Inorganic Paint Pigment Analysis in Ovaören Ceramics by Micro XRF Spectrometry

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Abstract

Ancient ceramics are the most common archaeological findings, which are highly significant objects for both antiquarian and scientific studies. Nuclear analytical techniques play important role in the determining the chemical characterization of cultural objects are made of the materials. In this regard, portable instruments contribute significantly to the in situ analysis of valuable cultural objects that cannot be transported to the laboratory. In this study; ceramics recovered in excavation from Ovaören archeological site, where is located to the west of Nevşehir city, are analyzed to determine elemental distribution of mineral paints by μ-XRF (Micro X-Ray Fluorescence) spectrometry. This study gives a first impression on the color pigments of Ovaören ceramic samples dated to Middle Bronze Age (2000-1650 BC), Middle Iron Age (850-600 BC) and Late Iron Age (600-330 BC). Estimation of both original colors and chemical contents of the archaeological samples is important to make suitable conservation study.

Keywords: Micro-XRF; In situ analysis; Ancient ceramics; Portable instruments; Non-destructive analysis, Middle Bronze Age, Iron Age.

1. Introduction

Ovaören is composed of Yassıhöyük and Topakhöyük excavation sites. Ovaören ceramic samples recovered at the Ovaören archaeological site are coming from these two different areas. Topakhöyük and Yassıhöyük lie between latitudes 38^0 36' 53'' and 38^0 36' 21'' N and longtitudes 34^0 18' 5'' and 34^0 17' 21'' E. Topographic map and aerial view of Ovaören archeological site are given in (Fig. 1a) and (Fig. 1b), respectively (Senyurt, 2008).

This excavation has been carried out under the leadership of S. Y. Şenyurt who is head of Gazi University Archeology Department and also Archeological Research Center of Environmental Values (GÜ-ARCED) since 2007. This excavation study continues in an area approximately 5 km radius (Senyurt, 2008).

Ovaören, continuously inhabited from the Chalcolithic to the Late Iron Age, is located at a strategically important intersection with Kings Highway and Silk Road. Ovaören provides important new findings about aforementioned periods with the ongoing excavations (Senyurt, 2008).

Topakhöyük represents the earliest settlement phase of the site, however a few painted Middle Bronze Age (2000-1650 BC) samples are included. Yassıhöyük is a fortified city neighboring Topakhöyük and the majority of samples are dated to Middle Bronze Age, Middle Iron Age (850-600B) and Late Iron Age (600-330 BC) (Senyurt,2008).

μ-XRF spectrometry is the most widely used technique due to a number of favorable analytical characteristics, such as non-destructive analysis, multi-element analysis, high sensitivity and applicability for a wide range of samples (Mantler et al., 2000; Van Grieken and Markowicz, 1993; Pillay et al., 2000; Scott, 2001; Williams-Thorpe et al., 1999; Punyadeera et al., 1997; Milazzo and Cicardi, 1997).

This paper is the first analytical study for Ovaören excavation site and also clarifies chemical content of the color pigments that are used for the purpose of decoration in order to help conservators to use suitable minerals.

2. Materials and Methods

The ceramic samples selected to cover the different color and also their different shades. They were washed with water and brushed in order to remove residues formed on the surface of the ceramics. The primary color of the figural decoration is blackish, brownish and reddish. The μ-XRF spectrometry, non-destructive analysis method, is preferred due to the archaeological importance of these ceramics. All samples are analyzed, mapped by using μ–XRF spectrometer in order to determine spatial distribution of elements and also tabulated (Table 1). The μ -XRF spectrometer (Bruker Artax 800 model), includes a X-ray tube with a Molybdenum anode, a polycapillary lens and a solid state Si(Li) Peltier-cooled detector (10 mm^2 active area), is used. Because of good optical arrangement, The X-ray beam size is 70 μm. The maximum tube voltage is 50 kV and maximum current is 1 mA (30 W). An optical microscope is used in order to choose and focus on the points of interest while scanning the ceramic's surface. μ -XRF spectrometry moves in distances of 5 cm in the X-Y directions and 2.5 cm in the Z-direction by 0.01 mm step size. All measurements were performed in air environment and no filters were used. All μ -XRF measurements were performed in a point scan mode (Fig.2).

3. Results and Discussion

The results obtained from the preliminary analysis of these ceramics are presented in Table 1. The analysis results of some exemplary the ceramic samples with different color are evaluated and discussed in detail.

3.1. Yassıhöyük ceramic (Sample Code: YH10 IL175 124-7): This ceramic's figure includes black color pigment and its picture is given in Fig. 3a. μ -XRF mapping analysis shows that this black pigment includes high Mn (Manganese) concentration as a major and As (Arsenic) and V (Vanadium) concentration as minor elements (Fig. 3b). The XRF spectrum of the ceramic material (Background) and black color pigment are given in Fig. 4. This shows that Mn (MnO) ore had been used as black pigments for decorating ceramics during the Late Iron Age (Goffer, 2007).

3.2. Yassıhöyük ceramics (Sample Code: YH 97 C15): This ceramic has black and red pigments. This ceramic picture is given in Fig. 5a. The XRF spectrum of ceramic materials (background), the black and red pigments is plotted with red, green and pink colors, respectively (Fig. 5b). μ-XRF mapping analysis shows that black color pigment includes high Mn (Manganese) concentrations as major and V (Vanadium) concentration as minor (Fig. 6a). Also, μ-XRF mapping analysis shows that the red color pigment has a high Fe (Iron) concentration as a major and V (Vanadium) and As (Arsenic) concentration as minor (Fig. 6b). This shows that Mn (MnO) and Fe (Fe2O3) ores had been used as black and red pigments in ceramics during the Late Iron Age (Goffer, 2007).

3.3. Topakhöyük ceramic (Sample Code: TH 07 H20-7): This archeological ceramic contains figures that are not easily visible to the naked eye (Fig. 7a). μ-XRF mapping analysis shows that this sample's color pigment includes high Mn (Manganese) concentration as major and As (Arsenic) and V (Vanadium) concentration as minor (Fig. 7b). We could easily determine the figures, its original color and pigments by μ -XRF mapping.

4. Conclusions

Painted decorations on ceramics from Ovaören generally seem have blackish, brownish and reddish colors. The analysis proves that the main colors are red and black. Mn (MnO) and Fe (Fe2O3) ore have been used as black and red pigments for decorating pottery (Goffer, 2007). Different shades of brown are obtained with a mixture of different proportions of black Mn (MnO) and Fe (Fe2O3) ore. Some black pigments have a brownish sheen though pigments include only Mn (MnO) ore. The analysis of Mn based black pigments in all periods indicates that similar techniques were possibly used for the decoration of ceramics between the Middle Bronze Age and Late Iron Age. Because ceramic pigments are affected by the physical environment, and ceramic materials contain generally Ca (CaO), its color may have changed from black to brownish shades. A proper conservation study can now be launched by estimating the original colors and its chemical contents of the archaeological samples.

Acknowledgment

The current project was supported by International Atomic Energy Agency and Turkish Atomic Energy Authority, in the frame of the Program "Nuclear Techniques for the Protection of Cultural Hertitage Artifacts in the Mediterranean Region (RER/1/006)". We would like to thank Archeological Research Center of Environmental Values (GÜ-ARCED) for archeological samples.

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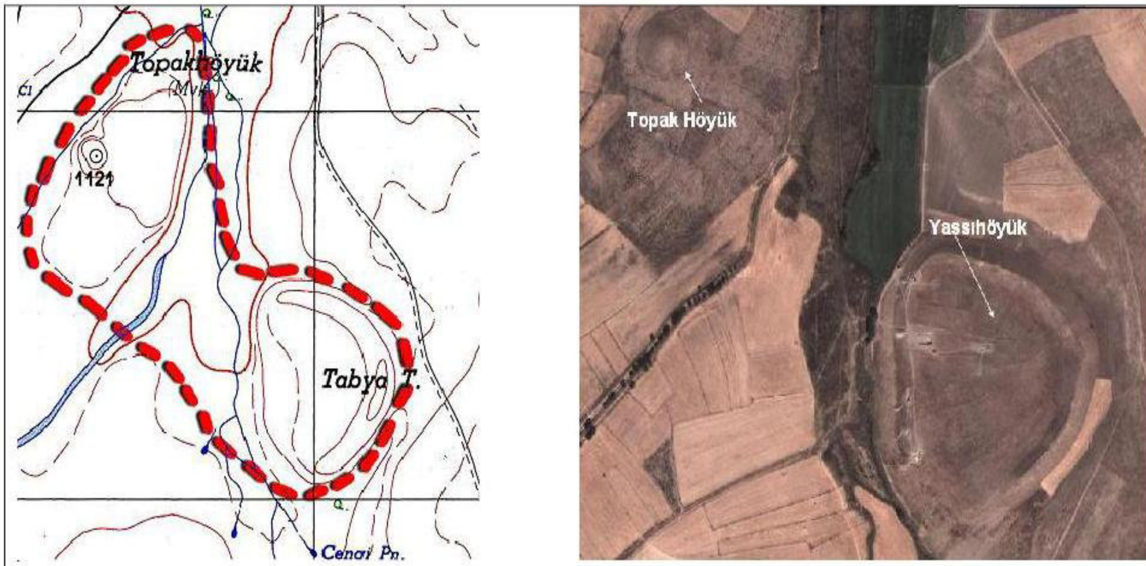

Fig. 1. a) Topographic map and b) Aerial view of Ovaören archeological site.

Figure 2 Artax 800 μ-XRF Instrument for rapid point analyses and elemental mappings

Fig. 3. a) Yassıhöyük ceramic (YH10 IL175 124/7) and b) its elemental mapping result.

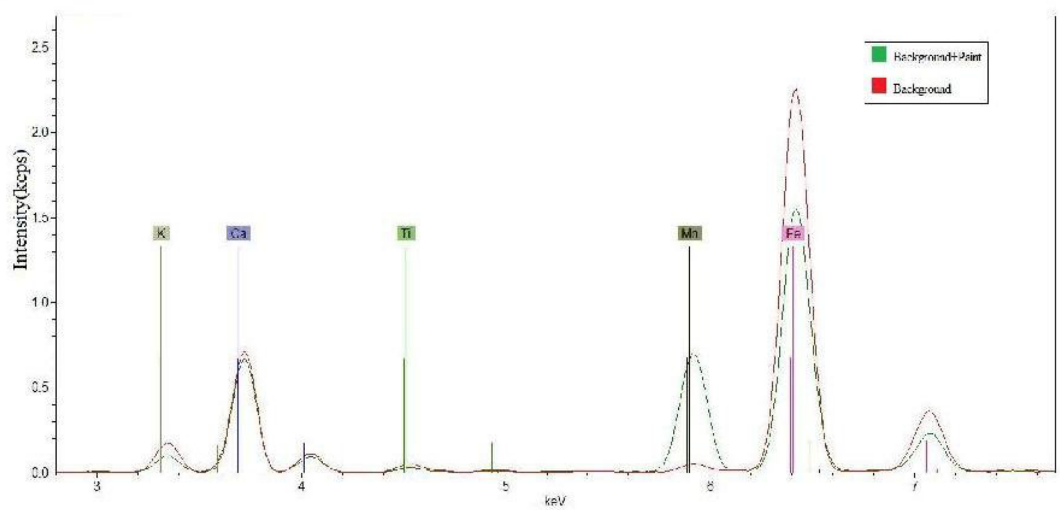

Fig. 4. Micro-XRF spectrum of Yassıhöyük ceramic (YH10 IL175 124/7).

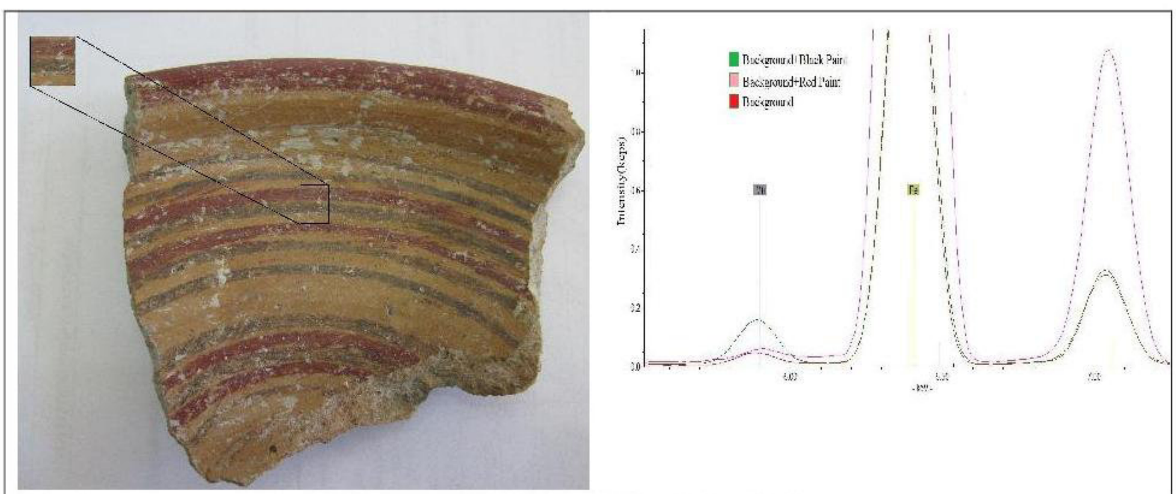

Fig. 5. a) Picture of Yassıhöyük ceramic (YH 97 C15) and b)its XRF spectrum.

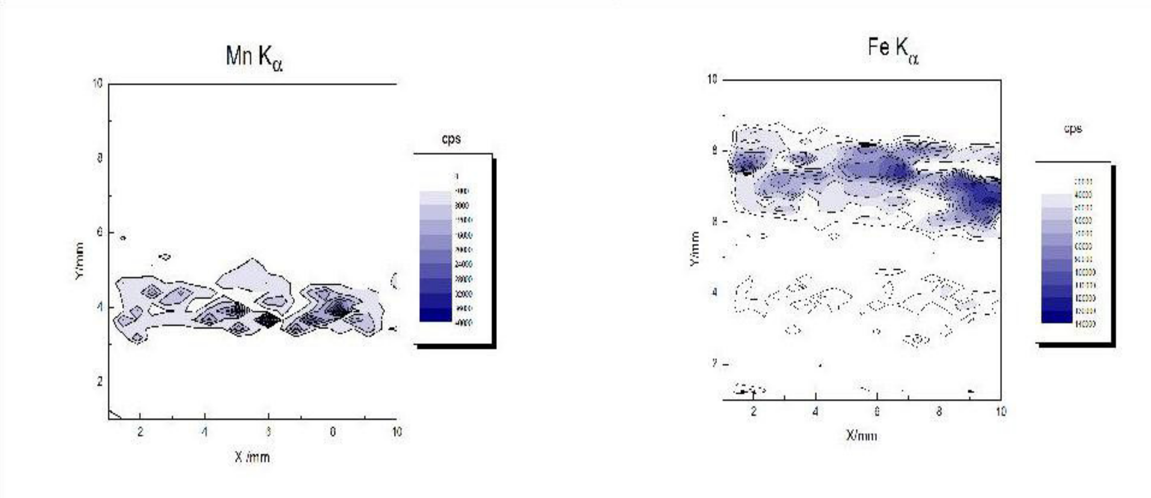

Fig. 6. a) Elementel mapping result of Yassıhöyük ceramic (YH 97 C15) for Manganese and b) its elementel mapping result for Iron.

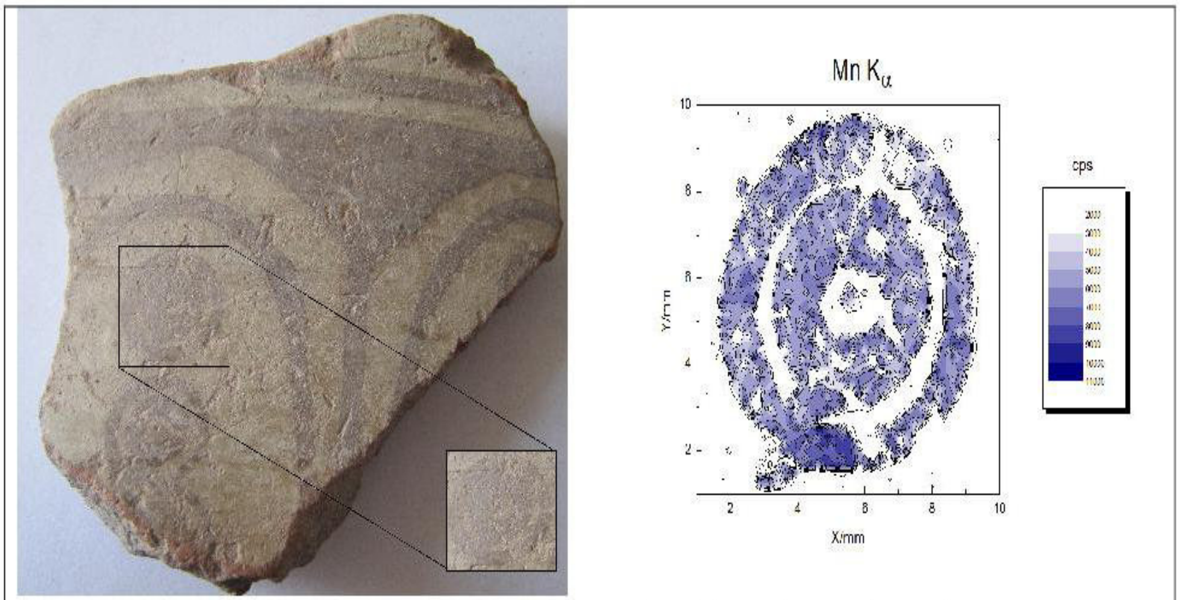

Fig. 7. a) Picture of Yassıhöyük ceramic (TH 07 H20-7)and b) its elemental mapping result.

Table 1 Yassıhöyük and Topakhöyük ceramics and their qualitative analysis results

Sample Code	Colour	Observed		Period	Sample Code	Colour	Observed		Period
		Major Elements	Minor Elements				Major Elements	Minor Elements	
AS09 GE-47 19-40	Red	Fe		Middle Bronze Age	YH 10 IK 175 59-4	Black	Mn	Ti, Ba	Late Iron Age
TH 07 GT 184	Black	Mn	Ni,Cr, V	Middle Bronze Age	YH 97 C3	Dark Brown	Fe+Mn		Late Iron Age
						Black	Mn		
TH 07 GT 183	Red	Fe	As	Middle Bronze Age	YH 10 IL175 75-1	Black	Mn	V	Late Iron Age
	Black	Mn			YH 10 IL175 10-4	Black	Mn		Late Iron Age
YH 10 SUR 2	Black	Mn	Ti	Middle Iron Age	YH 10 IK175 52-9	Black	Mn	Ti	Late Iron Age
TH 07 H 20-7	Black	Mn	Ti, V	Middle Iron Age	YH 07 6-85	Dark Brown	Fe+Mn	V	Late Iron Age
YH 10 IK175 80-1	Dark Brown	Fe+Mn		Middle Iron Age	YH 07 62-18	Dark Brown	Fe+Mn		Late Iron Age
YH10 IL175 124-7	Black	Mn	Ca, V	Middle Iron Age	YH07 E8 33-3	Dark Brown	Fe+Mn		Late Iron Age
YH07 B9-1	Red	Fe		Middle Bronze Age	YH 97 C15	Red	Fe	V, As	Late Iron Age
YH09 IJ175 40-1	Black	Mn		Middle Iron Age		Black	Mn	V	
YH10 IK175 207-12	Dark Brown	Fe+Mn	V	Middle Iron Age	YH07 2-79	Red	Fe	Cr, V	Late Iron Age
						Dark Brown	Fe+Mn		