets for the body and for the red pigment in the wavenumber range 400–4000 cm^{-1}, are presented in Figures 4 and 5.

The characterization of red pigment is complex because the red ochre is colored by iron oxide or hematite (α-Fe_2O_3). Ochre is a natural earth containing silica and clay. Therefore the identification of hematite is sometimes difficult if it is accompanied by silicates (for Si-O the stretching vibration is situated in the range 1100–900 cm^{-1}, and the bending vibration in the range 660–500 cm^{-1}) [21, 22].

The bands attributable to the typical Si–O vibrations (1084, 798, 777, 695 and 514 cm^{-1}) [16] are very well resolved in the FTIR spectrum of the GA02 sample (see Figure 4). The presence of quartz in the samples is confirmed by the two characteristic peaks appearing at 777 cm^{-1} and 695 cm^{-1} (see Figures 4 and 5). The presence of the iron oxide seems to be indicated by the peaks appearing at 797 cm^{-1}, 536 cm^{-1} and 470 cm^{-1} [23], shown in the Figure 5. In consequence, the red pigment could be attributed to iron oxide in the form of hematite. The 1432 cm^{-1} and 874 cm^{-1} bands, attributable to the functional group CO_3^{2-} [21], are present in the spectrum of red pigment for GA20 sample. The results of the FTIR analysis were confirmed by the XRD powder analysis. The bands centered at about 1600 and 3450 cm^{-1} are typical bands of H_2O [15].

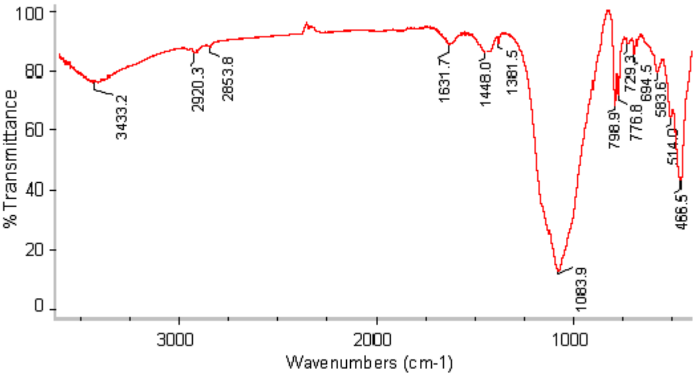


Figure 4. FTIR spectrum of the body for the GA02 sample.

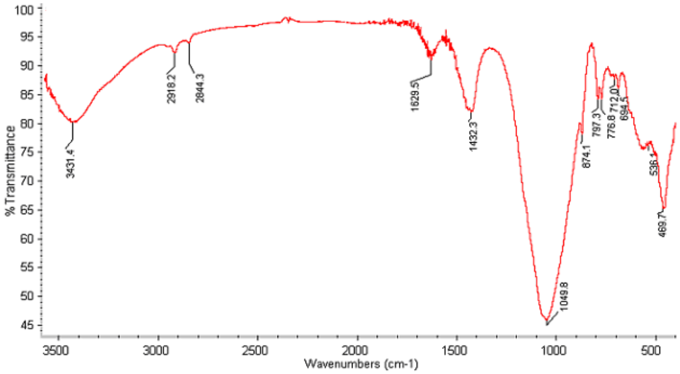


Figure 5. FTIR spectrum of the red pigment for the GA20 sample.

3.4. XRD

The XRD technique enabled us to identify the clay constituents, as well as the mineral phases formed during the firing of the ceramics. The mineral composition of the *Cucuteni* original samples includes quartz, K-feldspar, plagioclase, clinopyroxene, hematite, calcite and micas. A similar mineralogical composition was found for the fake ceramic samples. As a result, we may conclude that the pieces of ceramic were made using local raw material. The mineralogical composition of the investigated samples (semi-quantitative analysis) is presented in the Table 2. Among the minerals, quartz predominates in both original and fake ceramic [7]. Second in importance are K-feldspar and plagioclase. Clinopyroxene, hematite and micas are also present in the original ceramic shards, but in smaller quantities. The minor constituents identified in the sample GF66 were K-feldspar, plagioclase, clinopyroxene, hematite, micas and calcite.

Table 2. Mineralogical composition of investigated samples by XRD analysis: Qz = quartz, K-feld = K-feldspar, Plg = plagioclase, Cpx = clinopyroxene, Hem = hematite, Cal = calcite; + + + + (very abundant), + + + (abundant), + + (present), + (little present), tr (present in trace), – (not observed).

Sample (Phase)	Qz	K-feld	Plg	Cpx	Hem	Micas	Cal
GA02 (A)	+ + + +	+ +	+ +	+	+	+	tr
GA03 (A)	+ + + +	+ +	+ +	+	+	+	tr
GA13 (A)	+ + + +	+ +	+ +	+	+	+	tr
GA33 (B)	+ + + +	+ +	+ +	+	+	+	tr
GA35 (B)	+ + + +	+ +	+ +	+ +	+	+	+
GA41 (A)	+ + + +	+ +	+ + +	+ +	+ +	+	–
GA42 (B)	+ + + +	+ +	+ +	+	+	tr	tr
GA56 (B)	+ + + +	+ + +	+ + +	+ +	+ +	–	–
GF66 (A)	+ + + +	+	+	+	+	+	+

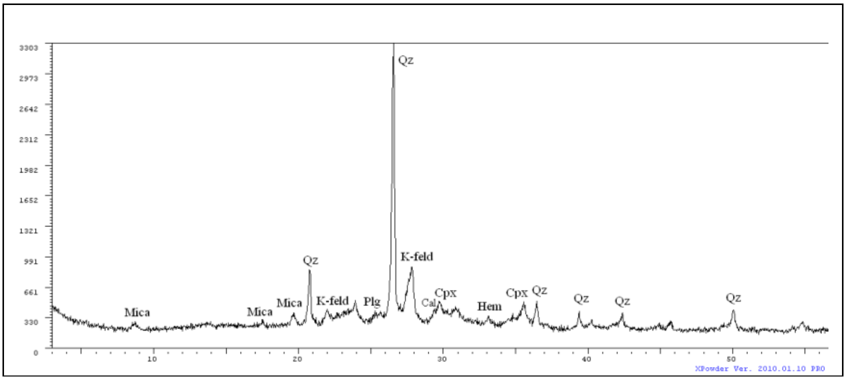


Figure 6. X-ray diffraction pattern of sample GA13.

The quartz could have been added as a temper, or it could have formed during the baking from the decomposition of the clay silicates. The presence of hematite indicates an oxidizing atmosphere during the ceramic baking [2, 7]. A representative X-ray diffraction pattern is shown in Figure 6.

4. Conclusions

The use of multi-techniques investigation applied for the characterization of both pigments and paste of the ceramics body allowed us to identify the composition of the materials employed in the production of the painted Eneolithic pottery from the *Cucuteni* culture, as indicated by the samples found in the Iaşi County (Romania). The species found present in the ceramic bodies are: quartz, K-feldspar and plagioclase, clinopyroxene, hematite, micas and traces of calcite.

The ED-XRF is suitable for determining only the elemental composition and not the chemical form of the analysed materials. This is an inconvenience, particularly in pigment analysis. However, the fact that iron is the major element (the ratio Fe/Mn is higher) in the red pigmented surface leads to the conclusion that local ochre was used for the manufacture of the ceramic objects. The different variation of both ratios Fe/Mn and Ca/K for the black surfaces revealed that the pieces of fake ceramic (obtained in the laboratory by experimental archaeology) were decorated using a different type of black pigment (probably a synthetic pigment). The ranges of these ratios could be used as objective criteria to distinguish original *Cucuteni* painted ceramic from fake ceramic samples.

However, further determinations performed on a larger selection of painted ceramic samples, if possible also belonging to other Eneolithic cultures, are needed in order to confirm the findings regarding the origin and the manufacturing techniques used for the production of *Cucuteni* ceramics presented in this exploratory study.

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