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APPLICATION OF ARCHEOMETRIC TECHNIQUES IN THE STUDY OF WALL PAINTINGS ON THE EXAMPLE OF FRAGMENTS OF FRESCO PAINTINGS FROM THE CHURCH OF ST. NICHOLAS (CRKVA SVETOG NIKOLE) IN BALJEVAC, SERBIA

ABSTRACT

During the archaeological research of the Church of St. Nicholas, in Baljevac, Serbia, fragments of wall paintings were found in Pit no. 1, located in the nave area. The fragments were determined to be from the second phase of the construction of the church (13th century). Several fragments of different and pure tones were selected to examine the composition of the mortar and pigments, as well as the painting technique. Analytical techniques and the results obtained by their use during the examination of the selected fragments are presented in this paper. With a suitable selection of analytical techniques, all the pigments that had been used were identified, the chemical composition of the mortar determined and a parallel made with the materials analysed so far from wall paintings from similar periods. The importance of modern archeometric tests in modern conservation-restoration practice is highlighted and guidelines for continuing research are presented.

KEYWORDS: EDXRF, FTIR, RAMAN SPECTROSCOPY, WALL PAINTINGS, ARCHAOMETRY, CULTURAL HERITAGE, FRAGMENTS, PIGMENTS, CHURCH OF ST. NICHOLAS IN BALJEVAC

INTRODUCTION

Laboratory and/or *in-situ* examinations, destructive or non-destructive, on samples or whole objects, provide data on the composition of materials, technology and manufacturing techniques,

causes of damage and degree of degradation of a given cultural property. The data obtained by analytical methods serves primarily to identify the materials used, which is why they can also help in the selection of a suitable conservation procedure. Additionally, generated analytical data can reveal

the authenticity of the materials used and everything that a given item has undergone over the course of time.

When it comes to wall paintings, the analytical techniques applied can be non-destructive, micro-destructive or destructive. Non-destructive and micro-destructive analytical techniques are preferable when working with archaeological and museum material, which is why special attention is paid to the selection of the appropriate instrumental technique that can provide answers to the questions asked. It is very important to know the possibilities and limitations of analytical techniques, in order to reach the most accurate results and high-quality interpretation.

The ruins of the medieval Church of St. Nicholas, in Baljevac near Raška, a single-nave basilica with façades, and an apse divided by blind arcades, has Romanesque properties, hence, it was included among the churches of the so-called coastal type very early on (Fig. 1). At first, it was believed that it was built at the end of the 12th century (Дероко 1932: 36–39), however, based on a detailed analysis of its secondary parts, primarily the windows, the dating was revised in more recent scientific literature to the middle of the 13th century (Чанак - Медић, Кандић 1995: 207–203). The fresco paintings in the interior of the church are only partially preserved, mostly in the lower zones, and they were dated into the 14th century on the basis of their style (Станић 1973: 64–67; Станић 1974: 53–74). From the 18th century, the church was in ruins, without a roof and exposed to atmospheric influences, which led to a lot of damage on the painted layer. The existing protective roof structure was built in 1935/36 and is one of the early examples of conservation practices in Serbia.

In 2016, Institute for the Protection of Cultural Heritage, Kraljevo, began archaeological research with the goal of gathering data for the formulation of a reconstruction project (Грујовић Брковић, Алексић Чеврљаковић 2016: 75). The research has shown that the building from the 13th century represents a restored older church with the same plan. During the archaeological campaign in 2017, under the level of the original floor in Pit no. 1 (Fig. 2) in the area under the dome, a fresco painting was discovered, corresponding to the second phase of the building of the church. This closed unit was created in the 14th century, after a

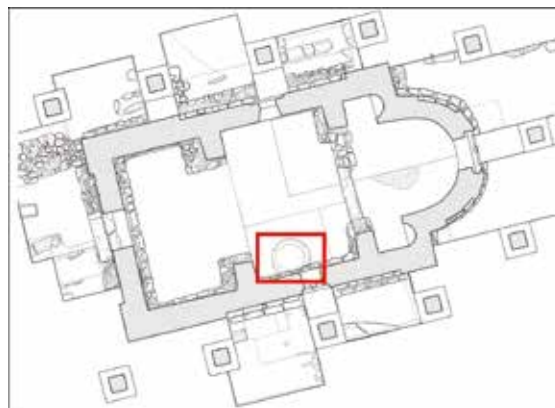


Fig. 1. Position of Pit no. 1 in the nave of the Church of St. Nicholas, in Baljevac (Drawing by A. Matović; documentation of the Institute for the Protection of Cultural Heritage, Kraljevo).

new painting of the walls (Berke 2009, 16; Turinski 1990: 5, 6), when the remains of older frescoes were set aside along with the Romanesque stone decorations, kitchen and table pottery,¹ stonemasons' tools and other movable finds, which clearly indicate a restoration context.²

In this paper, the importance of the previously mentioned archaeometric techniques in the study of the composition of the mortar and pigments of wall painting is shown precisely on the example of fragments found in the nave area of the Church of St. Nicholas, in Baljevac, which are kept at the Institute for Cultural Heritage Preservation, Kraljevo, today. The knowledge on the use of pigments in painting throughout history was very important for the drawing of relevant conclusions within this research, showing the necessity of a multidisciplinary approach to cultural heritage research.

PIGMENTS USED IN THE MIDDLE AGES

Information on paints from the Greek and the Roman period can be found in manuscripts by Theophrastus, Vitruvius and Pliny. Theophrastus (4th century BC) wrote the oldest treaty, *De lapidibus*, on rocks. Vitruvius (*Marcus Vitruvius Pollio*, 1st century BC), in his work *De architectura libri*

1 Certain bowl and pot fragments contain traces of pigments and were most probably used as paint palettes.

2 Unpublished archaeological research of V. Milutinović,

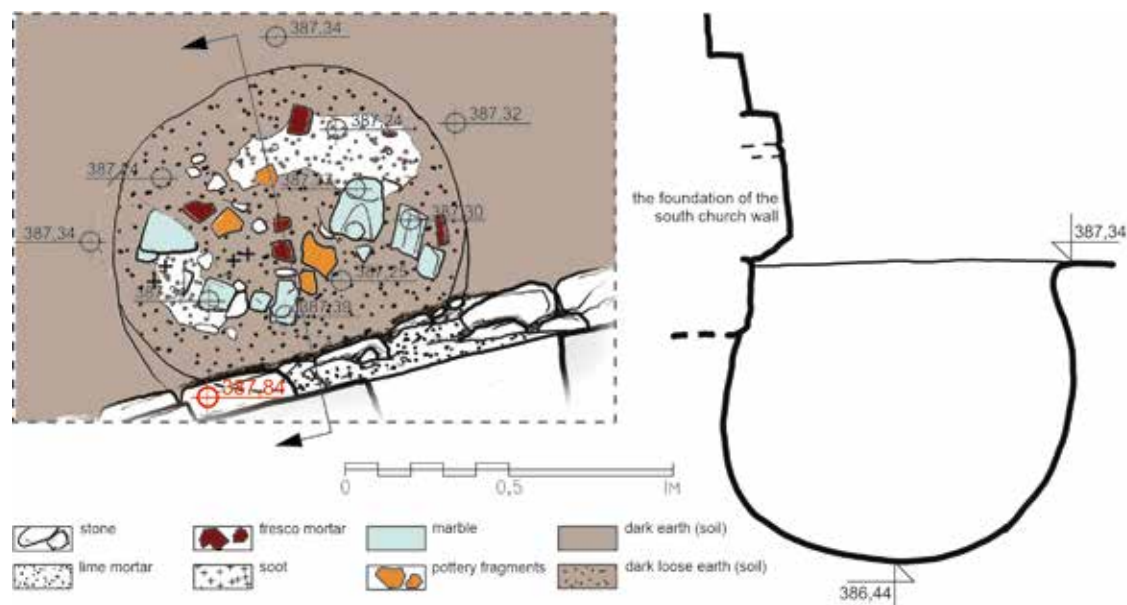


Fig. 2 Base of Pit no. 1 at the infill level, with a cross-section after it was emptied (Drawing by A. Matović; documentation of the Institute for the Protection of Cultural Heritage, Kraljevo).

decem, dealt with painting technologies and types and groups of paints, aside from architecture. Pliny the Elder (*Gaius Plinius Secundus Maior*, 1st century BC), in his book *Naturalis Historiae*, wrote about painting and colours, among other things. Those same colours continued to be used by painters from the medieval period as well, with the difference that Egyptian blue, one of the oldest synthetic pigments, ceased to be in use after the Roman period (Turinski 1990: 34; Mazzocchin et al. 2003: 129; Riederer 1997: 23–45; Rogić et al. 2012: 285–287). When it comes to blue, lapis lazuli was the shade that was used the most in the Middle Ages.

Data on pigments used in the Middle Ages come from a manuscript on painting and painting techniques, described by Heraclius in his three books *De Coloribus et Artibus Romanorum*. There, he described how different colours are obtained from plants and minerals. In this paper, the focus will be on the inorganic pigments that were used most often in medieval wall paintings. In his third book, Heraclius describes the preparation of the white tempera *Alumen*, which should be mixed with water and resin on marble, then dried and reduced to powder, and then mixed with egg whites. He also writes about the preparation of lead white *Cerus* and red lead *rubeum minium*. The lead white paint was prepared by placing lead plates in a vessel, pouring very strong vinegar into

it, then closing the vessel and putting it in a warm place for a month. Once the vessel was opened, everything would be scraped off the lead plates and placed in a new vessel, which was to be heated over a fire, and the contents would be stirred until they became as white as snow. If the paint was kept over the fire for a longer time and stirred, it would become red *minium*. If the *minium* was left on the fire for a longer time, without stirring, it would revert to lead white again. For the preparation of tempera from green earth, *Malvam* would be mixed with vinegar or “good wine”, green earth added to that mix, which would result in tempera, which would be used for wall paintings. To make green paint from copper or brass: copper plates were placed in a vessel with white wine vinegar and left there for 1–3 months, and after this period the pigment would be obtained (M. Medić 1999: 162, 197–201).³

The *List of various arts* by the German monk Theophilus Presbyter (*Schedula diversarum artium*) is an extensive manual on painting techniques from the early 12th century. He wrote about the use of lead white, red lead, cinnabar, ochre, arsenic, green earth, azurite, lampblack, vine black, etc. He described the process of making cinnabar

³ There is no data on Heraclius’ origins, but it is believed that he could have been Greek, or perhaps Italian from Lombardy, and that his books were written before the manuscript of Theophilus Presbyter, Heraclius XXXIX.

with sulphur and mercury over fire. He also gave a recipe for the preparation of “green salt” from copper plates, salt, oil, honey, and vinegar (hot urine was also used instead of vinegar). To obtain Spanish green, he used small copper plates and vinegar, and noted that scales should be used to measure the ingredients (M. Medić 1999, 247–295).

Some of the most commonly used pigments in the 12th century, which we assume could also have been used on fragments and samples of wall paintings from the Church of St. Nicholas near Baljevac, are calcium carbonate (chalk), ochres, red iron oxides – red earth, cinnabar, red lead, green earth – *Terre Verte* and black pigments:

Calcium carbonate (chalk). White pigments can be different forms of calcium carbonate, they can come from limestone, chalk, marble, mollusc shells or bird eggs (Siddall 2006: 28). The three natural types of calcium carbonate are: aragonite, calcite and vaterite. Natural chalk, calcium carbonate, is a natural inorganic pigment, used from prehistoric times to the present day. Chalk is the name of calcium carbonate from Crete, which has become the common term (Ling 1991: 209).

Ochres. Yellow ochre is a natural mineral consisting of silicon and clay, coloured by the iron mineral goethite, and may contain traces of gypsum or manganese. It is found all over the world. Tones range from cream and yellow to brown and greenish. A higher amount of iron and manganese gives ochre a dull tone. It gains a reddish hue from heating (Turinski 1990: 22). Ochres have been identified in cave paintings (Altamira, Lascaux), as well as in paintings from Egypt, Greece and Rome. Ancient ochre was first used by Polygnotus and Mykon (Плиније старији XXXIII, IVI. 158, translation taken from: Медић 1999: 143).

Red iron oxides – red earths. Red earth is a natural inorganic pigment. Red earths have been used in all parts of the world from prehistoric times to the present day. These pigments contain a large amount of iron oxide. They are most often light red (hematite, rust), but they can range from orange to yellow (lepidocrocite, also known as esmeraldite or hydrohematite) and from dark brown to black (maghemite). They appear under the names: English red, Pompeian red, *terra di pozzuoli*, *caput mortuum*, Spanish red, Neapolitan red, Persian red, Indian red, Venetian red and others (Kajrez 2011, 57). Red earths are extremely

lightfast and stable in all techniques (Andrejević 1983, 63).

Cinnabar. Cinnabar is a natural inorganic pigment, obtained from the mineral cinnabarite (mercury sulphide). This ore is dried, ground, washed and heated, and used as a pigment after being dried again. It is orange-red, with excellent covering power and good performance. The oldest example of a wall painting on which cinnabar was used comes from the Neolithic village of Çatalhöyük (7000–8000 BC). There is no data on cinnabar being used in Egyptian or Mesopotamian painting. It was mostly used in ancient Greece and Rome (Turinski 1990: 25). Cinnabar deposits can be found throughout Europe, Asia, Persia, the Balkans, Italy, and in Serbia, in the vicinity of Avala and Prijepolje (Бабич 2003, 221–222). Artificial cinnabar was created in the 8th century (vermilion). There is no chemical difference between natural and artificial cinnabar. The only visual difference is that the natural pigment has coarser grains and a cooler tone than the artificial one. Two names are used: vermilion and cinnabar. Vermilion is the standard name in England and America, referring to the mercury sulphide pigment. Cinnabarite is a name derived from mineralogists and crystallographers and refers to the crystalline form of mercury sulphide (Gettens, Feller, Chase 1972: 45).

Red lead. Red lead, or *minium*, is a red synthetic pigment with a fine texture and good coverage. It was found in silver mines, and was highly valued. According to Theophrastus, *minium* was discovered by the Athenian Callias, who was heating red earth from silver mines, trying to obtain gold (unsuccessfully), and *minium* was, thus, created. It was imported from Spain, raw. In Rome, the ore was prepared, and the state would determine the selling price (Ling 1991: 209–209; Плиније старији 2011, XXXIII, chapter 11, 121). A red pigment called *Usta* was obtained by accident during a fire in Piraeus, after a cerusite vessel was burnt (Плиније старији 2011: XXXV, chapter 6, 114; Плиније старији 2011, XXXV, хх. 38; translation taken from: Медић 1999: 147). Another type of *minium* used to be obtained from a lead-coloured stone that was found near certain metal veins in silver and lead mines. This stone would turn red after being calcified, and it was also used as an imitation of *minium*. Surfaces painted with *min-*

ium, as with those painted with cinnabar, had to be protected with Punic wax (Плиније старији 2011, XXXIII, chapter 8, 120–122).

Green earth – Terre Verte. It belongs to pigments of natural inorganic origin. These are clays with a large amount of silicates and the minerals glauconite and celadonite, hydrosilicate of potash, aluminium, iron and magnesium. The colour varies from cool bluish-green to warm yellow and olive hues. Green earth was used for painting in Egypt, Greece and Rome, and also in later periods. Deposits of green earth have been found in today's Czech Republic, Italy, France, Baltic countries, Cyprus, Poland, Hungary, England, Germany, etc (Aliatis et al. 2009: 532).

Black pigments. Black from grapevines – vine black, has a composition of almost pure carbon with admixtures of impurities. It is obtained by charring cane stalks and other plant residues (dehydrated stalks, fruit stones, pomace, etc.). Polygnotus and Mykon made black ink from grape skins in Athens and called it grape pomace ink (Плиније старији XXXV, xxv. 41, translation taken from: Медић 1999, 147). This kind of black is lightfast, compatible with all binders and has a good covering power (Andrejević 1983, 82; Turinski 1990, 38). Charcoal, soot black, has been used as a pigment from the earliest times to the present day. It is obtained by heating wood with limited air contact. Charcoal is a common name for all black pigments, which are traditionally produced by charring organic matter, such as wood.

Charcoal can also include lampblack, obtained by collecting soot from oil lamps, being a product of burning oil, candles or resin. The composition of it is pure carbon, with minimal oil admixtures. Such blacks are obtained by burning natural gas, resin or resinous wood, oil, fat, stone and brown coal (Andrejević 1983, 82). Vitruvius wrote about the black colour obtained from wine lees, prepared by drying wine lees, boiling them and mixing with glue. In this manner, an excellent colour for painting walls was obtained, as well as Indian ink (Vitruvius, book VII, X, translated by M. Lopac 1951, 161). Painters came to Serbia from abroad by invitation, but there were also painting workshops of local masters throughout the Middle Ages. Foreigners had a decisive role in the turning points in Serbia, when they brought the latest artistic concepts and high standards from developed milieux. Mostly, major painters from Constantinople or Thessaloniki worked in Serbia.

INSTRUMENTAL ANALYTICAL TECHNIQUES APPLIED DURING RESEARCH

Optical microscopy (observation of the wall paintings with a USB microscope). With the use of a USB microscope (Fig. 3), we can examine and document various pieces of the surface and save information regarding the properties of the surface of a wall painting. It is a very simple and practical observation method.



Fig. 3. Examination of the surface of the painted layers of fragments with a USB microscope (Photo by K. Ponjavić).

A digital USB microscope provides additional information that cannot be detected visually. With the option of manual focus adjustment, it records data at a magnification of between 50 and 500 times (Fig. 4). When connected to a computer, it is possible to take photos or make video recordings. Optical microscopy is very useful for studying the condition and physical structure, texture, various damage, interventions that occurred at a later point, granulation of pigments or aggregates,

advantages of this instrumental technique have enabled its development over the years, making it an indispensable step in any modern archeometric study (Gajić-Kvaščev et al. 2012, 1025–1033; Rogić et al. 2012: 268–290; Rogić 2014; Rogić 2017: 71–79). Some of the advantages that should be highlighted are: it is non-destructive, non-invasive, multi-elemental (information is obtained on almost the entire elemental composition of the examined material with just one analysis),



Fig. 4. Appearance of the painted layers of fragments with a magnification of ca 50x (Photo by K. Ponjavić).

deposits and the presence of craquelures. Optical microscopy is also used on samples prepared by a special procedure that allows for an analysis of the stratigraphy of the layers on a cross-section. The stratigraphy or cross-section of a sample can yield very interesting results in the form of underpainting and overpainting, as well as the thickness of colour layers. Additionally, mortar layers and their difference in thickness, as well as aggregate grain size can be clearly observed, which can be especially enhanced by polishing the sample. There are several types of microscopes used for such examinations that are owned by laboratories throughout Serbia. The choice of microscope depends primarily on the type of information one wishes to obtain from the examination, as well as the ability to sample and prepare the material in a suitable manner for the examination of cross-sections (either by microscopy at lower magnifications or even by using scanning electron microscopy with energy-dispersive spectroscopy SEM-EDS, which provides information on the elemental chemical composition, and is suitable for the analysis of both mortar and pigments) (Rogić 2017: 71–79).

Energy-dispersive X-ray spectroscopy (EDXRF spectroscopy). One of the most commonly used instrumental techniques for the analysis of materials from which works of art were made is energy-dispersive X-ray spectrometry. The many

there are devices with which the analysis can be performed *in situ*, handling of the equipment is simple, results of the analysis are obtained in a very short time and in the same place where the test was performed (no additional processing of the results is required, nor the use of databases of comparative spectra to establish the elemental composition, which is extremely important if it is necessary to repeat the measurement or choose a different measuring place, since that decision can be made very quickly), and it is extremely available and reasonably priced. The disadvantages of this instrumental technique are not easy to overcome, but they are not too great a hindrance for its widespread use in the examination of almost all inorganic materials from which cultural heritage objects are made. The main disadvantage of this method is the impossibility of detecting organic materials (since the detection range is usually from energies corresponding to the detection of silicon – Si), as well as chemical compounds in which the detected chemical element is included (because chemical bonds between molecules cannot be detected with this method). The method is sensitive to the sample matrix, which significantly complicates the quantitative analysis.

EDXRF spectrometry for a non-destructive characterisation of pigments on fragments of wall paintings was performed with the use of

XRF spectrometers with a millimetre-sized beam, which was developed in the Department of Chemical Dynamics at the Vinča Institute in Belgrade and is specifically intended for the analysis of cultural heritage objects. The EDXRF spectrometer consists of an air-cooled X-ray tube (Oxford Instruments, Rh-anode, max 50 kV, 1 mA) with a pinhole collimator and a Si-PIN characteristic X-ray detector (6 mm²/500 mm, Be window, 12.5 mm thick), connected to a DSP (X123, Amptek Inc.) for spectrum acquisition. Two laser pointers were used for the correct positioning of the analysed sample at the point of intersection of the incident beam and the axis of the detector (Fig. 5). The experimental conditions were as follows: 40 kV – no filter, 800 µA and measurement time 100 s. These parameters were kept constant during all measurements.



Fig. 5. Detail of an EDXRF spectrometric examination of the dark red pigment on a fragment of a wall painting (Photo by M. Gajić Kvašćev).

Fourier transform infrared spectroscopy (FTIR). Infrared (IR) spectroscopy is a frequently used instrumental technique with a developed methodology for examining materials of cultural heritage objects. In a similar way to XRF spectrometry, an initial excitation induces a physical effect in the examined material and the consequences of such an event are monitored. Fourier transform infrared spectroscopy, FTIR, is most commonly used for a qualitative analysis of a wide range of organic and inorganic samples, and is also suitable for archaeological and museum objects because it requires a very small amount of the sample, and there are also instrumental solutions that make this analysis completely non-destructive for the

tested material. Three areas of electromagnetic radiation can be used for material excitation: near infrared, 13000–4000 cm⁻¹, mid infrared, 4000–200 cm⁻¹, which is most often used for testing materials of cultural heritage objects, and far infrared, 20⁰–10 cm⁻¹. By detecting the vibrational changes of the atoms around the balanced position in the molecule, one can talk about the crystalline or non-crystalline mineral properties of the examined material. This technique is multi-informative, and can also be used in the field for *in situ* analyses. The result of such an analysis is an extremely complex spectrum that requires multiple levels of processing and comparison with a spectrum database in order to determine the composition and characteristics of the material, based on the position and shape of certain spectral areas.

Raman spectroscopy. Raman spectroscopy is another instrumental technique that can be implemented in non-destructive modes of operation. As with FTIR analysis, Raman spectroscopy enables analyses of both inorganic and organic materials (identification of pigments, bearers and binders, precious stones, etc.) (Grujić-Brojčin et al. 2013, 111–117; Paternoster et al. 2005, 21–28). The basic principle of Raman spectroscopy is very similar to infrared and these two techniques are considered complementary in terms of the result obtained by these analyses. In Raman spectroscopy, the excitation is achieved by a laser beam, with the inelastic scattering on molecules of the examined material allowing a determination of their structure. Some of the advantages of Raman spectrometry are the fact that it is non-destructive, non-contact, it can be performed in air and without sample preparation, although there are versions of instruments for which analyses are performed in a non-invasive way and *in situ*. A simple analytical procedure, short analysis time, very small areas that can be analysed (e.g., the size of a pigment grain) are some of the characteristics of this method. The resulting spectrum is analysed through comparison with reference spectra from spectrum databases. A special database of reference spectra has been developed for the application of Raman spectroscopy for analyses of cultural heritage objects. The application of this technique has yielded significant results in the characterisation and identification of pigments, results that have led to a better understanding of

the nature of colour degradation, also in the study of material stratigraphy, the study of the state of conservation of the substrate or, for example, the characterisation of new restoration products.

RESULTS OF THE EXAMINATIONS OF FRAGMENTS

Seven fragments of wall paintings were selected for the examination using the EDXRF spectrometric non-destructive technique for pigment analysis (Fig. 6). Figure 7 shows that iron and calcium were detected in the sample as main elements and

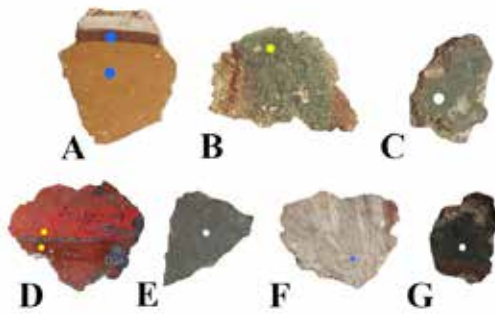


Fig. 6. Non-destructive examinations of pigments on fragments were performed in places marked by dots on the picture (Photo by K. Ponjavić).

potassium, titanium and manganese as trace elements. This EDXRF spectrum is characteristic of earth pigments, which suggests, in this case, that red earth was used as a painting pigment. It can be seen in Figure 8 that the same composition of chemical elements is present in the point recorded on the ochre colour (iron and calcium in addition to potassium, titanium and manganese, which are present in traces). This elemental composition suggests the use of yellow ochre, another pigment from the range of earth pigments. By comparing these two spectra (Fig. 9), we see that the calcium intensity is slightly higher in the EDXRF spectrum recorded on ochre, while the height of the iron peak remains constant. This result suggests that there may be a difference in the thickness of the ochre layers and the dark red painted layer. A spectrum was recorded on sample B (Fig. 10), in which chemical elements were identified, indicating that an earth pigment, green earth, was used (Fe, Ca as main elements, and K, Sr, Ti and Mn as trace elements). Similar to fragment B, the elemental composition of the pigments analysed on fragments C and G indicates the use of an earth pigment, green earth (Fig. 11). The difference in the height of peaks of the main chemical elements, iron and calcium, and the visual evaluation of the

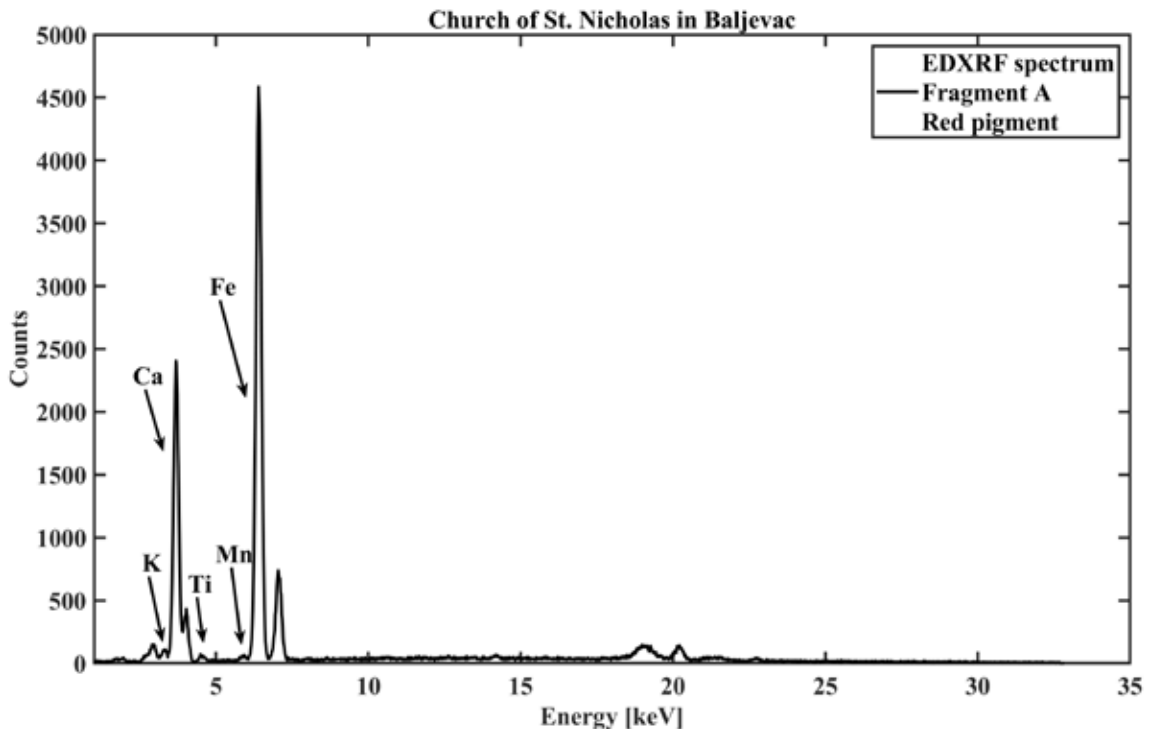


Fig. 7. EDXRF spectre of fragment A, red pigment.

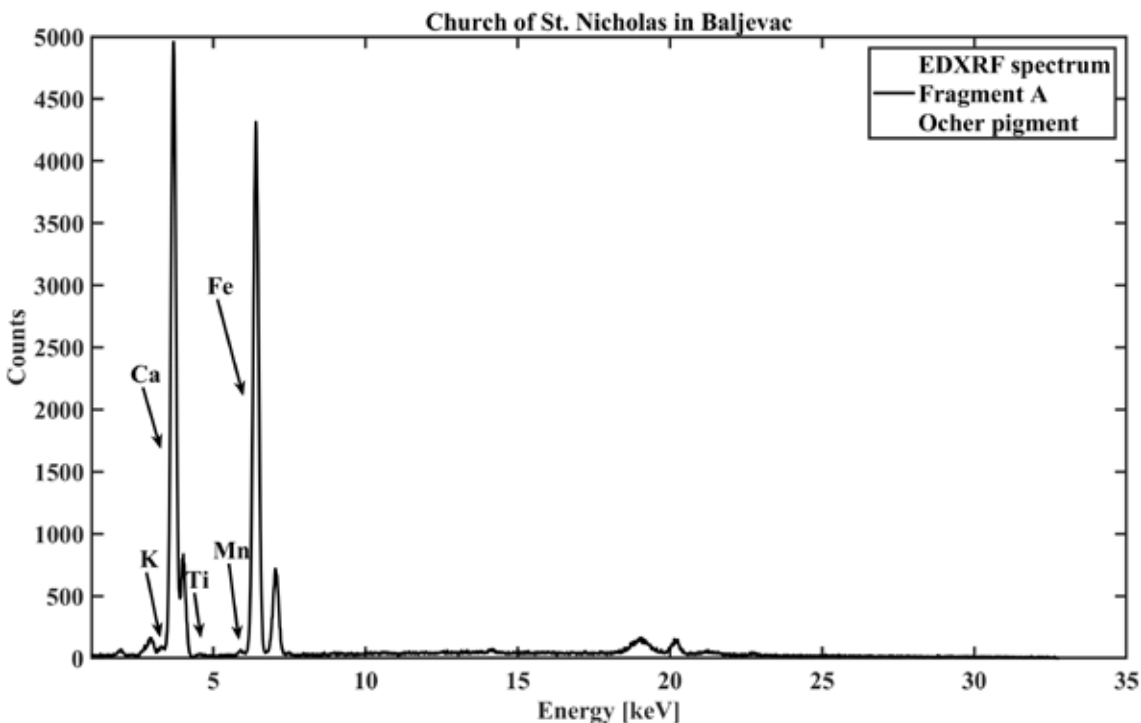


Fig. 8. EDXRF spectre of fragment A, ochre pigment.

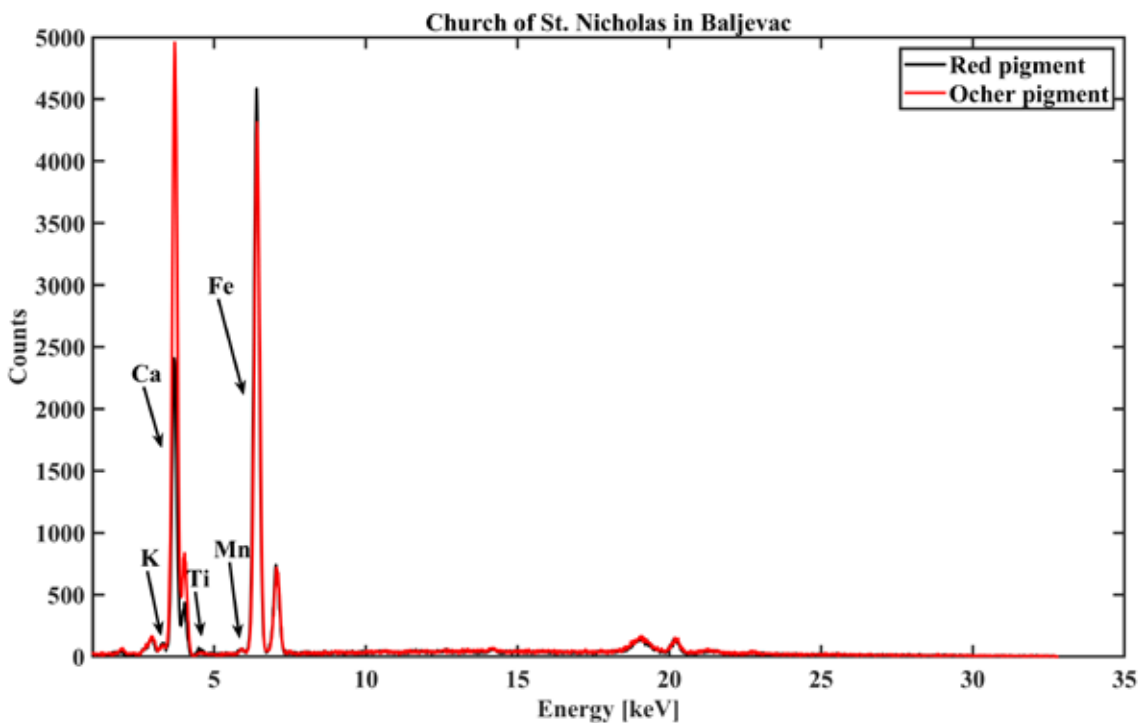


Fig. 9. Comparative EDXRF spectra of fragment A, dark red and ochre pigment.

shade of the analysed spot indicate a mixing of the green pigment with, most likely, a darker pigment that does not change the EDXRF spectrum (black pigment). The heights of calcium peaks in-

dicate different thicknesses of painted layers on these fragments. The EDXRF spectrum recorded on fragment F can serve as a reference spectrum for mortar (Fig. 12). Considering the height of the

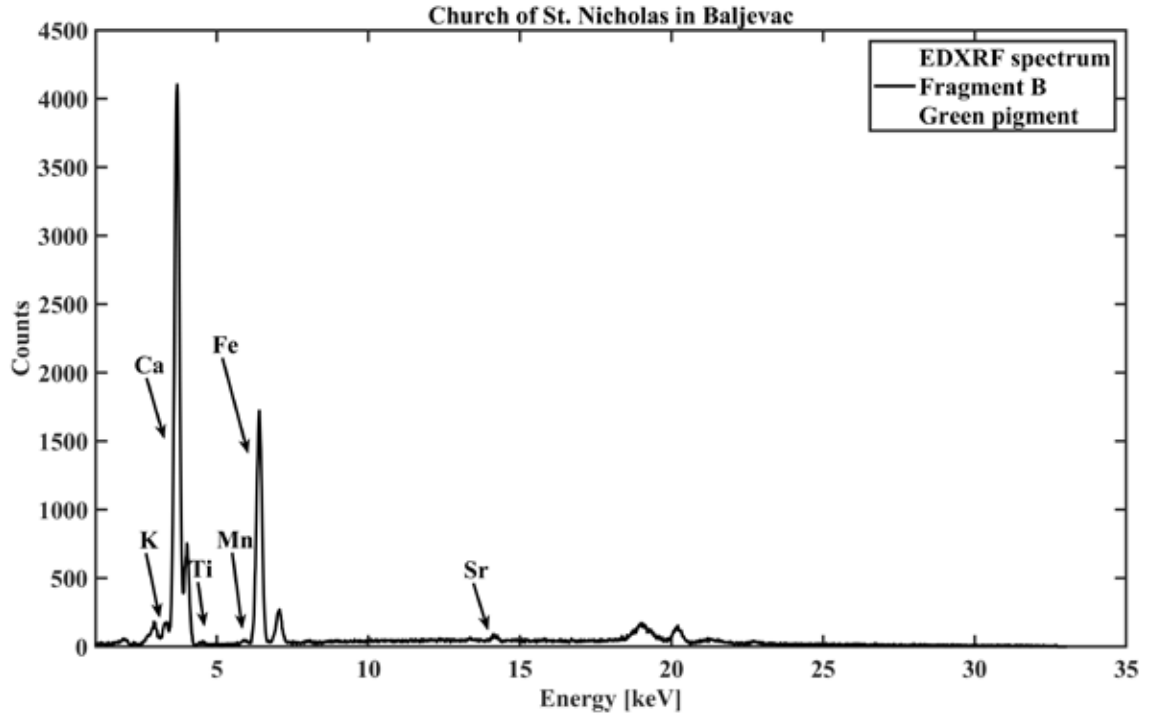


Fig. 10. EDXRF spectre of fragment B, green pigment.

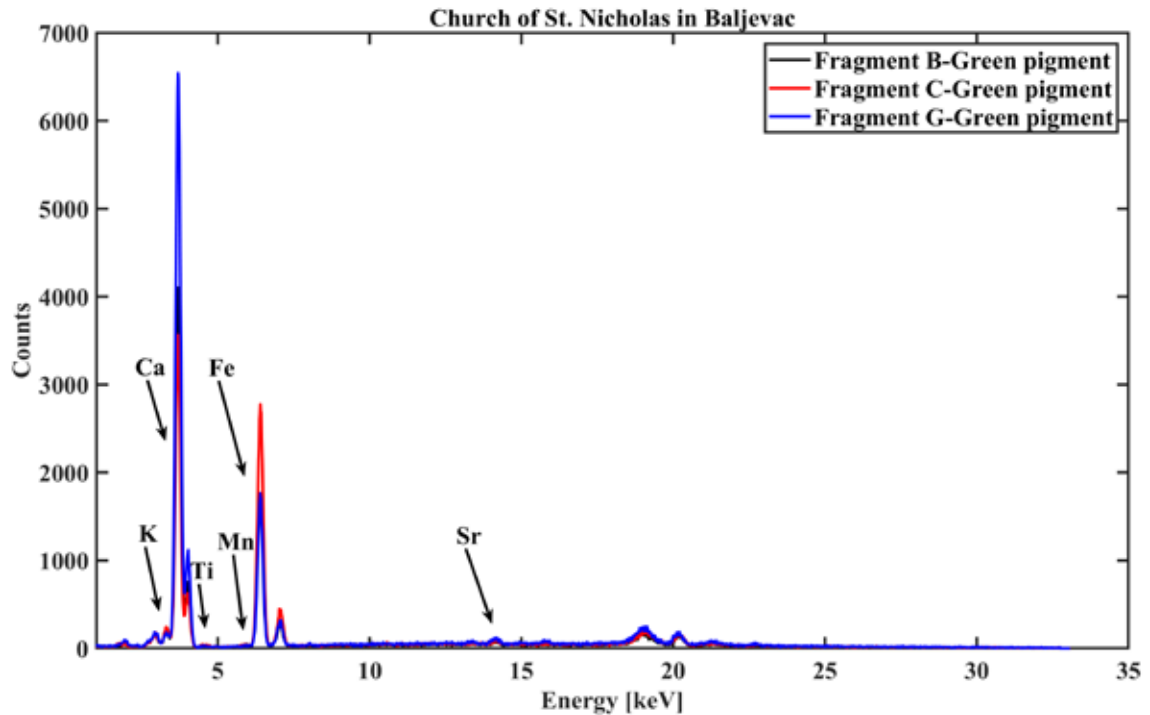


Fig. 11. Comparative EDXRF spectra of fragments B, C and G, green pigment.

iron peak, this chemical element can be considered a “companion” of the materials that make up the mortar. The height of the peak at an energy level of 2.3 keV indicates the use of calcium car-

bonate, chalk. The EDXRF spectrum recorded on the red part of fragment D, which is lighter in tone, indicates that cinnabar was used. Aside from the characteristic elements of mercury and sulphur, of

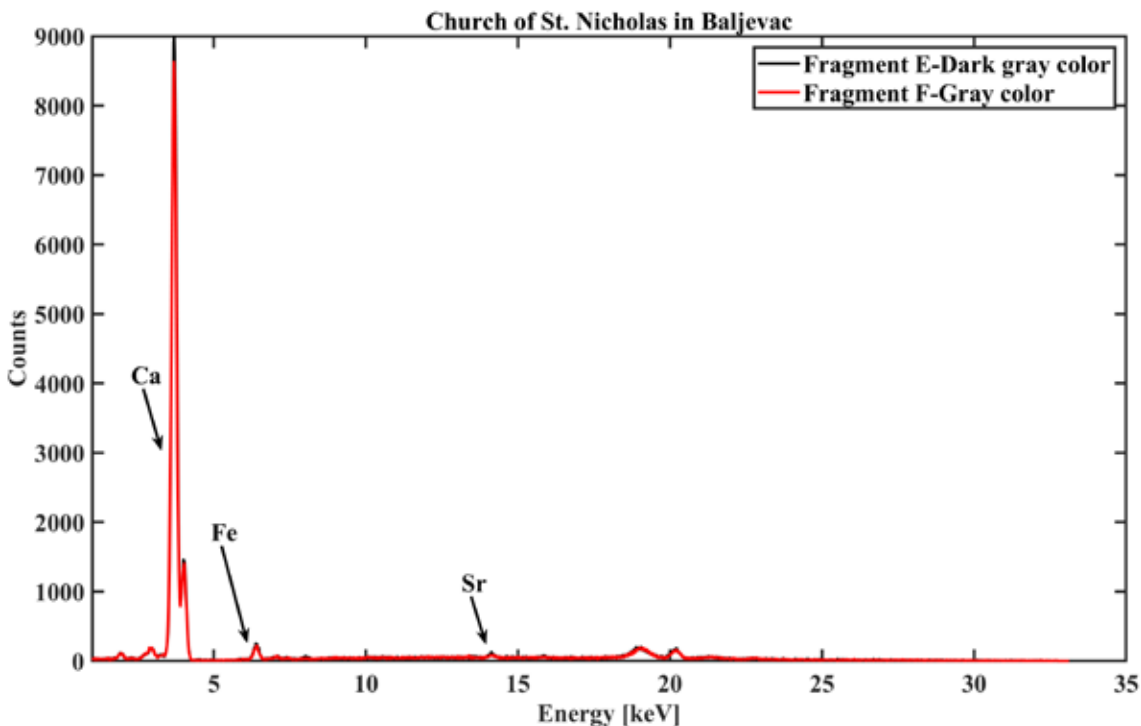


Fig. 12. Comparative EDXRF spectres of fragments E and F, grey.

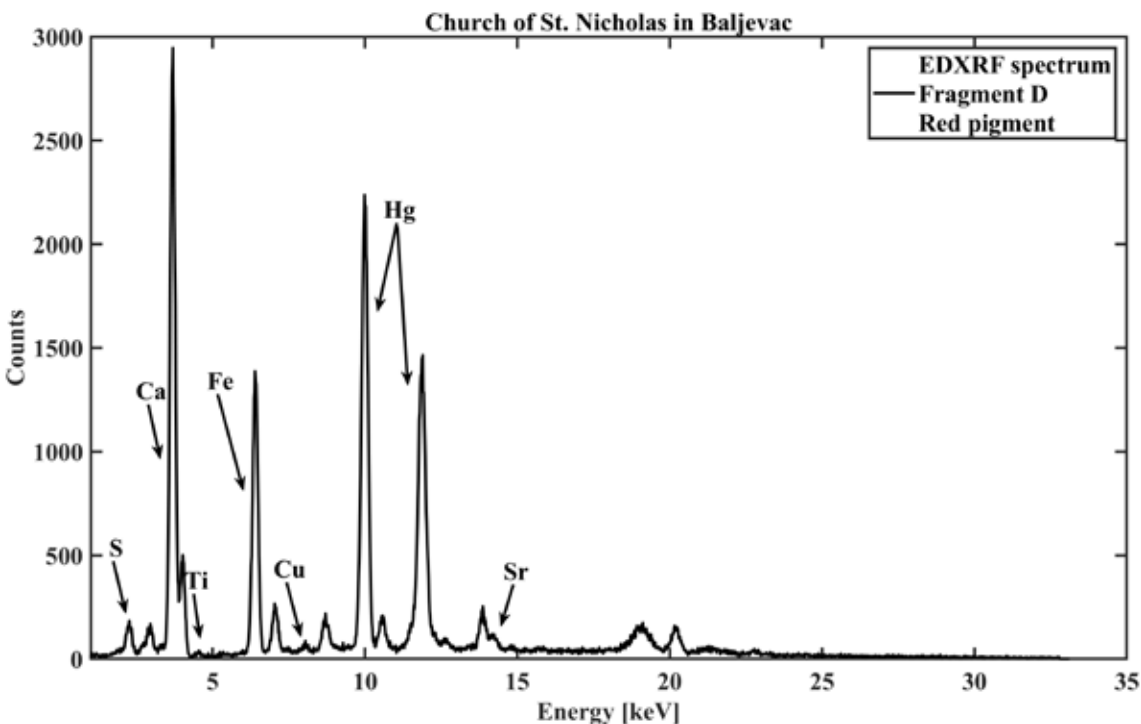


Fig. 13. EDXRF spectre of fragment D, red pigment.

which the cinnabar pigment consists, calcium was also detected as a main element, as well as titanium, copper (which can be a companion of cinnabar from cinnabarite ore) and strontium (Fig. 13).

The darker red tone on fragment D consists of iron and lead as the main elements, which can help determine which red pigment was used (Fig. 14). It can be deduced that two pigments were used,

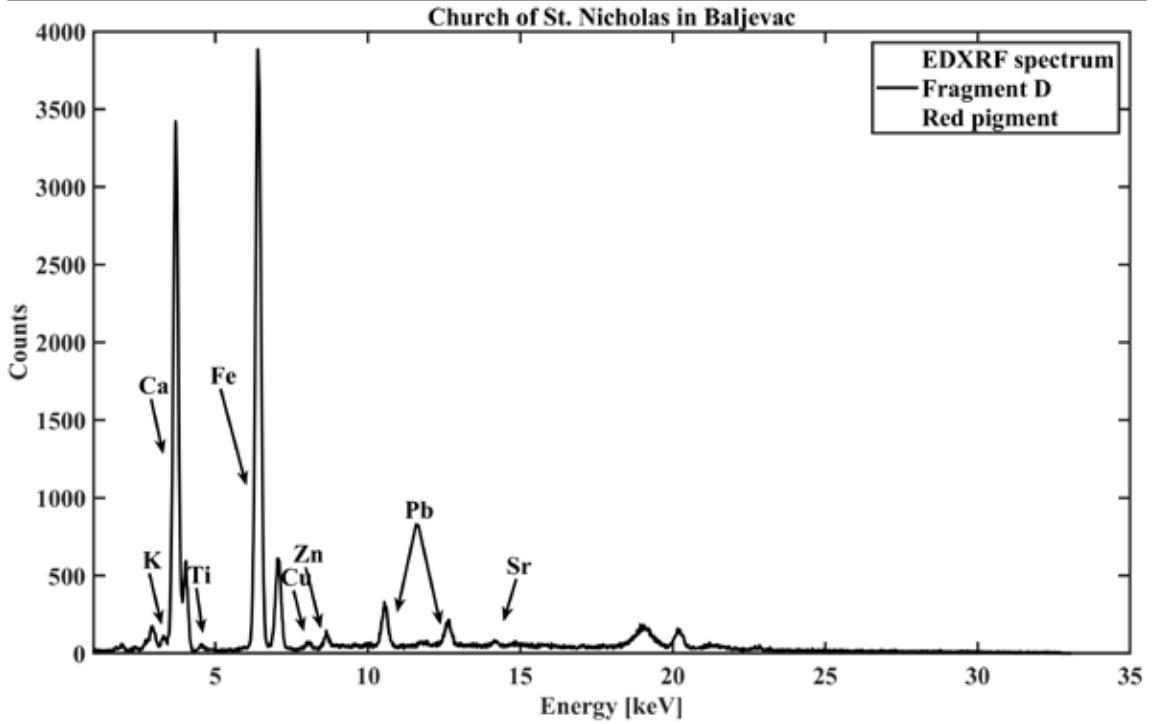


Fig. 14. EDXRF spectre of fragment D, red pigment.



Fig. 15. Sample 1, mortar with no traces of colour. Cross-section of the sample with a magnification of ca 180x, without a painted layer on the surface (Photo by T. Tripković).

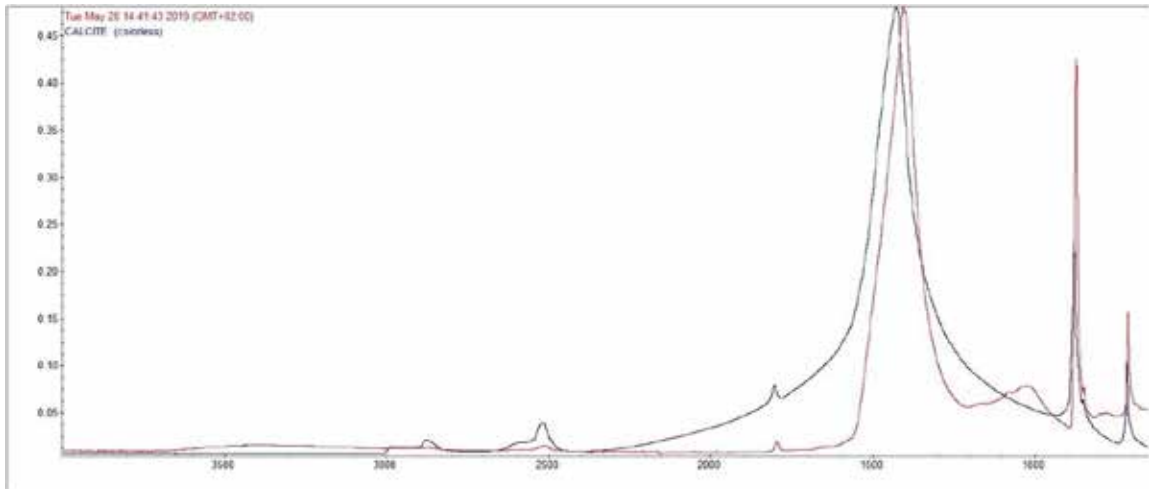


Fig. 16. Sample 1, FTIR mortar spectre shown in parallel with the calcite spectre.



Fig. 17. Sample 2, red painted layer. Cross-section of the sample with a magnification of ca 350x (Photo by T. Tripković).

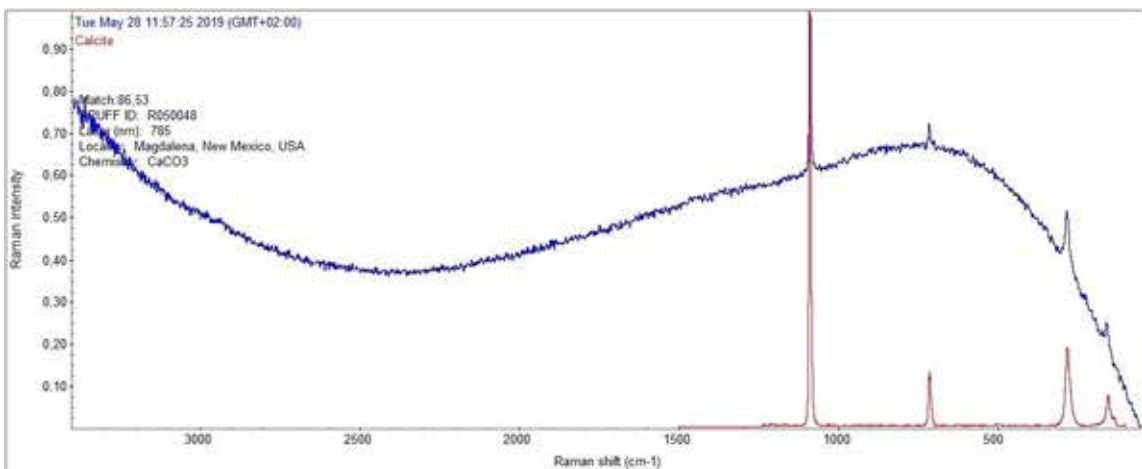


Fig. 18. Raman spectre of the white layer from sample 2 shown in parallel with the calcite spectre.

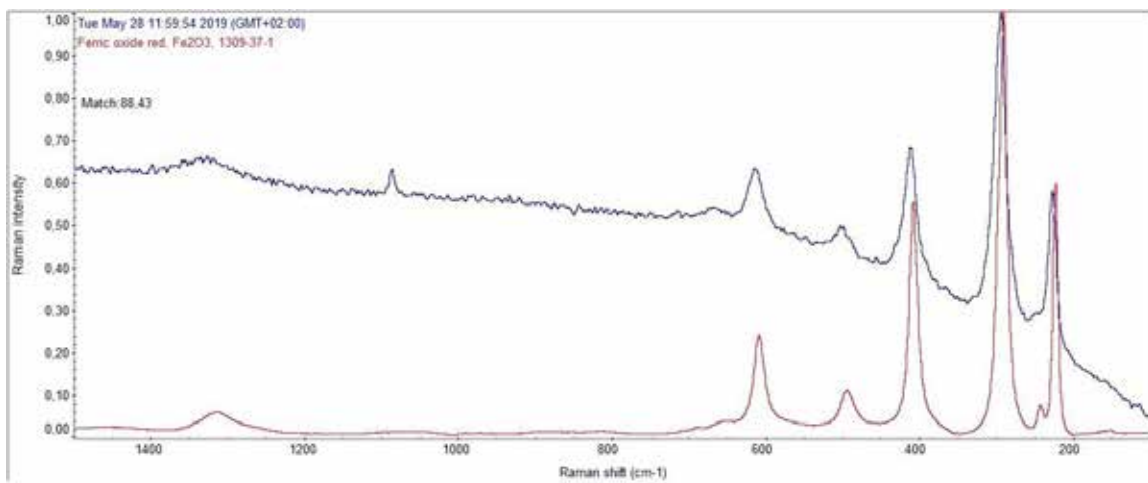


Fig. 19. Raman spectre of red pigment particles from sample 2 shown in parallel with the iron (III) oxide spectre.

earth red (as indicated by the trace elements K, Ti and Sr), as well as red lead – *minium* (with Cu and Zn as elements that can accompany lead).

In addition to these non-destructive analyses, optical microscopy and infrared spectroscopy (FTIR spectroscopy) were performed on one mortar sample (Fig. 15).⁴ On the basis of the appearance of the cross-section of the sample, it can be concluded that the mortar is made of both a lime binder and limestone aggregate (Fig. 16). Based on the FTIR spectrum, it can be concluded that the composition of the mortar is calcareous (calcium carbonate) and that it contains aggregates of the same chemical composition. This analysis confirmed the XRF spectrometry findings, namely, that chalk was used.



using optical microscopy (Fig. 20). The result (Fig. 21) showed an interesting stratigraphy, which enables us to discuss the painting technique and the mixing of pigments. Two layers of paint are clearly visible on the cross-section of sample 3. The first layer above the fresco mortar contains more particles of red ochre (iron (III) oxide), while there is a whitish layer on the surface containing a smaller concentration of red ochre mixed with calcium carbonate.

Optical microscopy, as well as Raman spectroscopy, are excellent methods (when it is possible to take a sample) for identifying pigments that have chemical elements in their composition that cannot be detected by non-destructive XRF spectrometry, such as with parts of materials painted



Fig. 20. Sample 3, red or blue painted layer with a white coating. Cross-section of the sample with a magnification of ca 350x (photo by T. Tripković).

Another sample was analysed using destructive Raman spectroscopy and optical microscopy (Fig. 17), in order to learn about the painting technique and confirm the use of an iron-based red pigment. The cross-section of sample 2 is characteristic of the fresco technique. A darker layer of deposited impurities can be seen on the surface of the painted layer. On the basis of the Raman spectroscopy of the sample, it was determined that calcite, calcium carbonate, is present in the substrate (mortar) (Fig. 18), while red ochre was used as a red pigment for painting – iron (III) oxide (Fig. 19). Another sample of red paint was analysed by

⁴ We would like to thank PhD Tatjana Tripković, chemist, adviser at the Republic Institute for the Protection of Cultural Monuments of Serbia - Belgrade for providing the results of the following analyses: optical microscopy, infrared spectroscopy and Raman spectroscopy.

black, as was the case with the sample in Fig. 21. The cross-section of the sample in Fig. 21 is characteristic of the fresco technique. The painted layer consists of black particles diffused into the layer of fresh plaster, so they give the appearance of a dark blue coloured layer. Using Raman spectroscopy, it was determined that the black pigment particles are amorphous carbon by composition (Fig. 22).

By means of the analytical techniques applied, it was discovered which aggregate was used for the preparation of the mortar, as well as which chemical elements and chemical compounds made up the pigments used for the wall paintings from the 13th century in the Church of St. Nicholas, in Baljevac. The composition of the mortar is lime (calcium carbonate) and it contains aggregates of the same chemical composition. Calcium carbonate was also used to lighten the tone of some



Fig. 21. Sample 4, black. Cross-section of the sample with a magnification of ca 350x (photo by T. Tripković).

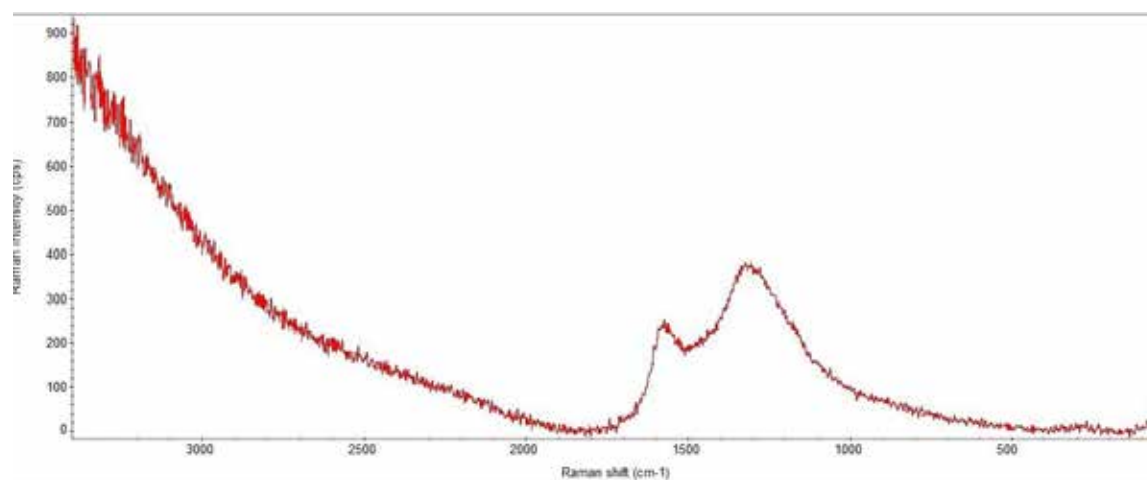


Fig. 22. Raman spectrae of the black layer in sample 4 contains peaks typical of amorphous carbon.

lighter red tones. pigments, by being mixed with them. The most commonly used pigments are earth pigments of all colours: red – red earth, hematite, ochre – yellow ochre, brown – ochre and green – green earth. Darker red tones were obtained using red lead pigment – *minium*, while cinnabar was used for

CONCLUSIONS

At the end of the 20th century, a wide-spread application of analytical techniques in the field of the study and protection of cultural heritage began in the world, resulting in a wide range of data on the physical-chemical composition and origin of various materials. In the past decades, during the research of wall paintings from both the Roman and the medieval period in the territory of Serbia, the emphasis was often on iconography and the archaeological context. In the past, analyses of materials were not available, and cooperation between experts from different fields in the process of the study and protection of the cultural heritage was rare. At that time, one could only guess at which pigments were used, based on the knowledge of painting technology. However, such conclusions were often wrong.

By means of physical-chemical analyses, it is possible to obtain exact data on pigments used.⁵ The techniques applied in the analysis of painted layers are varied, and the following were used in this paper: pEDXRF, FTIR, and Raman spectrometry, as well as OM. For experts dealing with cultural heritage protection, it is most important to know what certain analytical techniques can reveal. Often, it is not necessary to apply a large number of different techniques, but rather to have a clear goal and choose those techniques that can provide the necessary data. Through a comparison of the results obtained by applying the aforementioned analytical techniques with knowledge from the field of painting technology, archaeology, history of art and architecture, scientifically invaluable conclusions can be reached (Mora, Mora, Philippot, 1984, 22). In order to obtain the most accurate results possible, it is important to choose an adequate sample, and to keep in mind that any information obtained from the sample must be additionally confirmed. It was noticed that samples with pure, intense and thicker colour layers yielded better results than lazure.

When it comes to the fragments from the Church of St. Nicholas, in Baljevac, the following colours were detected by visual observation: light

and dark red, orange, pink, blue, green, various shades of ochre and brown, white and black, as well as various shades of mixtures of these colours. By using the analytical techniques of pEDXRF, Raman and FTIR spectrometry, it was concluded that the following pigments were used during the painting of the second phase of the Church of St. Nicholas, in Baljevac: yellow ochre, red earth, cinnabar, red lead, green earth, lime white and charcoal black. Unexpected results were obtained in two blue samples. Green earth was detected in one sample. Green earth can also have a bluish hue. In the case of the second sample, which seemed blue, it was concluded, on the basis of the obtained results, that charcoal black was used, making it seem blue due to the fresco technique and calcium carbonate. Iron oxide red – red earth with cinnabar and red lead, was also combined. The mortar consists of a limestone aggregate. Based on the cross-section of the fragments and microscope recordings, it can be concluded that the fresco painting technique was applied. The best comparison references for pigments from a similar period are those that were used to paint the monastery of Žiča.⁶ Almost the same pigments were detected, the only difference being that no lapis lazuli was detected on the fragments from the Church of St. Nicholas, in Baljevac. It was interesting to note the use of cinnabar, a very precious and expensive pigment, even in the 13th century, which could represent additional research related to the historical and artistic context of these fresco paintings. Another finding that would be interesting for further research of these materials are the impurities from which elements detected in traces in the EDXRF spectrum of *minium* originate. By revealing information on the admixture types, it would be possible to discuss the technique of obtaining this pigment.

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⁵ For some of the first works on the analysis of painted layers from the Roman period in Serbia, see Rogić et al. 2012 and the unpublished PhD thesis by D. Rogić, "Tehnologija antičkog slikarstva na teritoriji Srbije" [Technology of antique painting in the territory of Serbia], 2014.

⁶ Physical-chemical analyses showed that iron oxides were used: hematite, goethite (red and yellow-ochre), cinnabar, lapis lazuli, charcoal or graphite black, magnetite brown and green earth. Холцлајтнер Антуновић, et al. 2015, 95.

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REZIME

PRIMENA ARHEOMETRIJSKIH TEHNIKA U ISTRAŽIVANJU ZIDNIH SLIKA NA PRIMERU FRAGMENTA FRESKO SLIKARSTVA IZ CRKVE SVETOG NIKOLE U BALJEVCU

KLJUČNE REČI: EDXRF, FTIR, RAMANSKA SPEKTROSKOPIJA, ZIDNE SLIKE ARHEOMETRIJA, KULTURNO NASLEĐE, FRAGMENTI, PIGMENTI, CRKVA SVETOG NIKOLE U BALJEVCU.

U radu su prikazane analitičke tehnike i rezultati koji su dobijeni njihovim korišćenjem prilikom ispitivanja izabranih fragmenata zidnih slika, pronađenih u Crkvi Sv. Nikole u Baljevcu. Prilikom arheoloških istraživanja crkve, u Jami br. 1, koja se nalazila u prostoru naosa, pronađeni su fragmenti zidnog slikarstva datovani u XIII vek. Odabrano je nekoliko fragmenata različitih i čistih tonova za ispitivanje sastava maltera i pigmenta, kao i tehnike oslikavanja.

Analitičke tehnike koje se primenjuju u ispitivanju zidnog slikarstva mogu biti nedestruktivne, mikrodestruktivne i destruktivne. Nedestruktivne i mikrodestruktivne analitičke tehnike su poželjne u radu sa arheološkim i muzejskim materijalom. Tehnike koje se primenjuju za analizu bojanih slojeva su raznovrsne, a u ovom radu su korišćene: pEDXRF, FTIR, i Ramanska spektrometrija, kao i OM. Za stručnjake koji se bave zaštitom kulturnog nasleđa najbitnije je da znaju šta pojedine analitičke tehnike mogu otkriti. Često nije neophodno primeniti veliki broj različitih tehnika, već imati jasan cilj i izabrati one tehnike koje nam mogu obezbediti potrebne podatke. Da bi rezultati bili što tačniji, važno je odabrati adekvatan uzorak. Poznato je da su uzorci čistih, intenzivnih i debljih slojeva boja daju jasnije rezultate nego oni sa lažurnim slojevima.

Kod fragmenata iz Crkve Svetog Nikole u Baljevcu, upotrebom analitičkih tehnika pEDXRF, Ramanska i FTIR spektrometrija, zaključeno je da

su pri oslikavanju druge faze crkve korišćeni sledeći pigmenti: žuti oker, crvena zemlja, cinober, olovno crvena, zelena zemlja, krečno bela i crna od uglja. Malter je po sastavu krečni (kalcijum karbonat) i sadrži agregate istog hemijskog sastava. Kalcijum karbonat je korišćen i za posvetljavanje tona nekih pigmenata, tako što je mešan s njima. Na osnovu poprečnog preseka fragmenata i snimanja pod mikroskopom može se zaključiti da je primenjena fresko tehnika slikanja.

Kod dva uzorka plave boje dobijeni su ne očekivani rezultati. Kod jednog od njih je detektovana zelena zemlja. Kod drugog uzorka, čija je boja označena kao plava, na osnovu dobijenih rezultata zaključeno je da je korišćena crna-ugljenik, koja zbog fresko tehnike i kalcijum karbonata stvara privid plave boje. Crvena boja – od oksida gvožđa je kombinovana sa cinoberom i olovno crvenom bojom. Najbolju analogiju za poređenje sa pigmentima iz sličnog perioda predstavljaju pigmenti korišćeni za oslikavanje manastira Žiča. U ovom manastiru su detektovani skoro isti pigmenti kao na ispitivanim fragmentima, osim lapis lazulija, koji je odsutan na fragmentima crkve u Baljevcu.

* * *

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