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A physicochemical study of Medieval and Post-Medieval ceramics from the Aegean

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CHAPTER 11 RAMAN SPECTROSCOPY

11. INTRODUCTION

Although around fifty measurements were implemented by Raman Spectroscopy analysis in the Institute of Nanoscience and Nanotechnology at the National Centre for Scientific Research ‘NCSR Demokritos’ in Greece, only eleven of them were interpreted due to fluorescence of the glazes. The Raman spectroscopy was performed with a Jobin-Yvon LabRam HR 800 system. A green laser with a 2 μm spot diameter has been used. This method was used in order to identify the chemical components of the pigments in combination with the Scanning Electron Microscopy (SEM-EDS).

Micro-Raman spectroscopy was here applied for the study of ceramic pigments showing different features and technological background. Especially, the Raman scattering measurements were performed at the surface of painted ceramics in order to analyze existing pigments. Raman spectroscopy did not call for sample preparation; entire fragments were analysed without further handling, provided they were small enough to be moved and arranged under the laser probe. Very thin ceramic coatings on a rather thick ceramic body were analyzed. Infrared spectroscopy yielded complementary information in combination with X-Ray Fluorescence Spectroscopy (pXRF) and Scanning Electron Microscopy (SEM-EDS).

11.1 RAMAN SPECTROSCOPY

Micro-Raman spectroscopy is a characterization and analysis method widely applied in the field of cultural heritage, history and art. It is a non-invasive and non-destructive method to investigate works of art and cultural heritage artifacts, because it can be applied in situ (Howell 2005). The identification of pigments on archaeological artifacts is critically important to understanding the history of an object and in the resolution of problems related to restoration, conservation, dating and attribution of artwork. Namely, Raman spectrum, as unique signature, is specific to the technology applied to a given mixture of starting materials and to the process of pottery production (Colomban 2004, 2005a,b; Colomban and Treppoz 2001; Colomban et al. 2001; Clark et al. 1997a, 1997b). Many techniques, both molecular and elemental, have been used for such studies, but the former is the more important since they lead to the identification of the pigment, which is usually a molecule rather than an element (Colomban 2005a,b; Colomban et al. 2001; Clark et al. 1997a, 1997b). Raman spectroscopy, significantly a molecular technique, has emerged out of recent advances in optics and detector technology as probably the most suitable of such techniques on account of its high spatial (ca. 1 μm) and high spectral (ca. 1 cm^{-1}) resolution, its molecular specificity, its excellent sensitivity by way of charge-coupled device (CCD) detectors, and the fact that most items may be analyzed non-destructively and in situ (Corset et al. 1989; Ferraro 2003; Smith and Clark 2004). FT-Raman has also been used with microscopes, typically in combination with near-infrared (NIR) laser excitation.

Raman spectroscopy relies upon non-elastic scattering of photons, known as Raman scattering. A source of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range is used, although X-rays can also be used. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted

up or down. The shift in energy gives information about the vibrational modes in the system. In the micro configuration the spatial resolution and the depth of field are a few micrometers. These features offer many advantages for the analysis of very thin micro-structures, as these can be spatially distinguished from the surroundings as well as directly characterized without interference from the material underneath (Stuart 2007). The acquisition of a statistically significant set of data points is, however, advisable in order to obtain compositional results representative of the structural item under study, whether this is a ceramic body or a coating.

The reasons turning Raman spectroscopy so apt for art and archaeological analysis are the versatility of selection of a range of laser excitation wavelengths to interrogate coloured specimens and the acceptance of specimens of a size range from milligram to kilogram, which contribute to the popularity of this method (Derrick 1999). The major advantages of the adoption of Raman spectroscopy for the analysis of artifacts and works of art are twofold: the technique is nondestructive and requires little or no chemical and mechanical pretreatments of the specimen, and the molecular signatures from both the organic and inorganic components are obtained in the same spectrum, hence affording the opportunity for assessing the interactions and relative stabilities to chemical, biological, and environmental changes operating on the specimen (Colomban 2019; Clark 2011; Stuart 2007). The examination of diverse range of artifacts and specimens using non destructive laser Raman spectroscopic analysis provides the acquisition of novel historical information about their origins and degradation suffered in a new light.

11.2 RESULTS AND DISCUSSION OF RAMAN SPECTROSCOPY

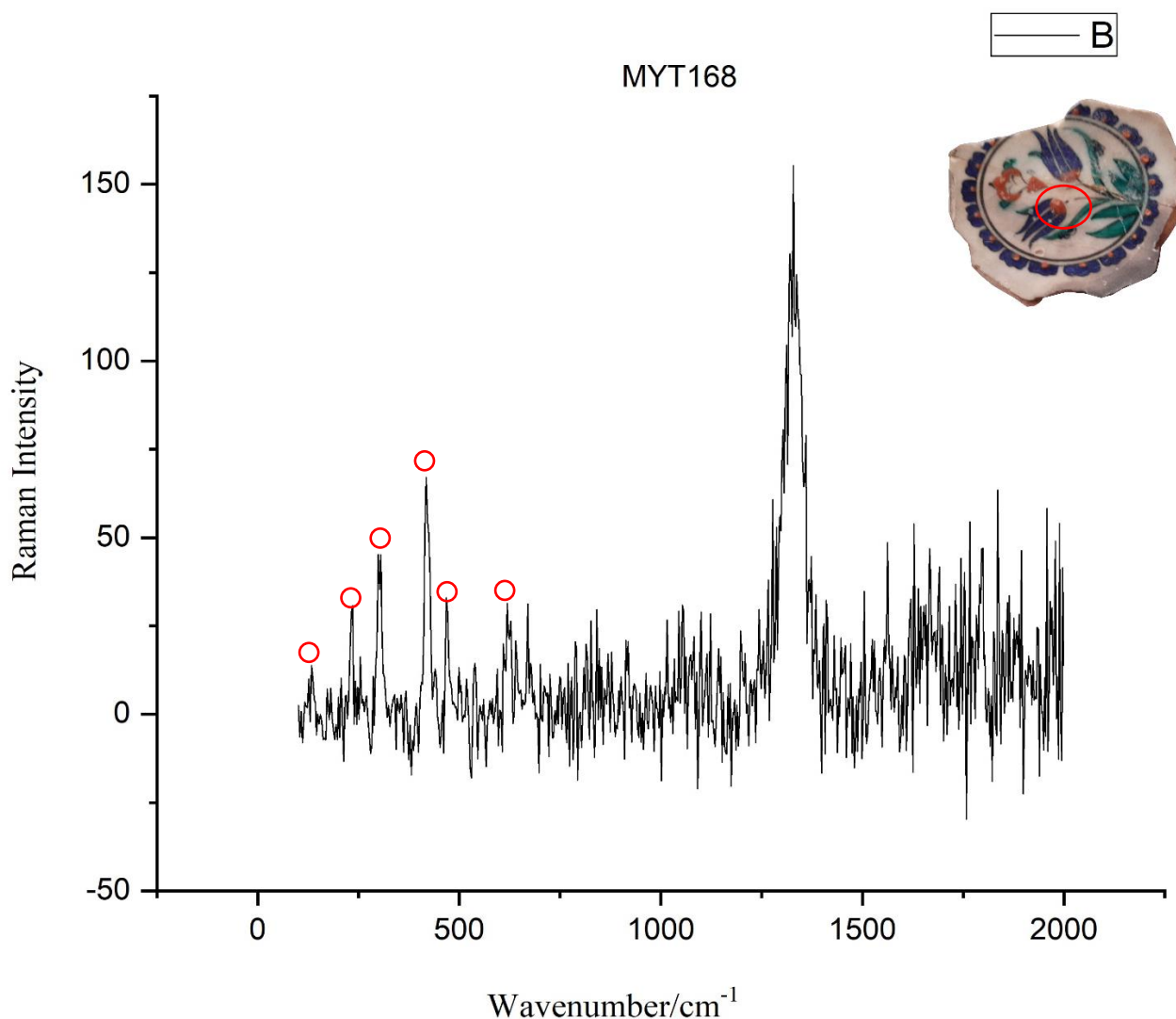


Figure 185 Red colour of sample MYT168 (Iznik Ware)

The red colour of the glaze came from the Hematite oxide, Fe_2O_3 , which can be detected at the peaks: 130nm, 230nm, 300nm, 415nm, 615nm (Burgio 2001) (Database of Raman spectroscopy, X-ray diffraction and chemistry of minerals (ruff.info)).

At the peak 465 (460), SiO_2 can be detected which did not completely dissolved during firing (Burgio 2001).

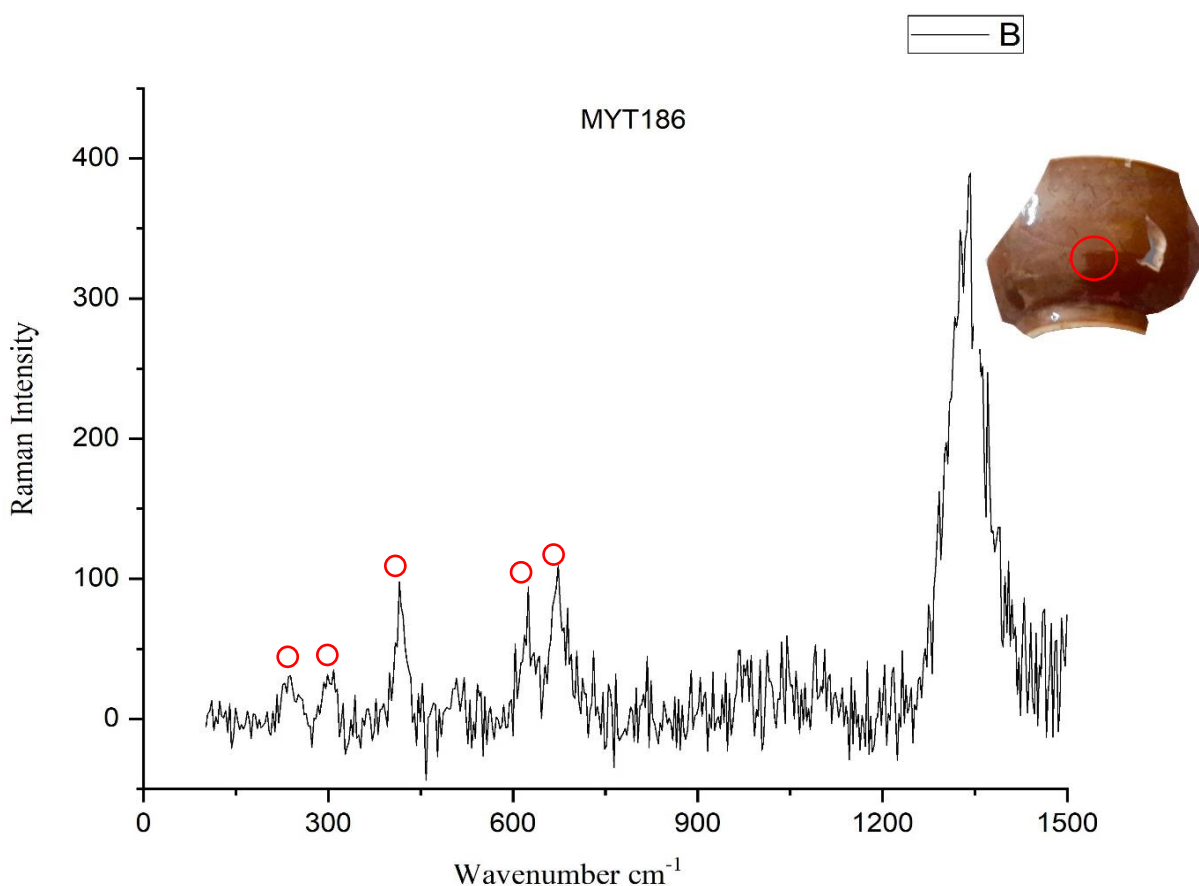


Figure 186 Brown colour of sample MYT186 (Porcelain).

The red colour of the glaze came from the Hematite oxide, Fe_2O_3 , which can be detected at the peaks: 230nm, 300nm, 415nm, 620nm and also from the Magnetite oxide, Fe_3O_4 , at the peak 670 (Burgio 2001; Colombari 2020) (Database of Raman spectroscopy, X-ray diffraction and chemistry of minerals (rruff.info)).

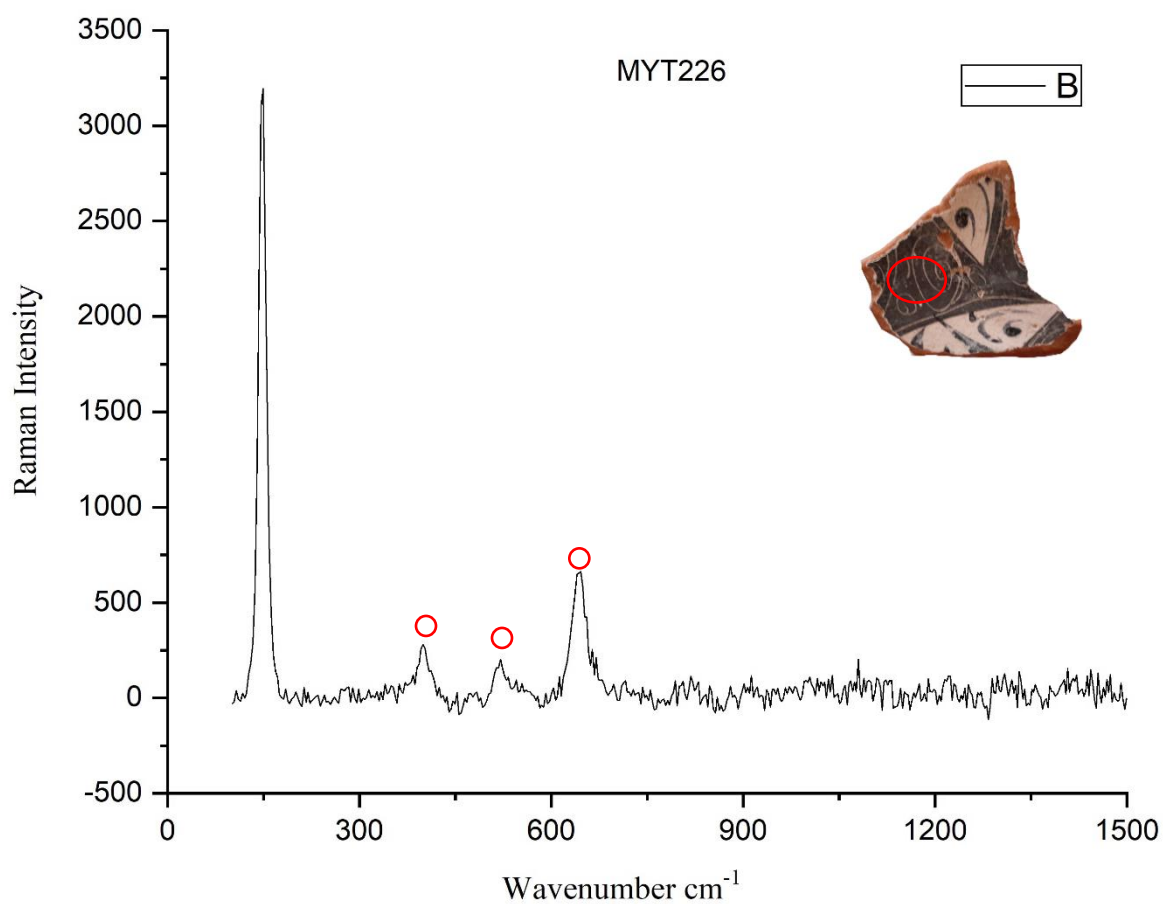


Figure 187 Black colour of sample MYT226 (Miletus Ware).

The black colour of the glaze is a combination of Magnetite oxide MgO , which can be detected at the peak 230nm, of Chromium oxide Cr_2O_3 at the peak 530(550)nm and of Hematite oxide Fe_3O_4 at the peak 400nm (Bell 1997; Colombari 2005a,b).

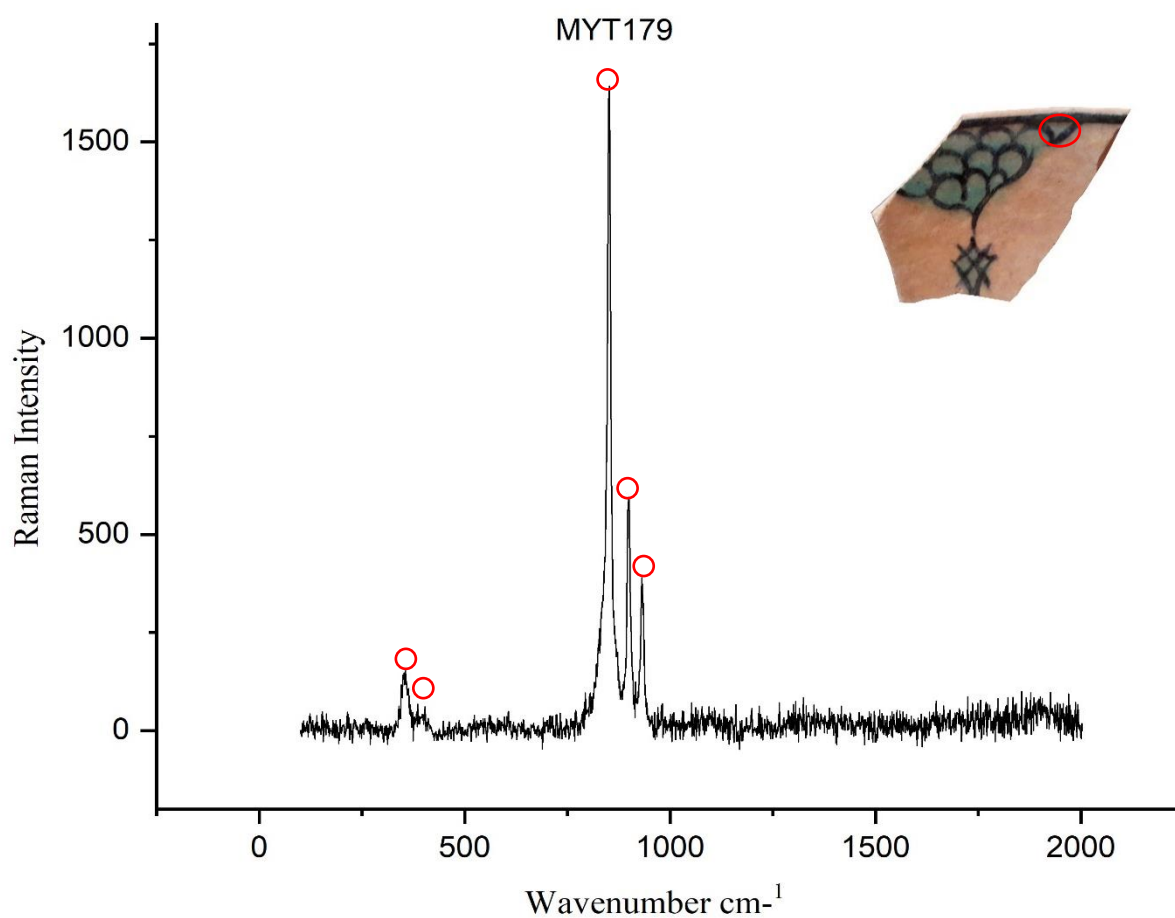


Figure 188 Dark line of sample MYT179 (Kütahya).

The Dark line is a combination with Cr, Al, Fe at the peaks 350nm, 405nm, 700nm, 845nm, 896(895)nm and 931(930)nm (Colomban 2005a,b; Colomban et al. 2005a).

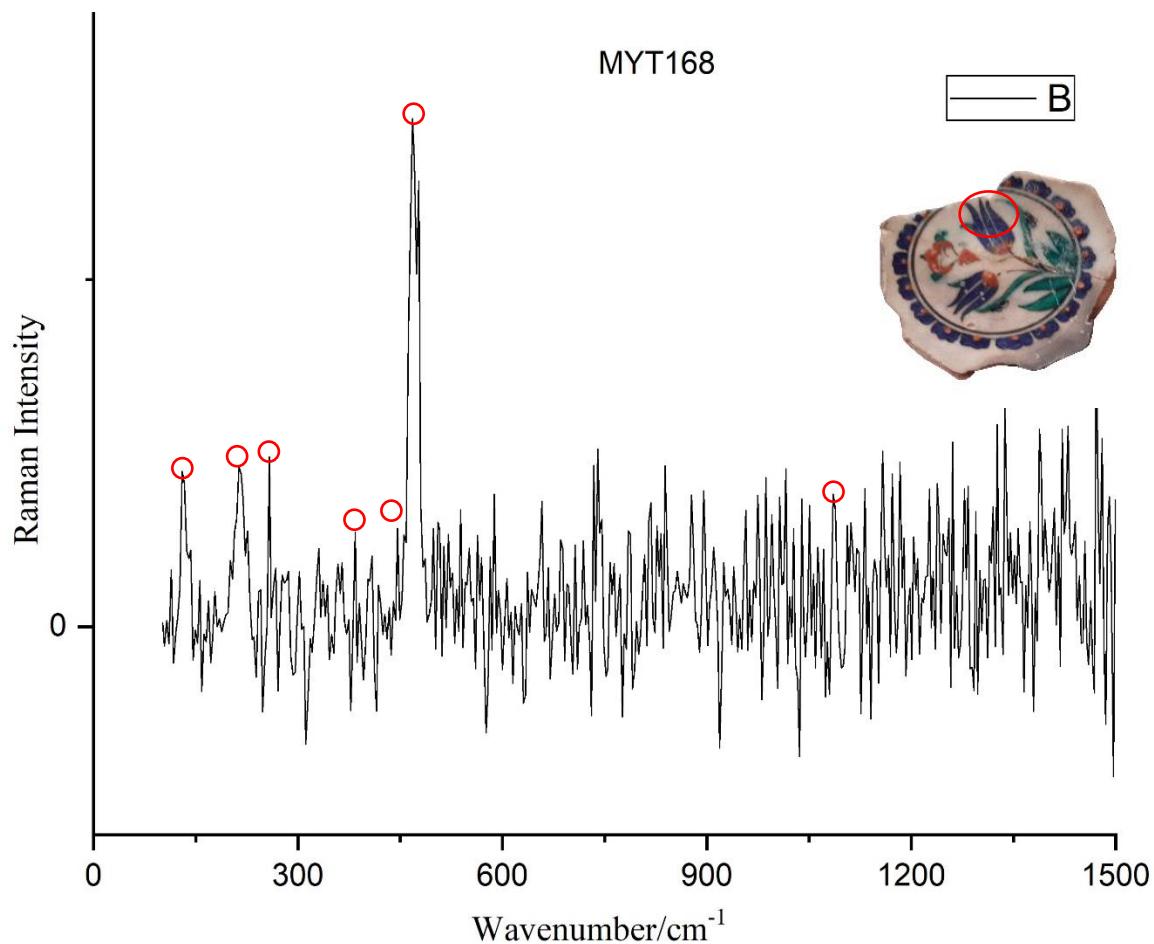


Figure 189 Blue colour of sample MYT168 (Iznik Ware).

The blue colour came from the Egyptian blue Calcium Copper (II) Silicate $\text{CaCuSi}_4\text{O}_{10}$, which can be detected at the peaks: 435(431)nm, 465(470)nm, 1090 (1086)nm (Bell 1997; Burgio 2001).

At the peaks 131(130)nm, 209(208)nm, 263(262)nm, 355(354)nm, 399(398)nm, 467(466)nm, Silica silicon oxide, SiO_2 , can be detected (Burgio 2001).

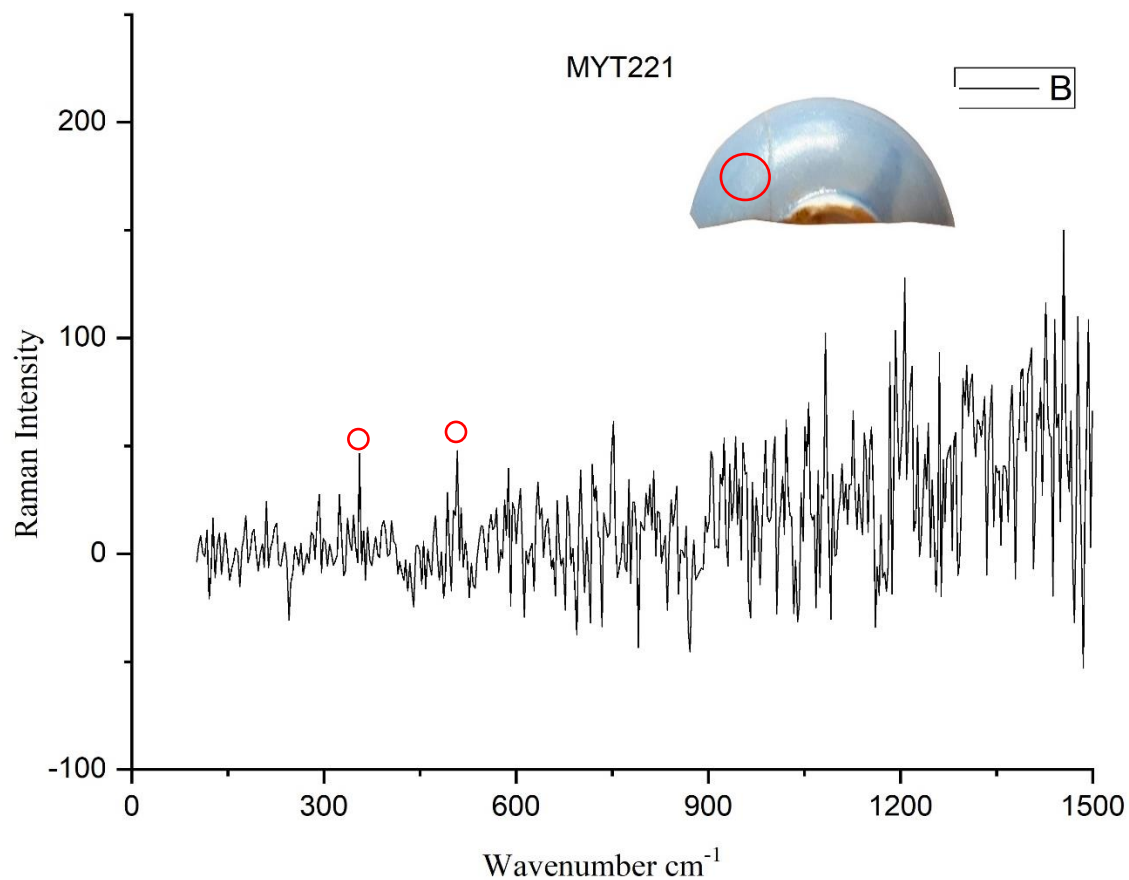


Figure 190 Blue glaze of sample MYT221 (Porcelain).

The blue glaze came from Lazurite oxide $\text{Na}_3\text{CaAl}_3\text{Si}_3\text{O}_{12}\text{S}$, which can be detected at the peaks: 355(352-378)nm, 520(549)nm (Bell 1997; Burgio 2001; Colomban 2020).

At the peaks 131nm, 209nm, 362nm, 400nm, 467nm, Silica silicon oxide, SiO_2 , can be detected (Burgio 2001).

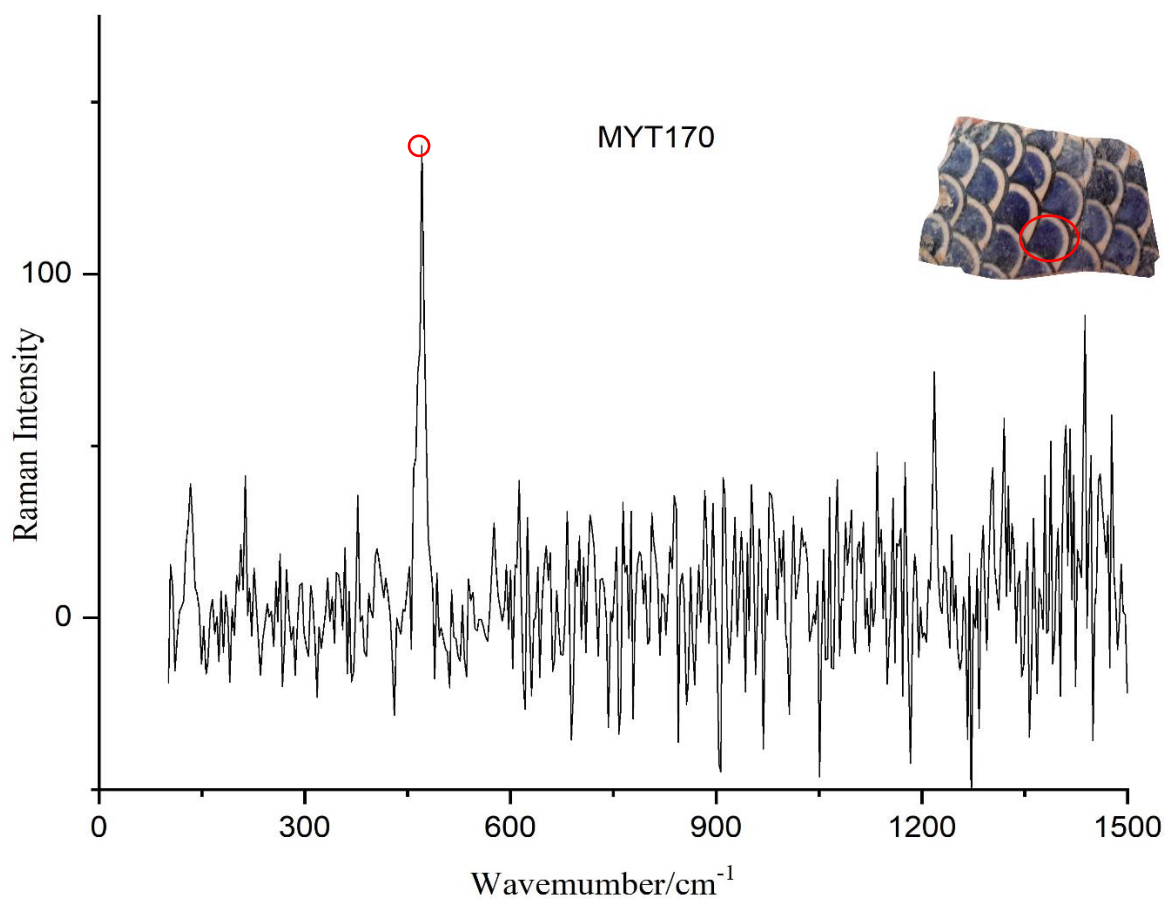


Figure 191 Blue colour of sample MYT170 (Iznik Ware).

The blue glaze came from the Blue Smalto Cobalt (II) silicate $\text{CoO} \cdot n\text{SiO}_2$, which can be detected at the peaks: 468(462)nm, 918(917)nm (Bell 1997; Clark 1998).

At the peaks 130nm, 208nm, 262nm, 360(354)nm, 391(398)nm, 466nm, Silica silicon oxide, SiO_2 , can be detected (Burgio 2001).

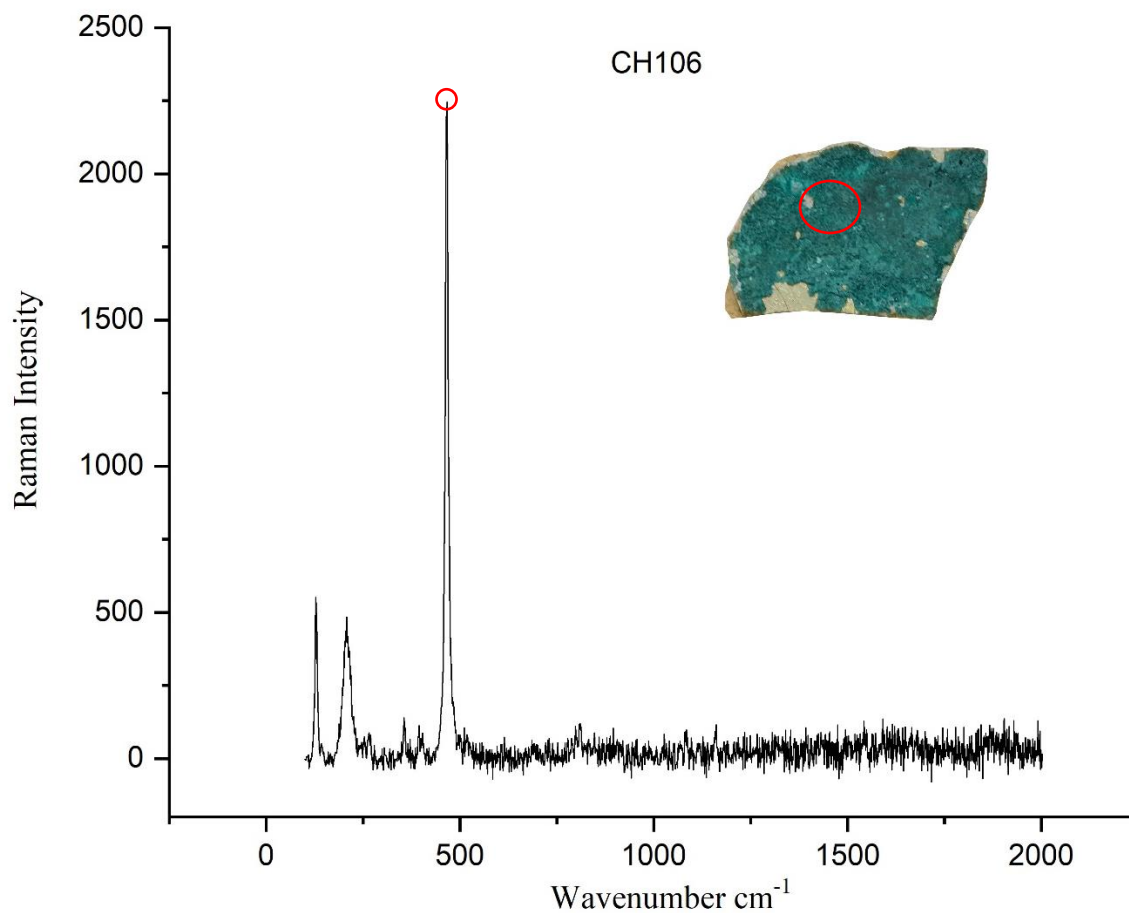


Figure 192 Turquoise colour of sample CH106 (Glazed Frit Ware).

According to Phillipe Colomban, the reaction of Cu in Pb glaze which can be detected at the peak 470nm (Colomban 2005a,b; Colomban and Screiber 2005b; Colomban 2011). This glaze consisted of a high amount of alkalis also. The reaction of Cu with the fluxes produced the turquoise colour.

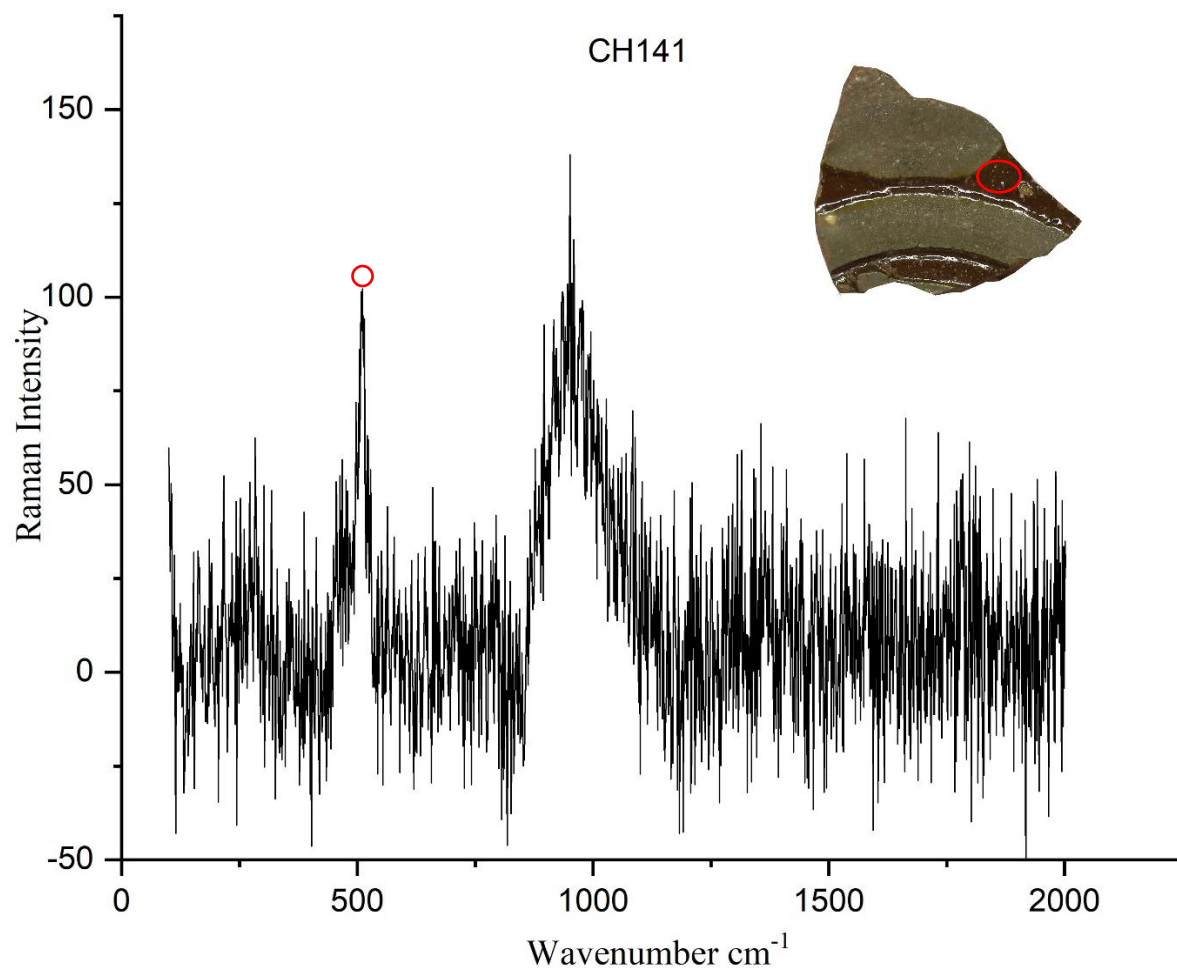


Figure 193 Green colour of sample CH141 (Champlevé Ware).

The green colour came from the Atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$, which can be detected at the peaks: 513nm and 911nm (Burgio 2001).

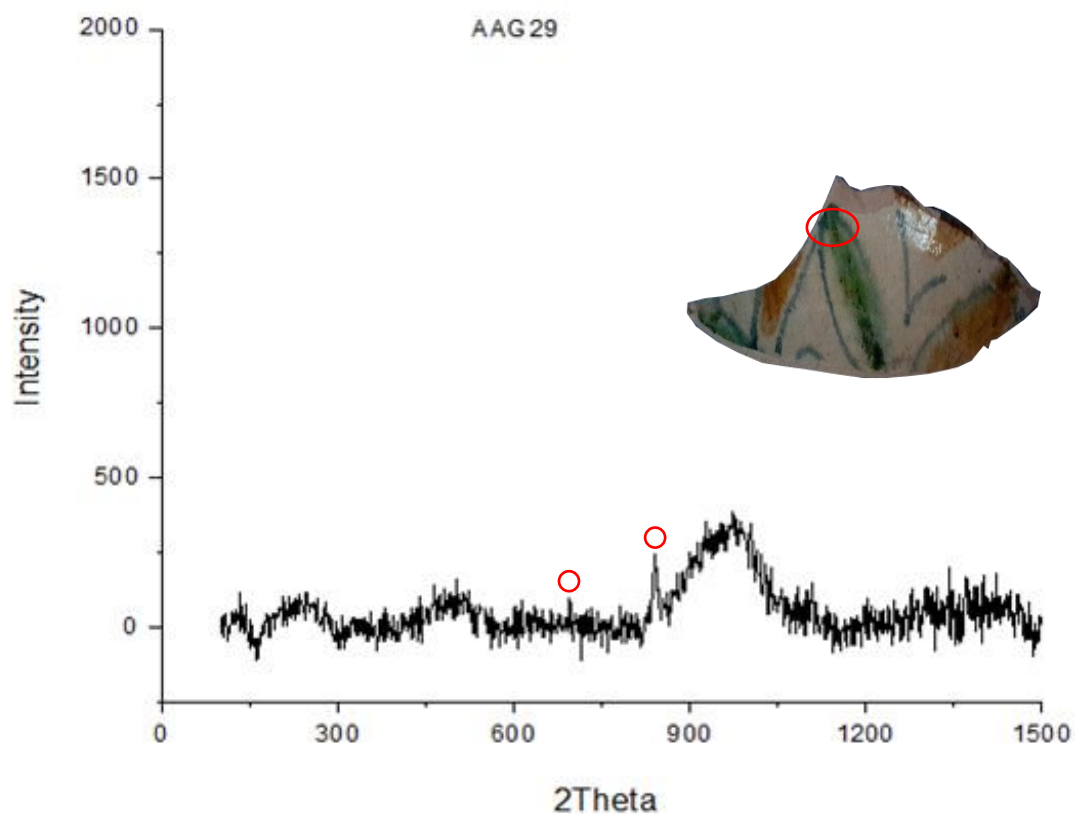


Figure 194 Green colour of sample AAG29 (Polychrome Painted Ware/Maiolica).

According to Phillipe Colomban, the green pigment is due to the reaction of Cu in Pb glaze which can be detected at the peaks: 550nm, 690nm, 854 (855)nm, 905nm, 936(935)nm, 985nm and 1050nm (Colomban 2005a,b; Colomban 2011).

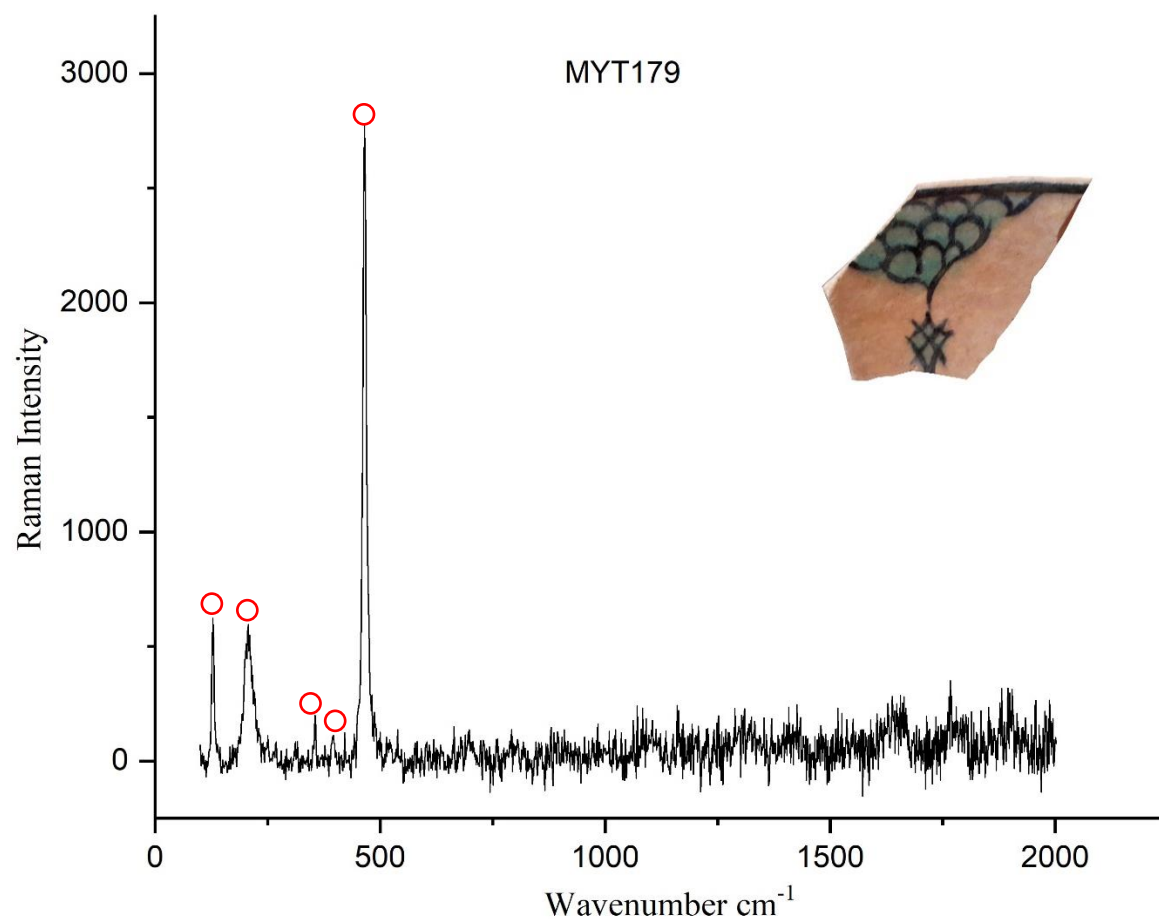


Figure 195 Glaze of sample MYT179 (Kütahya).

At the peaks 130nm, 209nm, 352nm, 398nm, 466nm, Silica silicon oxide, SiO_2 , can be detected (Burgio 2001; Coloman 2005c).

Although around fifty Raman analyses were implemented, only some of them were interpreted due to fluorescence of the glazes. A few pigments were detected in the glazed ceramics under study from **the Castle of Mytilene in Lesvos**.

The **Red colour** of Iznik Ware sample MYT168 came from Hematite oxide as well as the Red colour of Porcelain sample MYT223 (Figure 185). Theophrastus in his book ‘De Lapidibus’ mentioned ‘When the pots are thoroughly exposed to the fire, they cause the ochre to be baked, and the more they are burnt, the darker and more glowing the ochre becomes’ (Theophrastus 1965, p.79). The **Brown colour** of Porcelain sample MYT186 was a combination of Hematite and Magnetite oxide (Figure 186).

The **Black colour** of Miletus Ware sample MYT226 was a combination of Magnetite oxide, Chromium oxide and Hematite oxide (Figure 187). The Black line of Kütahya Ware sample MYT179 was a combination of Chromium oxide, Aluminum oxide and Hematite (Colomban 2005a,b) (Figure 188). The same chemical composition had the black pigment of Polychrome Painted Ware sample MYT215.

The **Blue colour** of Iznik Ware sample MYT168 came from the Egyptian blue calcium copper (II) silicate $\text{CaCuSi}_4\text{O}_{10}$ (Figure 189). The Blue colour of Porcelain sample MYT221 came from Lazurite oxide as well as the blue colour of Porcelain sample MYT223 (Figure 190). The Blue colour of Iznik Ware sample MYT170 came from the Blue Smalto as well as the blue colour of Porcelain sample MYT185 and of Polychrome Painted Ware sample MYT215 (Figure 191). The **Turquoise colour** of Kütahya Ware **samples** MYT179, MYT230 were due to Cu.

The **Green colour** of Porcelain sample MYT180 came from Atacamite as well as the green colour of sample Polychrome Marbled Ware sample MYT208 from Malachite.

Few pigments were detected in to the glazed ceramics under study from **Chalcis in Euboea**.

The **Turquoise colour** of Glazed Frit Ware sample CH106 was due to Cu in Pb with a high amount of alkalis (Figure 192). The **Green colour** of Champlevé Ware sample CH141 came from Atacamite (Figure 193).

Finally, the Green colour was only detected in the glazed ceramics under study from **the Athenian Agora in Attica**.

The **Green colour** of Polychrome Painted Ware/Maiolica sample AAG29 came from Cu in Pb glaze, as well as the Green colour of Monochrome Glazed Ware sample AAG37 (Figure 194).

Theophrastus at his book ‘De Lapidibus’ mentioned ‘Just as there is a natural and an artificial ruddle, so too there is a natural and a prepared cyanus, such as is made in Egypt. There are three kinds of cyanus, the Egyptian ($\text{CaCuSi}_4\text{O}_{10}$ or $\text{CaO} \cdot \text{CuO} \cdot 4\text{SiO}_2$), the Scythian, and lastly the Cyprian, the Egyptian being best for undiluted pigment-powders (Theophrastus 1965, p.79). Also, Theophrastus at his book ‘De Lapidibus’ mentioned that different recipes with Cu were applied for green colours (Theophrastus 1965, pp. 78-81).

Finally, the **SiO₂** of the glazes detected easily in some cases as at Kütahya MYT179 sample (Figure 195).