THE RAMAN STUDY OF WHITE, RED AND BLACK PIGMENTS USED IN CUCUTENI NEOLITHIC PAINTED CERAMICS

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Abstract

The white, red and black pigments from 50 ceramic sherds of the phase A of the Cucuteni culture were analyzed using Raman spectroscopy. For the white pigment, the Raman spectra indicated the presence of TiO₂ and quartz. CaCO₃ was not revealed in any of the samples. For the white pigment, a kaolinite white clay, rich in TiO₂ and quartz, formed from the weathering of acid igneous rocks, was used. For the red pigment, a clay rich in Fe oxyhydroxides, subjected to an artificial process of Fe oxyhydroxide enrichment, was used. The Raman spectra indicated the presence of hematite and quartz. As far as the black pigment is concerned, jacobsite and, in only one sample, black carbon or graphite were identified. The source of the manganese black pigment can be explained by secondary accumulations of Mn from the Iacobeni-Ciocânești region (Romania) and/or the manganese ore from Nikopol (Ukraine). The red ceramic paste also contains hematite and quartz, just like the red pigment. The raw black ceramic paste contains black carbon, which indicates that it was fired at temperatures lower than 700-750°C.

Keywords: Cucuteni – Trypolye, ceramics, pigments, jacobsite, black carbon, rutile, anatase, Raman spectra.

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Introduction

At its peak, the Cucuteni-Tripolye culture, one of the last brilliant cultural expressions of the Copper Age, spread over an area of 350,000 km², throughout Romania (Cucuteni), the Republic of Moldova and Ukraine (Tripolye). The culture is divided into three main phases (A, AB and B), which evolved over about 800 years (4300 - 3500 B.C.). The decorations of the Cucuteni pottery stand as proof of a remarkable aesthetic sense and of a very complex spiritual life (Constantinescu et al., 2007). The decorative motifs used in the painting of Cucuteni ceramics were mostly spirals, and rarely meanders, egg-shaped or other geometric forms. They are painted in three colours: white, red and black (dark brown). Since the discovery of Cucuteni pottery, the decorations have fascinated archaeologists, but the investigation of the pigments has been a secondary research theme, materialized in a relatively small number of studies.

The main results obtained previously on the pigments of Cucuteni ceramics by using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Synchrotron Radiation X-Ray Diffraction (SR-XRD) will be reviewed.

Stos-Gale and Rook (1981) and Niculescu et al. (1982) pointed out that the chromatophorous minerals of the white, red and dark brown pigments of a number of Cucuteni-Tripolye sherds were calcium silicate, hematite and jacobsite.

Burghelea et al. (2002) conducted a XRD study on trichromatic ceramic sherds belonging to the Cucuteni A2 phase. They have identified α-quartz, plagioclase feldspar, calcite, magnetite, and haussmanite in the black pigment, and hematite in the red one. The presence of quartz and plagioclase feldspar both in the pigment and in the ceramics, lead the authors to the conclusion that the pure pigments were finely dispersed into a clay suspension.

Through XRF and SR-XRD measurements, Constantinescu et al. (2007) analized a series of painted (red-white-brown-black) Cucuteni sherds found in Moldova (a province of Romania), at sites situated in the Bistrița Valley (Izvoare, Calu, Cășăria, Ghelăești), belonging to the Cucuteni A phase. The XRF measurements indicated that the main chemical elements in the black pigment (dark brown or chocolate black) are Mn and Fe. By the Mn/Fe ratio, the authors suggested that Mn minerals from Iacobeni, a locality situated in the NW region of Moldova, were used for this pigment. In the white pigment, Ca was established as the main element. For this reason, the authors suggest that kaolin was used as raw material for the white pigment (however, Ca is not the main element in kaolin – Si and Al are). In the red pigment, Fe and Ti were identified, which led to the conclusion that the pigment is an iron-rich, clay-based one, with Ti used as reinforcing agent. The SR-XRD analysis shows the presence of jacobsite (Mg-jacobsite), pyroxmangite or magnetite (+quartz) in the black pigment, hematite (+quartz) in the red one, and, in one sample, Ca (+quartz) in the white pigment. In the case of the black pigment, Constantinescu et al. considered that a type of primitive trade is obvious.
Analytical procedure

The Raman spectra were obtained at room temperature with a Horiba Jobin-Yvon RPA-HE 532 Raman Spectrograph with a multichannel air cooled (-70°C) CCD detector, using a wavenumber doubled Nd-Yag laser, 532 nm and nominal power 100 mW. The spectral resolution was 3 cm⁻¹, and the spectral range between 200 and 3400 cm⁻¹. The Raman system includes a “Superhead” fibre optic Raman probe for non contact measurements, with a 50X LWD visible objective Olympus, NA = 0.50 WD = 10.6 mm. The sulphur and ciclohexane bands were used for the calibration of the frequencies of the Raman spectra. Data acquisition was performed through 2 - 40 seconds exposure, 20 – 100 acquisitions, at a laser magnification of 90 – 100%, to improve the signal-to-noise ratio. Recording a clear Raman spectrum was a tedious task, as the spectra are superimposed on a strong fluorescence and background noise. The pigments were dispersed in clay suspension, which caused a powerful noise and a weak Raman signal. Nevertheless, Raman spectra with clear bands were recorded and this allowed to identify the minerals present in the pigments beyond any doubt.

Samples

A number of 50 ceramics sherds from the archaeological sites found at Hoiseşti, Scânteia and Ruginoasa (Iaşi) were analyzed, all samples belonging to Cucuteni phase A. The sherds from Hoiseşti are painted fine ceramics (samples 1-16) and raw ceramics, unpainted or color spotted (samples 18-40). The samples from Scânteia and Ruginoasa are painted fine ceramics.

The painted coating is dichromatic (white and red or red and black) or trichromatic (white, red and black). The decorative motifs are either spirals, angular or unidentifiable. All trichromatic sherds, whether the red motifs are painted on a white background or straight on the pot surface, have the limits between white and red hidden by the black pigment.

Results and discussions

Measurements using Raman spectroscopy were made on all three characteristic pigments of Cucuteni pottery (white, red and black).

The Raman spectra of the white pigment are defined by background noise (BN) and strong fluorescence (F). The lack of any Raman bands, even weak ones (fig. 1), is due to a kaolinite clay. Constantinescu et al. (2007) have shown through XRD studies that the white pigment is a light clay (type kaolin), but the same authors mention Ca as the major chemical element in the white pigment (kaolinite clay has a low concentration of Ca, the main elements being Si and Al). Calcium carbonate is certainly absent from the white pigment, because it has a good Raman signal, at least at 1087 cm⁻¹ (Buzgar and Apopei, 2009).
However, the large number of spectra acquisitions on the white pigment allowed the detection of some minerals in the kaolinite clay, quartz and TiO$_2$ (rutile and, rarely, anatase). The presence of quartz is indicated by the Raman band at $\sim$465 cm$^{-1}$, which is the most intense line of quartz (fig. 2). The other Raman bands are hidden by the BN&F.

Rutile gives a good Raman signal, even when it appears as very fine crystals. For this reason, the presence of rutile in the white pigment (fig. 3) is obvious, based on the two specific Raman bands (Buzgar et al., 2009).

Fig. 1 Raman spectrum of the white pigment  (Cucuteni pottery from Scânteia)

Fig. 2 Raman spectra of the white pigment (Cucuteni pottery from Hoisești)
The presence of TiO$_2$ in the white pigment on artefacts was indicated by Middleton et al. (2005). The analysis of a sample of white paint from a ceramic pot of Roman age, using FT-Raman spectroscopy, indicated that a component of the white paint was anatase.

An issue is the high frequency of appearance of rutile in relation to anatase. We believe that almost all artefacts made of fine ceramics from Hoiseşti were fired at ~900°C, which determined the transformation of anatase into rutile. Another argument which supports this theory is that the black raw ceramics from Hoiseşti present artificial white temper, made of small quantities of white kaolinite clay, where anatase and certainly not rutile is present. Moreover, in this case, the firing process was conducted below 700-750°C (above this temperature, black carbon is destroyed).

![Raman spectra of the white pigment](image1)

The presence of quartz and TiO$_2$ in the kaolinite clay may suggest that the clay used as white pigment has a residual nature, formed by the weathering of igneous rocks. Clay deposits of this kind are very rare and generally occur near volcanic neogen sites (Parva and Cornăiţa - Bistriţa Năsăud region; Haita, Pietrosul and Stejar Valleys – Suceava county).

We believe that the anatase-rich kaolinite used as white pigment during the Roman age (Middleton et al., 2005) is of the same genetic type, many sources of kaolinite clay formed by weathering occurring on the territory of the Roman Empire.

The red pigment studied contains hematite and, more frequently, quartz. The Raman spectra recorded on fine sherds from Hoiseşti (fig. 4) and Scânteia (fig. 5) are very similar and present the main bands of hematite. The diffuse shape of the Raman bands is caused by the fine granulation of hematite. Also, this is confirmed by high intensity peaks in the 200-
300 cm\(^{-1}\) region and a low intensity at 1320 cm\(^{-1}\), which is the most intense Raman band of hematite in large crystals (Zoppi et al., 2008; Buzgar et al., 2009).

Fig. 4 Raman spectra of the red pigment (Hoisești artefacts); the Raman spectrum of Hematite_5371 is from Buzgar et al. (2009)

Fig. 5 Raman spectra of the red pigment (Scânteia artefacts); the Raman spectrum of Hematite_5371 is from Buzgar et al. (2009)
A Raman study on some pigments of Cucuteni painted ceramics

Fig. 6 Raman spectra of the red pigment; quartz is present with the main band at 465 cm\(^{-1}\)

The presence of quartz is proved by the most intense band at \(\sim 465\) cm\(^{-1}\) (fig. 6). Quartz gives a Raman signal which is more intense than that of hematite, therefore hematite bands are less obvious in the Raman spectra.

The presence of both hematite and quartz in the red pigment excludes the use of Fe oxyhydroxides as pure red pigment. For the red color, red clay, washed several times, a process that enriched the clay with Fe oxyhydroxides (+quartz), was used. This known process is used even nowadays by pottery artisans. The source of this clay is not a special issue, as it is commonly found interbeded throughout sedimentary deposits of the Moldavian Platform.

The black pigment studied contains jacobsite (fig. 7). This mineral was also reported by Constantinescu et al. (2007). It is possible that it originates from the weathering crust of the Mn accumulations from Suceava county, as shown by Constantinescu et al. (2007), but we believe otherwise for two reasons. Firstly, in all samples, spectra indicated the presence of jacobsite as the only Mn mineral (absence of Mn carbonates or silicates). Secondly, several samples of black Mn corpuscles were provided by archaeologists from the “Ștefan cel Mare” University of Suceava. These Mn corpuscles were used as pigments in the Cucutenian age. Preliminary data (morphology, mineralogical composition) indicated the Nikopol manganese ore basin from Ukraine as source of these corpuscles.

The Raman spectra of the red ceramics (fine and raw) show the presence of hematite and quartz, just like the spectra of the red pigment (fig. 4 and 6). For the raw black ceramic from Hoisești (and one sample from Scânteia), the paste used was a clay rich in organic substance. Through the firing process, the organic substance turned into black carbon. The
Raman spectra of these samples clearly indicate the presence of black carbon (fig. 7), being similar to the spectrum of a black ceramic sample from Isaiia (Precucuteni culture).

![Raman spectra of black raw ceramics from Hoisești, a sample of black ceramic from Isaiia and a sample of red ceramic with dark-brown pigment from Scânteia (Cucuteni A). The spectrum of graphite used as standard is from Buzgar et al. (2009).](image)

Fig. 7 Raman spectra of black raw ceramics from Hoisești, a sample of black ceramic from Isaiia and a sample of red ceramic with dark-brown pigment from Scânteia (Cucuteni A). The spectrum of graphite used as standard is from Buzgar et al. (2009).

![Raman spectra recorded on the white spots embedded into black raw pottery from Hoisești. Raman spectrum of anatase_5316 (Buzgar et al., 2009).](image)

Fig. 8 Raman spectra recorded on the white spots embedded into black raw pottery from Hoisești. Raman spectrum of anatase_5316 (Buzgar et al., 2009).
The firing process was incomplete, as proven by the fact that the black coating is superficial, rarely reaching the upper height of the pottery walls. The temperature did not exceeded 700-750°C because, above this temperature, in an oxygen-rich atmosphere, black carbon burns out.

Several Raman spectra were recorded onto the white spots (artificial white temper) embedded into the raw black pottery from Hoiseşti. These spectra indicated the presence of anatase. Therefore, we have concluded that this artificial white temper is made of white kaolinite clay, that was also used as white pigment (fig. 8).

Conclusions

In order to elucidate the composition of the white, red and black pigment, 50 sherds from Hoiseşti were analyzed by Raman spectroscopy. The Raman signal recorded for most of the samples is weak due to a strong BN and F.

The minerals identified showed clear or barely visible bands, depending on the ratio signal/BN and the influence of F.

The Raman spectra of kaolinite clay do not have clear bands. If other minerals are included in the white pigments, the Raman lines of these minerals appear clearly. Thus, rutile, anatase and quartz Raman lines were present in the Raman spectra of the white pigment. Typical Raman bands of CaCO₃ did not appear in the spectra. Hence, we consider that the white pigment was made of kaolinite clay rich in oxides of Ti and quartz. This kind of clay, resulting through the weathering of igneous rocks (acid rocks), does not have a wide distribution. Significant deposits of this type of kaolinite clay are found in several places throughout the Bistriţa-Năsăud, Suceava and Harghita counties (Romania). The white pigment is encountered on sherds of fine pottery, hence, we concluded that this was a type of primitive trade. The prevalence of rutile in relation to anatase should indicate that, during the firing process, the temperature exceeded 900°C, when anatase turned into rutile.

Hematite and quartz are the main ingredients of the red pigment. The Raman spectra have a strong noise and fluorescence. Red clay rich in Fe oxyhydroxides was used as red pigment. Red clay is commonly found throughout sedimentary deposits in the Moldovian region.

Jacobsite is present in the black pigment. The lack of other Mn minerals, along with the presence in the Cucuteni area of the manganifer corpuscles (made of manganite), leads to the conclusion that the source of the black pigment might be either Nikopol Mn ore deposits (Ukraine), or the Mn ore deposits from the Iacobeni-Ciocâneşti area. One sample from Scânteia indicated the presence of graphite mixed with hematite (dark brown pigment). The source of this pigment may be the graphitic schist clastes which may be found along the Siret riverbed.

The raw black pottery from Hoiseşti contains black carbon and was fired below 750°C. The process of firing was incomplete, as the black color is only superficial, rarely reaching the half of the thickness of the pottery walls.
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References


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