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Original scientific paper

MICRO-RAMAN SPECTROSCOPIC STUDIES OF BYZANTINE CULTURAL HERITAGE IN REPUBLIC OF MACEDONIA*

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In the last decade, micro-Raman spectroscopy is recognized as one of the powerful non-destructive analytical techniques for physical-chemical characterization of cultural heritage artifactsartefacts. Activities regarding the use of micro-Raman spectroscopy in characterization of archaeological objects were recently carried out in Republic of Macedonia.

As a pilot project, pigment analysis (1) in the underlayer and overlayer (from the 17th and from the 19th century, respectively) of the wall paintings in *Sveta Bogorodica Church* in Lešok and (2) in the paints (blue, red, orange, green and yellow) used in six icons painted by Dičo Zograf, in three different churches in the Skopje region, was undertaken. The pigments used, as well as their mixtures, were identified using micro-Raman spectroscopy.

In order to achieve some understanding and characterization of the materials of the Byzantine glazed ceramic finds in Republic of Macedonia, as well as to obtain information on their manufacturing technology, micro-Raman spectra of fifteen glazed fragments, all dated from 12th to 15th century, were recorded. Based on their Raman spectra, it was possible to estimate the firing temperature of the analyzed glazes.

Key words: micro-Raman spectroscopy; pigments; Byzantine glazed ceramics; icons and wall paintings

ПРИМЕНА НА МИКРО-РАМАНСКАТА СПЕКРОСКОПИЈА ВО ИСПИТУВАЊЕ НА ВИЗАНТИСКОТО КУЛТУРНО НАСЛЕДСТВО ВО РЕПУБЛИКА МАКЕДОНИЈА

Во последната деценија, микро-раманската спектроскопија е прифатена како моќен недеструктивен аналитичкиі метод за физичко-хемиско карактеризирање на културното наследство. Преземени се активности во врска со воведување микро-раманската спектроскопија како техника за карактеризирање на некои археолошки објекти во Република Македонија.

Во рамките рамките на пилот-проектот е направена анализа на пигментите (1) во долниот и горниот слој (од XVII и XIX век) од ѕидното сликарство на црквата Св. Богородица во Лешок и (2) во боите (сина, црвена, портокалова, зелена и жолта) од шест икони сликани од Дичо Зограф во три цркви во скопскиот регион. Идентификацијата на пигментите и нивните смеси е направена користејќи микро-раманска спектроскопија.

Овој недеструктивен метод е применет и при карактеризирање на византиската глазирана керамика, најдена во Република Македонија, со осврт на технологијата на производство. За таа цел беа снимени рамански спектри на петнаесет примероци глазирана керамика, датирани од XII до XV век. Врз основа на раманските спектри, е утврдена температурата на печење на анализираните глазури.

Клучни зборови: микро-раманска спектроскопија; пигменти; византиска глазирана керамика; икони и ѕидно сликарство

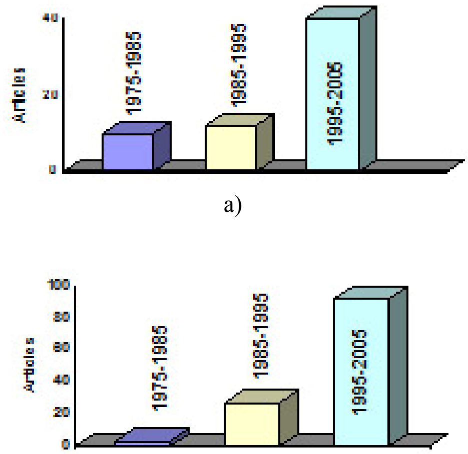
* Dedicated to Academician Bojan Soptrajanov, the leader of the Molecular Spectroscopy Group in Macedonian, on the accession of his 70th birthday.

INTRODUCTION

Situated on the crossroads of the ancient civilizations, Republic of Macedonia is very rich in archaeological sites and artefacts originating from the Neolith up to the medieval times. Although a considerable work is done in conservation of the archaeological sites and objects by the experts involved in cultural heritage preservation and conservation, the physical-chemical characterization of the artefacts in the past was mostly done using traditional, destructive analytical approaches and techniques.

Due to the value and uniqueness of the cultural heritage objects, the emphasis nowdays is on application of non-destructive analytical methods and techniques in artifacts characterization. A large number of different non-destructive methods and micro-techniques for characterization of the materials used have been developed. Among these micro-techniques, the "laser-assisted" Raman spectroscopy has attracted attention as an experimental method suitable for the study of a wide variety of archaeological and art objects, due to the non-destructive approach in characterizing the physical-chemical properties of the materials [1−4]. In the last decade, micro-Raman spectroscopy has proved to be invaluable for analyzing almost every kind of artefact, from gems to different painted materials, fibres (natural and synthetic, dyed or raw), ceramics and glasses. Its main advantages are: non-destructiveness, possibility for analyzing very small samples, high selectivity and sensitivity. , The very few its main disadvantages are is mainly due to the high level of background fluorescence. These attributes positioned micro-Raman spectroscopy as one of the most important analytical and diagnostic tools for investigation of precious objects in art and archaeology. To illustrate this, the growth of the number of publications on Raman spectra of pigments and ceramics over the last three decades are presented on Figs. 1-a and 1-b.

The use of non-destructive methods in investigation, testing, and characterization of museum objects in Republic of Macedonia is in its initial phase. In order to improve the preservation and conservation of cultural heritage in the Republic of Macedonia through non-destructive analysis and testing, activities regarding the use of micro-Raman spectroscopy in characterization of archaeological objects have been undertaken. In the initial stage, we have focused on the following pilot studies:



a)

b)

Fig. 1. Comparative analysis of the number of articles published in the last three decades on (a) Raman spectra of pigments and (b) Raman spectra of ceramics.
Source: Elsevier science – Science Direct (all journals)

The use of non-destructive methods in investigation, testing, and characterization of museum objects in Republic of Macedonia is in its initial phase. In order to improve the preservation and conservation of cultural heritage in the Republic of Macedonia through non-destructive analysis and testing, activities regarding the use of micro-Raman spectroscopy in characterization of archaelogical objects have been undertaken. In the initial stage, we have focused on the following pilot studies:

(1) *Pigment analysis in wall paintings and icons in some churches in Republic of Macedonia*

As part of the micro-Raman spectroscopic study of pigments, in this paper we report a pigment analysis in the underlayer and overlayer of the wall paintings from the 17^{th} and 19^{th} century, respectively, in *Sveta Bogorodica Church* in Lešok (North-Western Macedonia) and a comparative analysis of the pigments used in five paints (blue, red, orange, green and yellow) in six icons, from three different churches in the Skopje region, painted by the well known painter Dičo Zograf.

In general, the identification of pigments by micro-Raman spectroscopy is, at present, well elaborated, and is mainly based on the comparison between the recorded Raman spectra and a database of reference spectra. Several useful reference libraries of natural and synthetic pigments and minerals have been published in the recent years [5−8].

(2) *Analysis of Byzantine glazed ceramics from Republic of Macedonia*

In order to achieve some understanding and characterization of the materials and provenance of the Byzantine glazed ceramic finds in Republic of Macedonia, as well as to achieve technological information on the manufacturing of these objects, fifteen fragments, all dated from 12^{th} to 15^{th} century, found in the vicinity of Prilep (Markovi Kuli and Sv. Atanas) and Skopje (Skopsko Kale and Markovi Kuli − Kruvče) were analyzed.

Glazed caramics are silicate containing materials that differ from each other in the amount of crystalline materials they consist of. Recently, Philippe Colomban *and co-workers et al*. [9−11] developed a method for identifying different "families" of glassy silicates as a function of their composition. The method is based on defining the polymerization index (I_p) of SiO_4 groups [9], and on the cation impurities. The polymerization index is given as a ratio between the integrated area of the Raman bands due to the bending Si−O−Si vibration (A_{500}) and to the stretching Si−O vibration (A_{1000}) in glazed ceramics and glasses ($I_p = A_{500}/A_{1000}$) [10]. On the basis of this polymerization index, Colomban *and coworkerset al.* [9−11] proposed seven "families" of glassy silicates, with the I_p reaching up to 7. Different values of the polymerization index correspond to different firing temperature and can thus provide information on the firing temperature of the glazed ceramics. Namely, a low value of the polymerization index (below 0.8) corresponds to the lowest firing temperature of the glazed ceramics (between 600−800°C) containing a large amount of fluxing PbO. The higher values of the polymerization index (from 0.8 to 7) would correspond to higher firing temperatures, containing larger amount of alkaline or alkaline earth metals [11].

EXPERIMENTAL

Micro-Raman spectrometers

(1) The Raman spectra of the pigments in wall paintings were recorded on the micro-Raman spectrometer FORAM-685-2 with He-Ne laser excitation, focal length $f \times 20$ and resolution 7 cm^{-1}, in the region of 2000−400 cm^{-1}.

(2) The Raman spectra of pigments in icons were recorded on: (a) Raman spectrometer MArtA, a modified portable Raman imaging microscope (PRIM) spectrometer (Spectracode, West Lafayette, Ind., USA) using 785 nm diode laser excitation line and 70 mW power at the sample. The probe head is equipped with an infinity corrected objective lens $f \times 6$. Resolution: 7 cm^{-1}. , and on (b) Raman spectrometer Renishaw 1000 with 785 nm laser line and 5 mW power at the sample, with focal length $f \times 50$. Resolution: 4 cm^{-1}. The spectra were recorded in the 4000−150 cm^{-1} region.

(3) The Raman spectra of the glazed ceramics were recorded with micro-Raman multichannel spectrometer LabRam INFINITY (Jobin-Yvon Horiba) with 532 nm YAG laser line, power of 7 mW and focal length $f \times 50$, in the 4000−100 cm^{-1} region. Resolution: 4 cm^{-1}.

Evaluation of the spectra: Automatic baseline correction was applied to most of the spectra (in order to reduce the fluorescence background). Origin peak-fitting module (Microcal Software) [12] and AutoCAD 2005 were used for determining the integral area of the Raman bands envelopes for the glazed ceramic samples.

Samples: The pigments were analyzed from the small parts of samples fallen during the conservation treatment of the wall paintings or shreds from the icons. The glazed ceramics were analyzed directly from the fragments.

RESULTS AND DISCUSSION

The investigation of pigments by micro-Raman spectroscopy was performed on wall paintings and icons in some of the churches in Republic of Macedonia. For identification of the pigments, we used the available reference library of Raman spectra of pigments [5].

a) In wall paintings

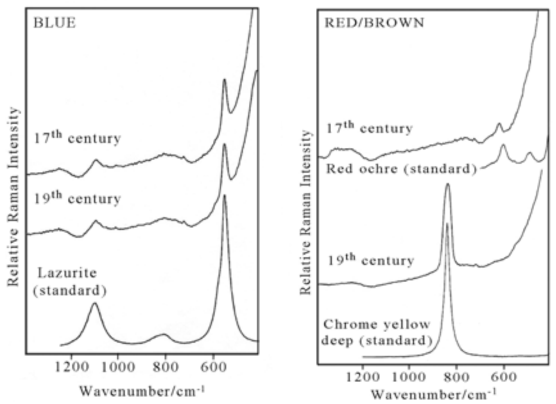
The aim of this study was to identify the pigments used in the under-layer and over-layer of the wall paintings from the 17^{th} and 19^{th} century, in *Sveta Bogorodica Church* in Lešok using micro-Raman spectroscopy [13].

The church was built in the 14^{th} century (in 1326). The first major reconstruction of the church took place in the 17^{th} century (in 1641) . when The the walls of the church were painted by an unknown author(s). In the second and last reconstruction, in the 19^{th} century (in 1879), the western annex was added and the walls were over-painted by the painter (*zograf*) Mihail Gjurčinov [14]. In order to follow the use of different pigments in the masters paints, four pigments (red/brown, blue, ochre / yellow and green) were taken for micro-Raman spectroscopic analysis from layers of the wall paintings dating from the 17th and the wall paintings dating from the 19th century.

Details of the two layers of the wall paintings from the 17th and 19th century are shown on Fig. 2, while the recorded Raman spectra of some of the pairs of pigments are shown on Fig. 3, together with the standard reference spectra [5]. The results of the pigment analysis are summarized in Table 1.

As presented in Table 1, there are differences between the Raman spectra of the pigments used in the 17th compared to the ones from the 19th century. One of the four analyzed pigments, the blue pigment, lazurite, has been used both in the 17th and 19th century wall paintings, while this is not the case for the three other pairs of pigments. Green paint was obtained by mixing lazurite and chrome yellow pigments. Two of the investigated pigments used in the 17th century wall paintings have not been identified in this analysis, most probably due to the limited spectral range of the used FORAM-685-2 micro-Raman spectrometer.

Fig. 2. Details of the two layers of paint from the 17th (middle layer) and from the 19th century (upper and lower layers) from one of the walls in *Sv. Bogorodica Church* in Lešok. (The colour can be seen on the on line Internet issue)



a) b)

Fig. 3. Micro-Raman spectra of the blue (a) and red/brown (b) paints from the 17th and 19th century wall paintings (in *Sv. Bogorodica Church*, Lešok) and the corresponding referent (standard) spectra of the pigments

Table 1

Identified pigments in the two layers of the wall paintings (17th and 19th century) in Sveta Bogorodica Church in Lešok

Pigment color	17th century	19th century
Blue	Lazurite	Lazurite
Red/brown	Red ochre	Chrome yellow deep
Ochre/yellow	No Raman signal	Chrome yellow
Green	No Raman signal	Mixture of lazurite + Chrome chrome yellow

As presented in Table 1, there are differences between the Raman spectra of the pigments used in the 17th compared to the ones from the 19th century. One of the four analyzed pigments, the blue pigment, lazurite, has been used both in the 17th and 19th century wall paintings, while this is not the case for the three other pairs of pigments. Green paint was obtained by mixing lazurite and chrome yellow pigments. Two of the investigated pigments used in the 17th century wall paintings have not been identified in this analysis, most probably due to the limited spectral range of the used FORAM-685-2 micro-Raman spectrometer.

In general, the problem of over layers, in which the wall paintings and/or icons are over painted, is frequently found in the Byzantine art works. The two layers of paint can be clearly seen on the cross section of a fragment of wall painting shown on Fig. 4.

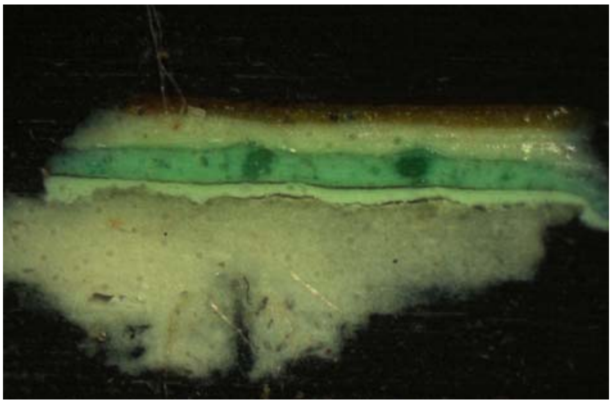


Fig. 4. An example of the cross section of two layers of paint in a wall painting

The introduction of non-destructive methods, such as micro-Raman spectroscopy, enables, in some cases, the evaluation of the under layer pigments, without damaging the upper layer, as already reported in the literature [15]. In order to develop an appropriate approach to the problem of over-layers of paint, referent samples mimicking the "real life" situation in the wall paintings/icons were prepared, according to the old recipes [16]. The recorded Raman spectra were then evaluated and analyzed.

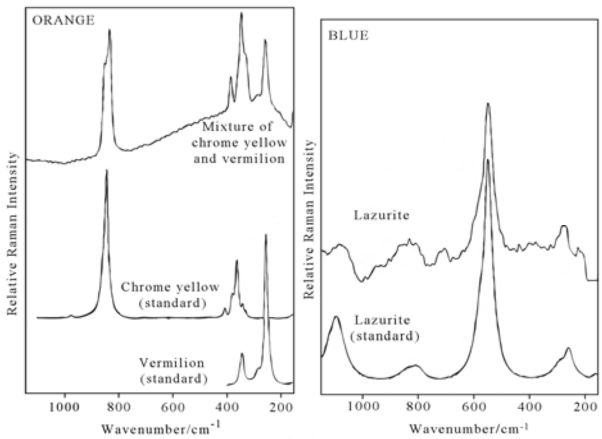
b) *In icons*

As part of the study of the pigments used in icons, six icons from three churches in the Skopje region, painted by the well known Macedonian painter, Dičo Zograf, were analyzed by micro-Raman spectroscopy [17].

Dičo Zograf is one of the most productive painters from the middle of the 19th century. The opus of Dičo Zograf is large and comprises numerous icons and iconostases in different churches in Republic of Macedonia [18, 19]. These icons are known to be rich in color: particularly characteristic are the blue and light blue, as well as red and orange (Fig. 5).

Fig. 5. Icon by Dičo Zograf: *Trite Arhierei* – Church Sv. Nikola, Ljubanci village (Skopje region). The analyzed paints are marked with arrows

Raman spectra of the five paints/pigments (blue, red, orange, green and yellow) in six icons from three churches in the Skopje region: *Sv Gjorgji* and *Sv. Ilija* in the village of *Banjani* and *Sv. Nikola* in the village of *Ljubanci* were analyzed. Shown in Fig. 6 are representative spectra of the two analyzed pigments in the icon *Trite Arhierei* (Fig. 5). For comparison, the referent Raman spectra of the corresponding pigments [5] are also given in Fig. 6. The results of the pigment analysis of six icons are summarized in Table 2.



a) b)

Fig. 6. Micro-Raman spectra of the orange (a) and blue (b) paint from the icon *Trite Arhierei* (Church Sv. Nikola, Ljubanci village)

As seen in Table 2, except in the case of the red pigment (vermilion), the painter often used mixtures of pigments, to obtain different hues of the prime color, which adds richness and vividness to the painted icons. He used traditional, inorganic pigments in his iconography, but also some synthetic pigments, already available in the middle of the 19th century, and often, a mixture of pigments, in order to obtain a desired color of the paint. For instance, for the blue color, in three out of six icons we have analyzed, he used lazurite, in two icons the blue paint was a mixture of massicot (orthorhombic PbO) and ivory black, while in one case, it was synthetic Prussian blue (Table 2). The orange paint was identified as a mixture of vermilion (HgS) and synthetic chrome yellow orange ($PbCrO_4 \cdot PbO$) (Fig. 6-a and Table 2), while the green color was a mixture of lazurite, vermillion and chrome yellow (Table 2).

Table 2

Pigments analysis of the six icons painted by Dičo Zograf

	Sv. Ilija		Sv. Gjorgji		Sv. Nikola	
	Sv. Petar & Sv. Pavle	Sv. Matej & Sv. Luka	Carski dveri	Apostol Petar	Trite arhierei	Bogorodica
RED	Vermillion	Vermillion	Vermillion	Vermillion	Vermillion	Vermillion
BLUE	Massicot + Ivory ivory black	Massicot + Ivory ivory black	Prussian blue	Lazurite	Lazurite	Lazurite
YELLOW	–	–	Chrome yellow orange	–	–	Chrome yellow deep + Carbon carbon black
ORANGE	Vermillion + Chrome chrome yellow deep	–	–	–	Vermillion + Chrome chrome yellow deep	Vermillion + Chrome chrome yellow deep
GREEN	–	Lazurite + Vermillion vermillion + Chrome chrome yellow	–	–	–	Carbon black +?

Glazed ceramics analysis

Raman spectroscopy is a powerful tool for characterizing ceramicss glazes, while other techiques (such as IR and XRF spectroscopy, XRD, SEM) are more useful for characterizing the ceramic body. In this work we have focused our interest on micro-Raman analysis of the ceramis glazes.

Fifteen fragments of Byzantine glazed ceramics, all dated from 12th to 15th century, found in archaeological sites in Prilep and Skopje region were analyzed using non-destructive, micro-Raman spectroscopy [20, 21]. All samples have an engobe (underglaze layer characteristic for Byzantine ceramics) and sgraffito slip decoration. The ceramic glazes are in brown, black, dark green or ochre colour, and some of them have specks (Fig. 7).

Although the glazes are coloured, they gave no significant Raman signature for pigments, possibly, due to the dissolution of the metal oxides in the glass matrix. On the other hand, for the ceramic sample MK8 (Fig. 8-a), the glazes and the engobes of the analyzed samples gave representative Raman spectra, as shown on Fig. 8-b. The three layers of the ceramic sample (the glaze, the engobe and the body), as well as the average thickness of the glaze and the engobe are indicated on the cross section photograph shown on Fig. 8-c. The Raman spectra of the engobe suggest the presence of plagioclase feldspars.

The baseline corrected Raman spectra of some of the recorded glazes, with the characteristic bands due to the stretching Si−O (~1000 cm^{-1}) and symmetric Si−O−Si bending (~500 cm^{-1}) modes, are shown on Fig. 9. The Raman spectra of these glazes show the strongest intensity band at ~1000 cm^{-1}, characterisc for structures with "isolated" and poorly connected tertahedra, and observed in any glassy network containing a large amount of fluxing oxides, such as PbO [10]. The Raman spectra of the analyzed glazes were used to calculate the index of polymerization (I_p) defined as a ratio of the integrated peak area (A_{500}/A_{1000}) related to the symmetric Si−O−Si bending (~500 cm^{-1}) and Si−O stretching (~1000 cm^{-1}) modes [9, 10]. On the basis of the calculated polymerization index and according to the approach developed by Colomban [11], it was possible to estimate the firing temperatures of the analyzed glazes. The determination of the integrated area of the Raman bands envelopes and the corresponding calculated

I_p values are shown on Fig. 10 for two analysed samples: MK8 and MK19. Most of the fragments of glazed ceramics have a polymerization index (I_p) below 0.5, wich corresponds to lead-rich (~ 50 %) silicates processed at low firing temperatures, below 700°C (Fig. 10-a).

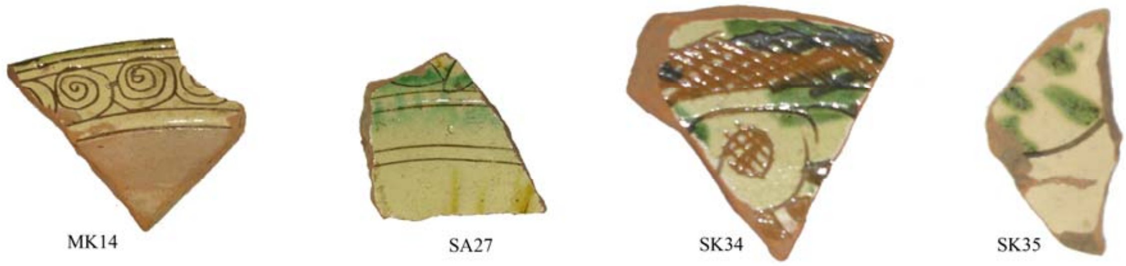
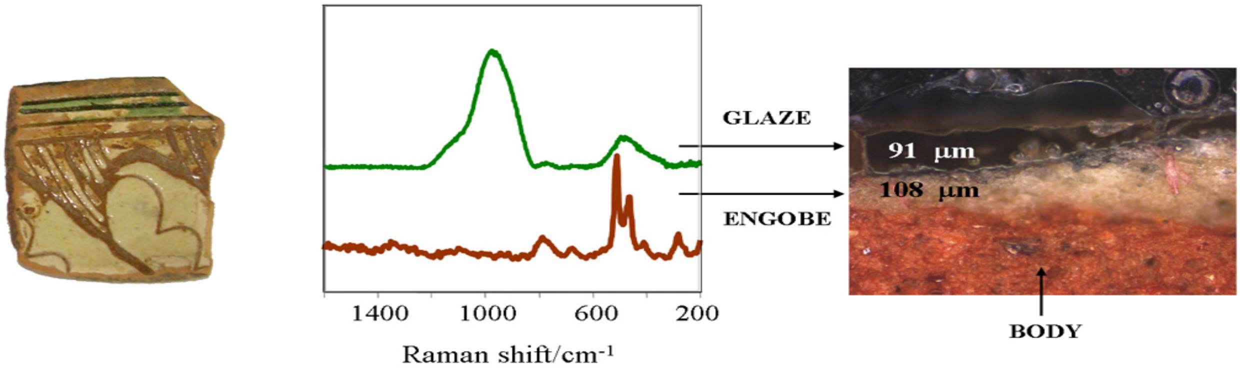


Fig. 7. Representative shreds of the analyzed glazed ceramic from Prilep (MK14 and SA27SA27) and Skopje (SK 34 and SK35).



a) b) c)

Fig. 8. Ceramic sample (MK8) from Markovi Kuli – Prilep (a); its corresponding micro-Raman spectra of the glaze and the engobe (b), and its cross section (c)

The baseline corrected Raman spectra of some of the recorded glazes, with the characteristic bands due to the stretching Si–O (~1000 cm^{-1}) and symmetric Si–O–Si bending (~500 cm^{-1}) modes, are shown on Fig. 9. The Raman spectra of these glazes show the strongest intensity band at ~1000 cm^{-1}, characterisc for structures with "isolated" and poorly connected tertahedra, and observed in any glassy network containing a large amount of fluxing oxides, such as PbO [10]. The Raman spectra of the analyzed glazes were used to calculate the index of polymerization (I_p) defined as a ratio of the integrated peak area (A_{500}/A_{1000}) related to the symmetric Si–O–Si bending (~500 cm^{-1}) and Si–O stretching (~1000 cm^{-1}) modes [9, 10]. On the basis of the calculated polymerization index and according to the approach developed by Colomban [11], it was possible to estimate the firing temperatures of the analyzed glazes. The determination of the integrated area of the Raman bands envelopes and the corresponding calculated I_p values are shown on Fig. 10 for two analysed samples: MK8 and MK19. Most of the fragments of glazed ceramics have a polymerization index (I_p) below 0.5, wich corresponds to lead-rich (~ 50 %) silicates processed at low firing temperatures, below 700°C (Fig. 10.a). However, in two analyzed fragments, the polymerization index (I_p) is between 0.5 and 0.8, which corresponds to lead-based (~ 35 %) silicates processed at medium temperatures (Fig. 10.b), at around 800°C [11]. These two samples also differ in ornamentation, having colored specks on the glaze. These results suggest different manufacturing sources.

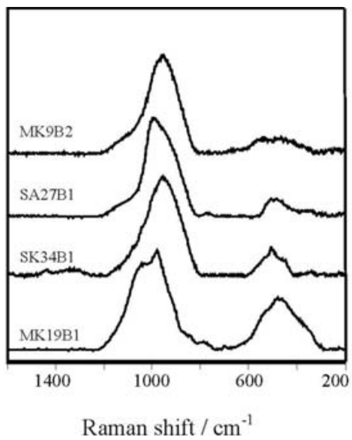
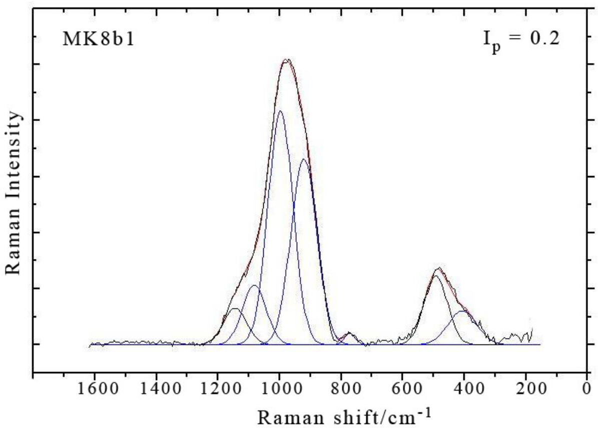


Fig. 9. Four representative micro-Raman spectra of ceramic glazes showing the strongest intensity band at around 1000 cm^{-1}



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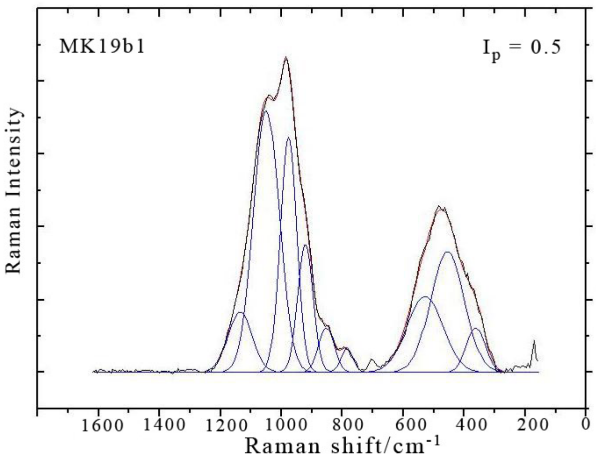

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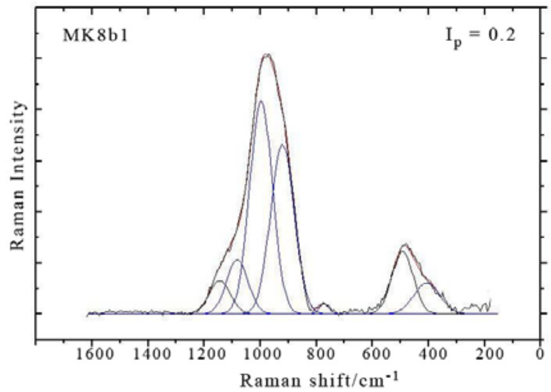

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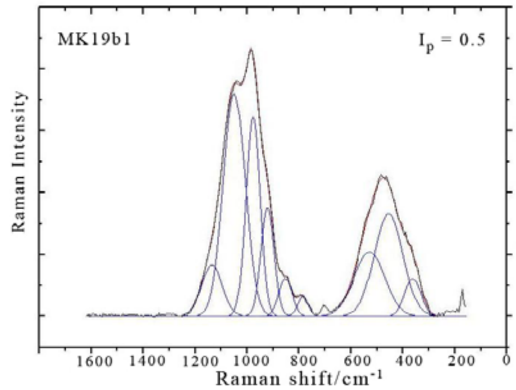

b)

Fig. 10. Determination of the integrated area of the Raman bands envelopes for the spectra of the samples MK8 and MK19 and the corresponding calculated I_p values

However, in two analyzed fragments, the polymerization index (I_p) is between 0.5 and 0.8, which corresponds to lead-based (~35 %) silicates processed at medium temperatures (Fig. 10-b), at around 800 ^{o}C [11]. These two samples also differ in ornamentation, having colored specks on the glaze. These results suggest different manufacturing sources.

CONCLUSIONS

Although the present micro-Raman studies on cultural heritage objects are in its initial stage, they have proved to be applicable for the study of pigments in wall paintings and icons as well as for glazed ceramics.

In regards to the pigment analyses, it was found that: (a) A distinction can be made between the pigments used in the 17th and 19th century for wall paintings. In the 19th century, new, synthetic, pigments were introduced. (b) Dičo Zograf used traditional, inorganic pigments in his iconography, but also synthetic pigments, already available in the middle of the 19th century, and often a mixture of pigments in order to obtain a desired color of the paint.

Systematic Raman spectroscopic study of the pigments used in medieval wall paintings and icons found in the churches in Republic of Macedonia, to the best of our knowledge, has not been performed as of todayyet. Therefore, creating a data base of pigments used in Byzantine wall-painting and icons in Republic of Macedonia will be one of the goals in our future studies.

The Raman spectra of the studied Byzantine ceramic glazes found in Republic of Macedonia suggest that they are lead-rich and fired at low temperature. Two manufacturing temperatures could be established: the majority of the samples have firing temperatures below 700°C, while two samples have firing temperature around 800°C. These results are in good agreement with the similar studies of the Byzantine ceramic finds, dated between 6th and 11th century, most of them excavated in Turkey [11].

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