VIBRATIONAL SPECTROSCOPIC AND SCANNING ELECTRON MICROSCOPIC STUDY OF PIGMENT RAW MATERIALS AND PAINTED CERAMICS EXCAVATED AT SZOMBATHELY-OLADI PLATÓ, HUNGARY

A „SZOMBATHELY-OLADI PLATÓ" ÁSATÁSBÓL SZÁRMAZÓ FESTÉKANYAGOK ÉS FESTETT KERÁMIÁK PÁSZTÁZÓ ELEKTRONMIKROSZKÓPOS ÉS REZGÉSI SPEKTROSZKÓPIAI VIZSGÁLATA*

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Abstract

Scanning electron microscopic (SEM-EDS), Raman (FT-Raman) and infrared (FT-IR) spectroscopic investigations were performed on raw pigment materials and polichrome painted ceramic fragments from the excavation of Szombathely-Oladi plató and Gór-Kápolnadomb.. In the raw yellow and red pigments we could identify goethite and hematite as colouring minerals, respectively. A special raw red pigment was found to be of 'pure' hematite. On the ceramic fragments decorated with red, the paint layer proved to be made of cinnabar (HgS) mixed with high-purity kaolin.

The white decoration proved to be pure, homogeneous calcite. To our knowledge, this is the first evidence of the use of cinnabar (HgS) for decorated pottery in Late Neolithic period in the region of Hungary. The use of cinnabar as painting material proved though to be rare among our samples from both archaeological sites.

Kivonat

Szombathely-Oladi plató és Gór-Kápolnadomb ásatása során napvilágra kerülő festékrögöket és több színnel (vörös, narancs, barna, sárga és fehér) festett kerámiatöredékeket vizsgáltuk pásztázó elektronmikroszkópos (SEM-EDS), Raman-spektroszkópiai (FT-Raman) és infravörös (FT-IR) spektroszkópiai módszerekkel. A sárga és vörös festékrögökben goethitet, illetve hematitot azonosítottunk. Az egyik jellegzetes vörös festékrög „tiszta" hematit-tömbnek bizonyult. A díszített kerámiákon – meglepő módon – vörös festékként nagy tisztaságú kaolinnal kevert cinnabaritot (HgS) mutattunk ki. A fehér festékréteg tiszta, homogén kalcitnak bizonyult.

Tudomásunk szerint először tudtunk cinóbert azonosítani magyarországi késő neolit festett kerámiákon, bár e festékanyag alkalmazása meglehetősen ritka a vizsgált minták között mindkét régészeti lelőhelyen.

Az AM jelen számában a cikk teljes magyar nyelvű változata is elérhető a következő címen: http://www.ace.hu/am/2013_2/AM-13-02-TZS.pdf

KEYWORDS: FT-RAMAN SPECTROSCOPY; FT-IR SPECTROSCOPY; SEM-EDS, LATE NEOLITHIC PAINTED POTTERY; CINNABAR; KAOLINITE

KULCSSZAVAK: FT-RAMAN SPEKTROSZKÓPIA; FT-IR SPEKTROSZKÓPIA; SEM-EDS, KÉSŐ NEOLIT FESTETT KERÁMIA; CINNABARIT; KAOLINIT

* The present study is the expanded and revised version of our earlier papers published in 2007 in the Wonderful Beauties exhibition catalogue and proceedings of the EMAC'07 conference in 2009.

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Fig. 1.: The site of Szombathely-Oladi plató

1. ábra: A szombathelyi Oladi plató feltárása összesítő térképének részlete

Introduction

The excavations in 2006-2007 on Szombathely-Oladi plató, Western Hungary revealed a Late Neolithic, Early Lengyel Culture settlement excavated by Gábor Ilon (Savaria Museum, Szombathely, County Vas). On the excavated 3 hectares area (**Fig. 1**) several hundreds of features represent the Lengyel Culture. Most of them are pits belonging to the settlement, but some are special features (Nos. 1, 184 and 370), probably associated with cultic activities. The early period of the Lengyel Culture is characterised by polychrome painted (red, yellow and white) pottery, as we can see in the already excavated settlements of Sé-Malomi dűlő (Kalicz 1998) and Gór-Kápolnadomb (Tóth 2006). Large amounts of painted pottery and fragments of pigments were found on the site, demanding the identification of the minerals in the pigments, in the painted layers and their possible binding materials. Only few pigment analysis results are available in Hungary, concentrating mainly on the territory of the Great Hungarian Plain (Raczky & Sándorné Kovács 2009, Raczky & Anders 2010). From the territory of the Lengyel Culture pigment analysis are available in lower number from abroad (Albustin & Albustin 2005, Draždák 1973-74). The painted decoration was widely used on everyday and special pottery (P. Barna 2014), as well as on the special objects, like figurines, altars and lamps.

Infrared and Raman spectroscopy, through their characteristic vibrational frequencies, can provide information on both organic and inorganic components, usually present as heterogeneous mixtures in artworks and archaeological finds. Raman spectroscopy (totally non-destructive, non-invasive technique, with no sample preparation requirement) and FT-IR microscopy (non-destructive or micro-destructive method) due to their high selectivity, good sensitivity and high spatial resolution became one of the most powerful tools in pigment identification (Casadio & Toniolo 2001; Derrick 1995; Smith & Clark 2004). That is the reason, why we decided for such investigations following the SEM measurements clearing the elemental composition of the samples (Mihály et al. 2009).

Samples

Several aspects were taken in account when choosing samples. Scanning electron microscopy was used primary to gain information on the

elemental composition. Based on literary sources (Draždák 1973-74, Kovárník 1987, Albustin & Albustin 2005, Raczky & Sándorné Kovács 2009, Raczky & Anders 2010, Bugoi et al. 2008) we rendered probable that mostly iron-oxide was used as colouring pigments, but we wished to document is with measurements. For this reason have we chosen samples from two western Hungarian archaeological sites, 25 sample (and 2 more added for Raman spectroscopy) from Szombathely-Oladi plató and 6 sample from Gór-Kápolnadomb (**Table 1.**). Both pigment nuggets, pigment remained on grinding stone and painted pottery shards were selected for study. Some of the samples surfaces were chemically treated during restoration, which were intentionally chosen for testing the effects on the measurement results.

The main aim of the infrared and Raman spectroscopy was the exact identification of the binding materials and pigments already detected by scanning electron microscopy.

Samples were chosen exclusively from intact archaeological features. Features were preferred which contained several different types of polychrome painted pottery shards in larger quantities spreading all over the excavated area.

Experimental

Scanning Electron Microscopy – Energy Dispersive X-ray Microanalysis (SEM-EDS)

The microscope part of the combined SEM-EDS instrument is used for imaging, and to choose the analytical region of interest (ROI) of the sample surface. The X rays generated by the electron beam (typically of 5-25 keV energy) of the SEM are then used for qualitative and/or quantitative elemental analysis of the excited volume (typically 1-10 μm deep under the ROI).

The limitations of the method: It works above Z=4 atomic number (no H detection). For quantitative analysis all elements have to be measured, and the sample has to be smooth, solid, homogeneous. Rough and porous samples yield semiquantitative results. Its detection limit is 0.1 – 1 wt%.

Advantage of the EDS method is that it requires no prior knowledge of the qualitative composition, making it ideal for unknown, complex samples.

In our measurement a JEOL-JSM25-SIII type SEM was used for imaging and excitation (with 25 keV beam energy). The X-ray spectra were collected by a RÖNTEC EDS hardware. A BRUKER Quantax software package did the data processing and the quantitative analysis.

Raman spectroscopy

The completely non-destructive Raman measurements were performed by the means of a BioRad (Digilab) dedicated FT-Raman spectrometer. The great advantage of FT-Raman in case of archaeological samples is that the use of visible (near infrared) exciting laser (Nd: YAG laser with radiation line at 1064 nm) theoretically eliminates the fluorescence coming from the sample or the impurities of the sample. FT-Raman spectra were collected using 150 mW laser power, 4 cm^{-1} resolution and co-addition of 1024 individual spectra.

Transmission infrared measurements were carried out in CsI pellet (~50-100 μg of sample) by means of a Bomem-120 spectrometer equipped with CsI optics and DTGS detector. 512 scans were collected at a resolution of 4 cm^{-1}.

Non-destructive reflection FT-IR analysis of painted ceramic surfaces was also performed by a Varian Scimitar 7000 spectrometer connected to an UMA 600 microscope system equipped with an MCT (HgCdTe) point detector and a focal plan array multidetector (FAP) system (with 64x64 MCT detector element) allowing a lateral resolution of ~5 μm.

Results and discussion

Study of pigment raw materials

The so-called earth pigments were used as polychrome pigments in this period. Red, yellow or brown pigments typically gain their colour from different iron oxide and iron oxy-hydroxide minerals (red and yellow ochre). **Fig. 3.** shows the FT-Raman spectrum of a raw yellow pigment. Beside characteristic bands of α-quartz (462, 199 and 124 cm^{-1}) and anatase (144 cm^{-1}), bands belonging to goethite ($Fe_2O_3.H_2O$) were identified at 696, 553, 39, 297, 255 and 242 cm^{-1} (Bikiaris et al. 2000). The results of preliminary SEM chemical microanalysis (EDS) are summarized in **Table 1**. It was established that beside iron (~4 mass%), high amounts of Al (7.57 mass%) and Si (36.54 mass%) are present, presumably in the form of alumino-silicates. Interestingly, Ti was identified in the case of only one point measurement.

FT-Raman measurements on a special red pigment revealed a ‘pure’ hematite. In the Raman spectrum (**Fig. 4.**) beside the well-defined hematite bands at 608, 495, 406, 290, 244, 221 cm^{-1}, the medium intense band at 654 cm^{-1} belongs to magnetite (Fe_3O_4) (Bordignon et al. 2007). Alternatively, this band can be attributed to disorder effects in the crystalline structure (Bikiaris et al. 2000). No Raman bands of quartz or anatase, typical impurities for clay minerals, were identified in the spectrum.

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Fig. 2a: Red pigment raw material: purified hematite (Feature nr. 22/A); **2b:** Red and orange decorated pottery fragments (Feature nr. 1); **2c:** White decorated pottery fragment (Feature nr. 171)

2. ábra: 2a: „Tiszta" hematit festékkrög (22/A obj.); **2b:** Vörös és narancssárga díszítésű kerámiatöredékek (1. obj.); **2c:** Fehér díszítésű kerámiatöredék (171. obj.)

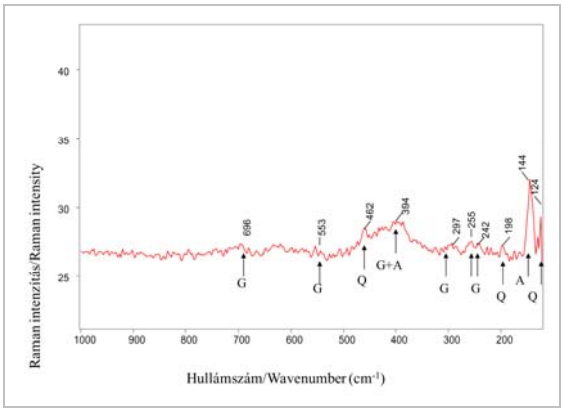

Fig. 3.: FT-Raman spectrum of yellow pigment raw material. G-goethite bands; Q-α-quartz bands; A-anatase (TiO_2) bands

3. ábra: Sárga festékkrög Raman-színképe. G-goethit sávok; Q-α-kvarc sávok; A-anatáz (TiO_2) sávok

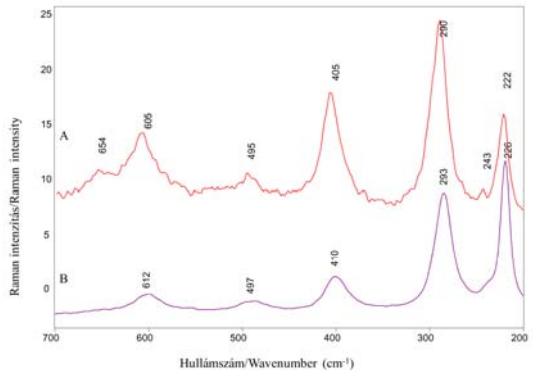

Fig. 4.: FT-Raman spectra of red pigment raw material (A) and pure hematite reference (B)

4. ábra: „Tiszta" hematit festékkrög (A) és hematit referencia (B) Raman-színképei

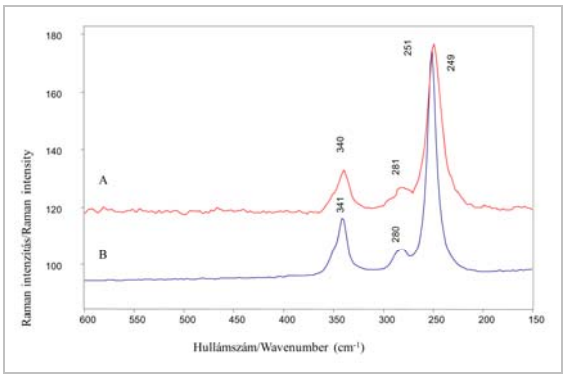

Fig. 5.: FT-Raman spectra of red paint on pottery surface (A) and natural cinnabar reference (B)

5. ábra: Kerámiafelületen lévő vörös festék (A) és természetes cinnabarit referencia (B) Raman-színképei

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Site	Sample ID	Feature/ Inv. nr.	Date	Type	Colour	Measurement	Result	Figure
Szombathely - Oladi plató	1	F. 11.	2006.08.15	pigment on grinding stone	red	SEM	iron oxide	
Szombathely - Oladi plató	2	F. 43.	2006.07.25	pigment nugget	red	SEM	iron oxide	
Szombathely - Oladi plató	3	F. 16.	2006.08.10	pigment nugget	yellow	SEM	iron oxide	
Szombathely - Oladi plató	4	F. 16.	2006.08.10	pigment nugget	red	SEM	iron oxide	
Szombathely - Oladi plató	5	F. 11.	2006.08.15	pigment nugget	white	SEM	calcite	
Szombathely - Oladi plató	6	F. 29.	2006.08.10	pigment nugget	red	SEM	iron oxide	
Szombathely - Oladi plató	7	F. 11.	2006.08.02	pigment nugget	red	SEM	iron oxide	
Szombathely - Oladi plató	8	F. 22/A.	2006.08.15	pigment nugget	red	SEM, Raman	hematite	**Fig. 2a**
Szombathely - Oladi plató	9	F. 16.	2006.08.11	pigment nugget	yellow	SEM, Raman	hematite	
Szombathely - Oladi plató	10	F. 16.	2006.08.11	pigment nugget	red	SEM, Raman	hematite	
Szombathely - Oladi plató	11	F. 16.	2006.08.11	pigment nugget	white	SEM	calcite	
Szombathely - Oladi plató	12	F. 11.	2006.07.21	pottery	red	SEM	iron oxide	
Szombathely - Oladi plató	13	F. 11.	2006.07.21	pottery	yellow	SEM	iron oxide	
Szombathely - Oladi plató	14	F. 11.	2006.07.19	pottery	red	SEM, Raman	iron oxide	
Szombathely - Oladi plató	15	F. 11.	2006.07.19	pottery	red	SEM	iron oxide	
Szombathely - Oladi plató	16	F. 11.	2006.07.19	pottery	yellow	SEM	iron oxide	
Szombathely - Oladi plató	17	F. 11.	2006.07.19	pottery	brown	SEM	iron oxide	
Szombathely - Oladi plató	18	F. 29.	2006.08.10	pottery	salmon	SEM	iron oxide	
Szombathely - Oladi plató	19	F. 29.	2006.08.10	pottery	red	SEM, Raman	cinnabar	**Fig. 2b**
Szombathely - Oladi plató	20	F. 1.	2006.08.18	pottery	red	SEM	iron oxide	
Szombathely - Oladi plató	21	F. 1.	2006.08.18	pottery	white	SEM	calcite	
Szombathely - Oladi plató	22	F. 2.	2006.08.10	pottery	orange	SEM	iron oxide	
Szombathely - Oladi plató	23	F. 11.	2006.08.11	chem. tr. pottery	green	SEM	calcite	
Szombathely - Oladi plató	24	F. 11.	2006.08.11	chem. tr. pottery	yellow	SEM	iron oxide	
Szombathely - Oladi plató	25	F. 11.	2006.08.11	chem. tr. pottery	yellow	SEM	iron oxide	
Gór - Kápolnadomb	26	Ő.2006.1.270.	¤	chem. tr. pottery	red	SEM	iron oxide	
Gór - Kápolnadomb	27	Ő.2006.1.270.	¤	chem. tr. pottery	white	SEM	calcite	
Gór - Kápolnadomb	28	Mixed layer above F. 1.	2002.10.21	pigment nugget	red	SEM	iron oxide	
Gór - Kápolnadomb	29	Ő.2006.1.280.	¤	chem. tr. pottery	yellow	SEM	iron oxide	
Gór - Kápolnadomb	30	Ő.2006.1.370.	¤	chem. tr. pottery	red	SEM	iron oxide	
Gór - Kápolnadomb	31	Ő.2006.1.370.	¤	chem. tr. pottery	red	SEM	cinnabar	
Szombathely - Oladi plató		Feature 1. section East	2006.09.26	pottery	yellow-orange-red	Raman	hematite	
Szombathely - Oladi plató		F. 171.	2006.08.23	pottery	white-red	Raman	hematite	**Fig. 2c**

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Table 1.: Archaeological data and applied measurement methods of the chosen samples

1. táblázat: A kiválasztott minták régészeti adatai és az alkalmazott mérési módszerek

Table 2.: EDS results on selected samples

2. táblázat: Kiválasztott minták EDS kémiai elemanalízisének eredménye

Elements	Sample 19			Sample 8			Sample 10			Sample 9		
Fe	9.12	8.06	15.67	**66.74**	**62.10**	**58.32**	**24.74**	**40.97**	**45.61**	3.30	4.05	2.53
Mg	0.85	1.09	0.73	0.37	0.25	0.10	0.24	0.21		0.29	0.75	0.52
Al	9.89	11.04	6.97	6.28	4.89	4.10	2.47	2.74	2.85	7.57	9.80	9.17
Si	13.88	20.67	18.45	5.53	7.82	4.55	6.90	12.05	11.91	36.54	21.78	16.99
K	1.53	2.33	0.87	0.66	0.61	0.62	0.17			5.28	4.14	2.16
C	*25.86*	*16.04*	*15.51*	3.54	4.53	5.72	*28.65*	*13.54*	*12.26*	11.12	19.58	28.97
Hg	**6.20**	**1.93**	**0.75**									
Ca	0.84	1.30	0.62	0.11						0.15	0.28	0.17
Ti					0.11					0.07	0.14	0.14
Zn						0.15	0.19	0.26				
P		0.75	0.78	0.11	0.11	0.12	0.35	0.54	0.59	0.08	0.14	0.05
S	**1.77**											
Na							0.24		0.24			
Mn				0.55	0.48	0.42						
Cu								0.26	0.18			
Ni								0.23	0.23			

Transmission FT-IR analysis of a small amount of removed samples reveals also that we are dealing with a 'pure' hematite raw material. The FT-IR spectrum are dominated by characteristic bands of Fe_2O_3, while spectrum of a 'normal' red raw material (Feature nr. 16., sample 10) show typical bands of clay minerals and quartz (spectra not shown).

Study of painted pottery fragments

Preliminary SEM microanalysis (**Table 1.**) revealed the presence of mercury in the red pigment on the examined ceramics (**Fig. 2b.**). FT-Raman measurements unambiguously identify the red pigment as cinnabar (HgS) (**Fig. 5.**).

The use of cinnabar for ceramics decoration is quite unusual in this archaeological period throughout Europe. The only known archaeological site were cinnabar was used is Vinča, where it was proved by micro-Raman, FT-IR spectroscopy as well as X-ray powder diffraction (Mioć et al. 2004).

This is not really surprising though, because already in Neolithic times well-known cinnabar quarry is situated nearby.

Quasi-destructive FT-IR measurements (~50 μg removed red paint was pressed in a CsI pellet) and non-destructive FT-IR microscopic reflection study provided additional information: the cinnabar was mixed with kaolin and fixed on the ceramic surface. **Fig. 6.** compares absorbance spectra of removed red paint (A) with cinnabar (B) and kaolinite (C) references. Since the previous FT-Raman investigation did not reveal bands of typical impurities of kaolin (α-quartz and anatase) we can assume that high-purity kaolin was used.

FT-IR microscopy with high lateral resolution (~5 μm) is suitable for homogeneity (or inhomogeneity) studies. In the reflection spectra, collected from painted surfaces, bands of outer and inner hydroxyl groups (3699, 3669, 3655 cm^{-1}, and 3623 cm^{-1}, respectively) indicate a homogenous presence of kaolinite. The homogeneous nature of the painted surface suggests a deliberate mixing of the pigment with kaolin, rather than unintentional mixing. The aim of this technology is to mix the pigment with very fine, wet clay.

As a result, the paint was distributed in the clay evenly and for this reason the application of the paint became easier and more complex and fine motifs could be made.

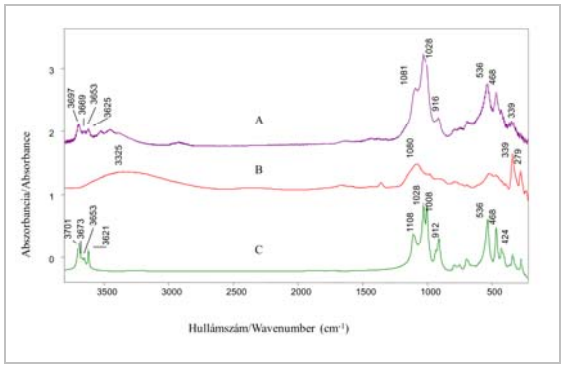

Fig. 6.: FT-IR spectra of red paint removed from pottery surface (A), natural cinnabar reference (B) and kaolin reference (C)

6. ábra: Kerámiafelületről lekapart vörös festék (A), természetes cinnabarit referencia (B) és kaolinit referencia (C) CsI pasztillában felvett FT-IR színképei

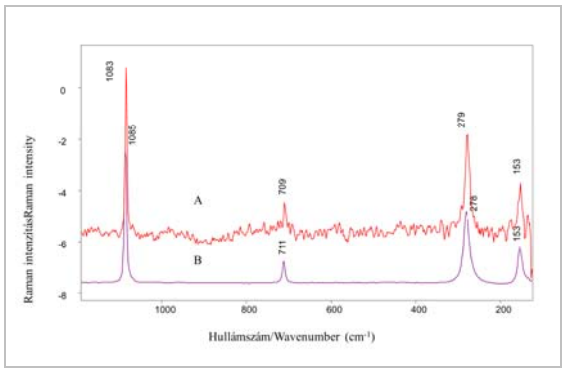

Fig. 7.: FT-Raman spectra of white paint on pottery surface (A) and calcite ($CaCO_3$) reference (B)

7. ábra: Kerámiafelületre felvitt fehér festék (A) és kalcit ($CaCO_3$) referencia (B) színképei

Analysing the orange paint layers (Feature nr. 1.) by in situ FT-IR reflection spectroscopy, the characteristic –OH vibrational bands of kaolinite in the 3700-3600 cm^{-1} wave number region are absent. Transmission FT-IR spectra of removed paint are dominated by clay and quartz bands, however, typical bands of inner and outer hydroxyl-groups of kaolinite are missing, too. Cinnabar was also not detectable. We can assume that the orange layer was developed applying red or yellow ochre.

The pigment on a pottery decorated with white bands was found to be pure calcite ($CaCO_3$) (**Fig. 7.**). FT-IR microscopic mapping revealed a uniform, compact paint layer.

Detailed study of the paints on ceramics or possible layered structure of the painting such as the identification of first coat painting, pigments and binding materials need further investigations.

Conclusion

Combined application of SEM-EDS, FT-Raman and FT-IR spectroscopy allowed a detailed identification of mineral content of raw pigment materials and painted layers on Late Neolithic ceramics from Szombathely-Oladi plató. Beside goethite and hematite containing yellow and red ochre raw pigment materials, a piece of 'pure' hematite was also evinced. This may be the result of a purifying process suggesting a purposeful preparation of the raw material (the presence of magnetite may suggest a reductive heat treatment). Surprisingly, on ceramic fragments the red decoration's colouring component was found to be mercury sulphide (HgS) mixed (diluted) with kaolinite. To our knowledge, this is the first evidence of the use of cinnabar (HgS) for decorated pottery in Late Neolithic period in the region of Hungary.

The above presented study of pigments and painted pottery shards yielded archaeologically very interesting results. General view was the aim of the scanning electron microscopy investigations for both sites (Szombathely-Oladi plató and Gór-Kápolnadomb). We were interested in the elemental composition of the pigment nuggets and pigments found on painted pottery shards. Besides this, we were curious about the effect of the chemicals used during the restoration process on the measurement results performed. The information gathered with SEM-EDS was completed by vibrational spectroscopic investigations, identifying the exact pigment materials, their compositions and the binding materials used for fixing on the ceramic surface. The study gave the result, that in the most cases truly earth pigments (iron-oxide and hydroxide) were used as red and yellow pigments, but rare cinnabar could be identified as well. Cinnabar painting occurs on both archaeological sites, which means conscious choice. The chemical products and treatments used during the restoration process verified to have a bad effect on vibrational spectroscopic investigation, but didn't influence SEM measurements, which means, that for vibrational spectroscopic study untreated pottery fragments are needed.

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