

XRD and FTIR characterisation of historical green pigments and their lead-based glazes

Eglė Gražėnaitė¹,

Jonas Kiuberis²,

Aldona Beganskienė¹,

Jūratė Senvaitienė²,

Aivaras Kareiva^{1*}

¹ Department of Inorganic Chemistry,
Vilnius University,
Naugarduko St. 24,
LT-03225 Vilnius, Lithuania

² Department of Applied Chemistry,
Vilnius University,
Naugarduko St. 24,
LT-03225 Vilnius, Lithuania

In this study, the applicability of X-ray powder diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy to investigate historical green pigments and their glazes was evaluated. In order to verify the ability to detect pigments in their glazes of the above techniques, the XRD and FTIR analyses were performed on the model samples. The investigation was pursued on nine pigments (Kremer Pigmente): malachite, verdigris, cobalt green, cobalt bottle green, chrome oxide green, Egyptian green, Victorian green, Florentine green and green jasper. The same pigments together with lead oxide and silica were used to prepare lead-based glazes. The results revealed that the XRD analysis is a useful tool for qualitative determination of the composition of glazes, although in some cases other analytical techniques should be involved. However, FTIR spectroscopy in the high wavenumber range (4 000–600 cm⁻¹) does not give reliable results in the determination of green pigments in glazes.

Key words: green pigments, glazes, characterization, XRD, FTIR

INTRODUCTION

The variety of green historical pigments is numerous. Green pigments can be based on copper, iron, chromium, cobalt and other metals. Green copper-based pigments were widely used since the ancient Egypt times for various art techniques, such as mural-painting, painting and ceramics until the 19th century. Due to their disadvantages (low hiding power and intensity, bad resistance to atmospheric effects, toxicity) later they were almost completely replaced by other green pigments. Iron-based pigments are usually earth pigments and are named by their provenance. Earth pigments are also characterised by a low covering power and intensity, but good resistance to alkalis, light and atmospheric effects. Besides, they are non-toxic. These pigments are used since the ancient times and can be applied in all kinds of art. Usually, chromium-based green pigments are synthetic, only volkonskoite (Cr₂O₃ · FeO · CaO · Al₂O₃ · SiO₂ · H₂O) is a natural mineral. Synthetic chromium oxides were discovered in 19th century and quickly replaced the less resistant and more toxic copper-based pigments. Chromium-based pigments find applications in all art techniques

and have a good resistance to light, atmospheric effects, alkalis and acids, and aggressive gas. One of the main historic cobalt-based green pigments is cobalt green (CoO · nZnO), sometimes known as Rinman's green or zinc green. It was produced in the end of 18th century. Despite its chemical stability, cobalt green was not very popular among the artists, since it created relatively weak colours and its production was too expensive. Other cobalt-based green pigments contain chromium, nickel, titanium and other elements [1, 2].

Various pigments were used to colour ceramic glazes. By the end of the 1st millennium BC, lead-based glazes appeared in China and in the eastern Roman Empire, although there are records of detection of it back to 5th–4th millennium in Egypt [3]. The use of lead-based glazes spread widely to the Middle East and Europe [3, 4], and humanity has inherited a generous amount of stoneware and ceramics with lead glazes which interest historians and conservation scientists. Numbers of research groups have been investigating ceramic glazes by various methods, such as XRF, SEM-EDS, PIXE, IR spectroscopy, ICP and others [5–11]. The investigation of cultural heritage should be non-destructive; hence the X-ray fluorescence spectroscopy is a promising method to measure directly from the historical object without fragmentation of the object itself.

* Corresponding author. E-mail: aivaras.kareiva@chf.vu.lt

However, it is only an elemental analysis and it does not disperse phase composition, whereas the X-ray diffraction analysis does. Recently, there have been published studies on the application of the X-ray powder diffraction (XRD) method to characterize the historical pottery and diversely coloured glazes [8, 9, 12, 13]. But in these papers the investigation of green coloured glazes was done merely in several cases. Therefore, in this study we examined only the green historical pigments. The first aim was to determine the composition of green inorganic pigments with unknown constitution. The second task was to investigate the detectability of pigments in their lead-based glazes using the XRD analysis and FTIR spectroscopy.

EXPERIMENTAL

Nine historical green pigments along with lead oxide and silica, all of them analytical grade reagents, purchased from Kremer Pigmente, were investigated and used to prepare lead-based glazes. For the preparation of glazes, in all cases the same molar ratio of ingredients has been selected: $\text{Pb}_3\text{O}_4 : \text{SiO}_2 : \text{pigment} = 2.85 : 1.9 : 0.25$ [12, 13]. The analysed samples are described in the Table. The amount of unknown composition pigments (No. 8 and No. 9) was picked to be 1.40 weight %. In this paper all pigments were called according to manufacturer's catalogue.

Individual pigments and their mixtures were investigated by the X-ray powder diffraction (XRD) analysis in the range from 10 to 80 2θ degrees and by the infrared spectroscopy (FTIR) in the range of 4 000–600 cm^{-1} . The XRD was performed with a Rigaku MiniFlex II using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). For FTIR studies a Perkin Elmer Spectrum BX spectrometer with an ATR accessory was used. Transmittance (%) was taken by the co-addition of 10 scans with a resolution of 2 cm^{-1} .

RESULTS AND DISCUSSION

XRD analysis of individual green pigments and their mixtures for glazes

The X-ray powder diffraction analysis of individual pigments exposed their composition. The XRD patterns of the C–O bond containing pigments are shown in Fig. 1. All diffraction peaks of pigment No. 1 correspond to the standard pattern of malachite $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ (PDF [72-0075]) (Fig. 1a). The

formula of verdigris presented in the catalogue of Kremer Pigmente is given as $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$. However, the XRD analysis data (Fig. 1b) confirmed that the purchased reagent is monophasic copper acetate monohydrate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (PDF [27-0145]).

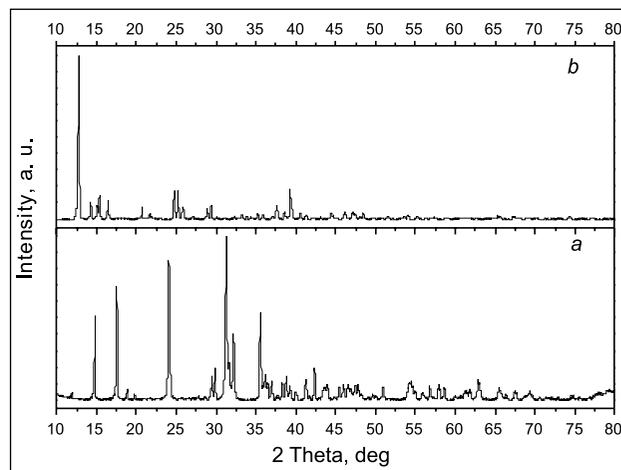


Fig. 1. XRD patterns of the C–O bond containing the green pigments: malachite (a) and verdigris (b)

XRD patterns of oxide pigments are given in Fig. 2. Cobalt green pigment with a sophisticated chemical composition presented by Kremer Pigmente is composed of nickel zinc titanium oxide NiZnTiO_4 (PDF [35-1372]) as the main phase and barium sulphate BaSO_4 (barite, PDF [83-1718]) and metal oxides TiO (PDF [02-1196]), CoO (PDF [02-1217]) as the secondary phases (Fig. 2(a)). Unfortunately, no crystalline phases containing aluminium were determined, in contrast to the declaration of the producers (Table). The XRD pattern of cobalt bottle green pigment corresponds exactly to the XRD pattern of cobalt chromium oxide CoCr_2O_4 (PDF [80-1668]) (Fig. 2b). Finally, according to the XRD pattern of chrome oxide green (Fig. 2c), all peaks coincide with the pattern of chromium(III) oxide Cr_2O_3 (eskolaita, PDF [38-1479]).

XRD patterns of the rest four green pigments (Egyptian green, Victorian green, Florentine green and green jasper) are presented in Fig. 3. The most complex pigment to identify was Egyptian green (Fig. 3a). Egyptian green is usually obtained from Egyptian blue pigment $\text{CaCuSi}_4\text{O}_{10}$ (cuprorivaite) by

Table. Historical green pigments (Kremer Pigmente) and their weight percentages in the lead-based glazes

| Sample No. | Catalogue No. | Pigment | Chemical formula according to producer | Weight, % |
|------------|---------------|---------------------|---|-----------|
| 1. | 10300 | Malachite | $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ | 2.60 |
| 2. | 44450 | Verdigris | $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$ | 5.81 |
| 3. | 44100 | Cobalt green | Co, Al, Ti, Ni, Zn oxides | 5.74 |
| 4. | 44130 | Cobalt bottle green | CoCr_2O_4 | 2.67 |
| 5. | 44200 | Chrome oxide green | Cr_2O_3 | 1.80 |
| 6. | 10064 | Egyptian green | Cu silicate | 1.47 |
| 7. | 44190 | Victoria green | $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ | 5.70 |
| 8. | 11152 | Florentine green | ? | 1.40 |
| 9. | 11200 | Green jasper | ? | 1.40 |

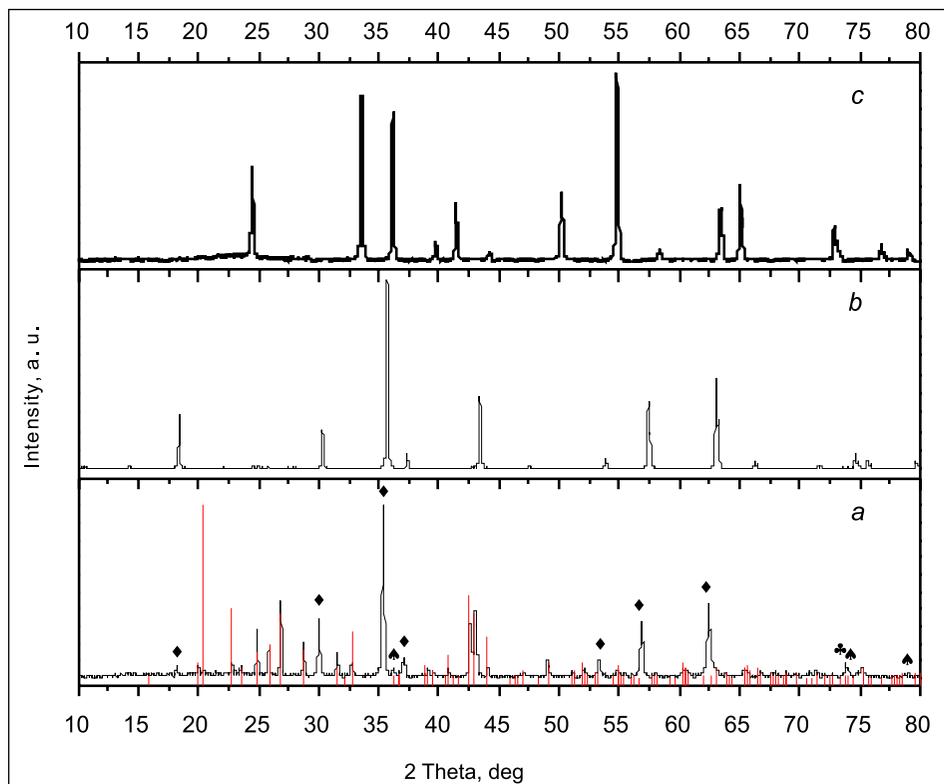


Fig. 2. XRD patterns of the green oxide pigments: cobalt green (a), cobalt bottle green (b) and chrome oxide green (c). The phases are marked: \blacklozenge – NiZnTiO_4 ; \blacktriangle – TiO_2 ; \bullet – CoO and vertical lines represent the standard diffractogram of BaSO_4

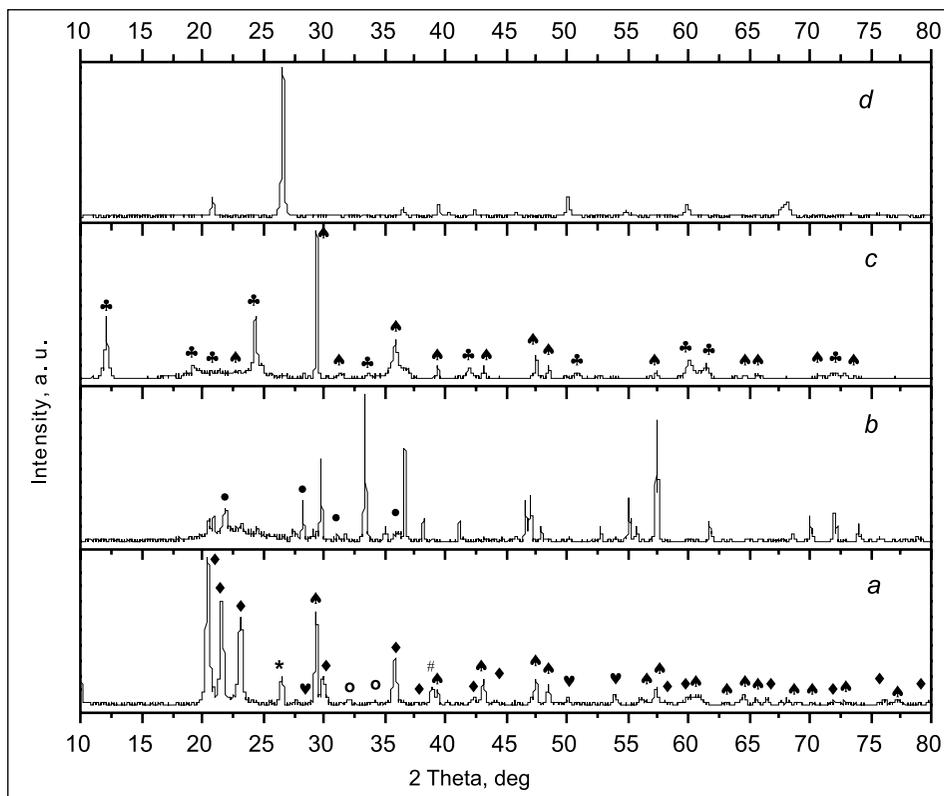


Fig. 3. XRD patterns of green silica containing the pigments: Egyptian green (a), Victoria green (b), Florentine green (c) and green jasper (d). The phases are marked: \blacktriangle – CaCO_3 ; \blacklozenge – SiO_2 (tridymite); \heartsuit – Na_2CO_3 ; $*$ – Mg_2SiO_4 ; \bullet – K_2CO_3 ; $\#$ – CuO ; \bullet – SiO_2 (cristabolite) and \blacktriangle – Mg-Fe-Si-O

heating it or its raw materials, such as CuO , CaCO_3 , SiO_2 and Na_2CO_3 , above 1 000 °C [14–16]. The XRD results revealed that this pigment contains calcite CaCO_3 (PDF [47-1743]), tridymite SiO_2 (PDF [75-0638]), sodium (PDF [86-0297]) and potassium (PDF [71-1466]) carbonates, magnesium silicate Mg_2SiO_4 (PDF [87-2036]) and copper oxide CuO (PDF [74-1021]). Presumably the XRD pattern of Egyptian green shows only raw materials with Mg_2SiO_4 and K_2CO_3 phases as impurity since no newly formed phase was determined. According to the data in the catalogue of the manufacturer, Victoria green pigment should be calcium chromium silicate. Although the X-ray diffraction analysis (Fig. 3b) confirmed the presence of $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ (uvarovite, PDF [87-1007]) as the main phase, it also showed that an extra phase of silica SiO_2 (cristabolite, PDF [77-1317]) was present in the material investigated. Unfortunately, even after XRD measurements the phase composition of green pigment Florentine green still remained unclear. The results revealed that Florentine green (Fig. 3c) contains calcite CaCO_3 (PDF [47-1743]) and magnesium iron silicate Mg-Fe-Si-O (PDF [22-0710]). However, all diffraction peaks of green jasper (Fig. 3d) coincide only with silicon oxide SiO_2 (PDF [85-0457]) and no phases of chromophore were identified. Considering green jasper is a green earth pigment, the chromophore should be iron [17, 18] or chromium [19] compounds.

After the examination of XRD patterns of the prepared lead-based glaze mixtures containing different historical green pigments, it turned out that most of them are very similar since the main detected phase in glazes was lead oxide Pb_3O_4 (PDF [41-1493]). Nevertheless, a historical green pigment verdigris could be easily detected in the glaze mixture by the XRD method. The XRD pattern of the glaze mixture prepared with green pigment verdigris is given in Fig. 4. The intense peak at $2\theta \approx 12.8^\circ$ and a few weak peaks at $2\theta \approx 24.7^\circ$, 37.6° and 42.5° could be easily attributed to copper(II) acetate monohydrate (PDF [27-0145]). Besides, a weak peak of silicon oxide (quartz, PDF [86-1560]) from the glaze mixture is observable at $2\theta \approx 20.8^\circ$.

Malachite (Fig. 5a), all three oxide-based pigments (Fig. 5b–d) and Victoria

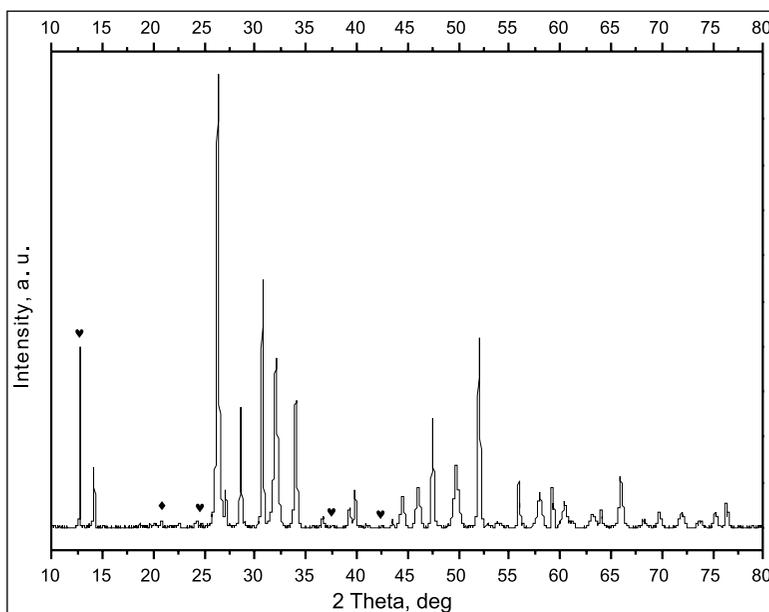


Fig. 4. XRD pattern of glaze mixture containing the green pigment verdigris. The phases are marked: ♥ – $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and ♦ – SiO_2

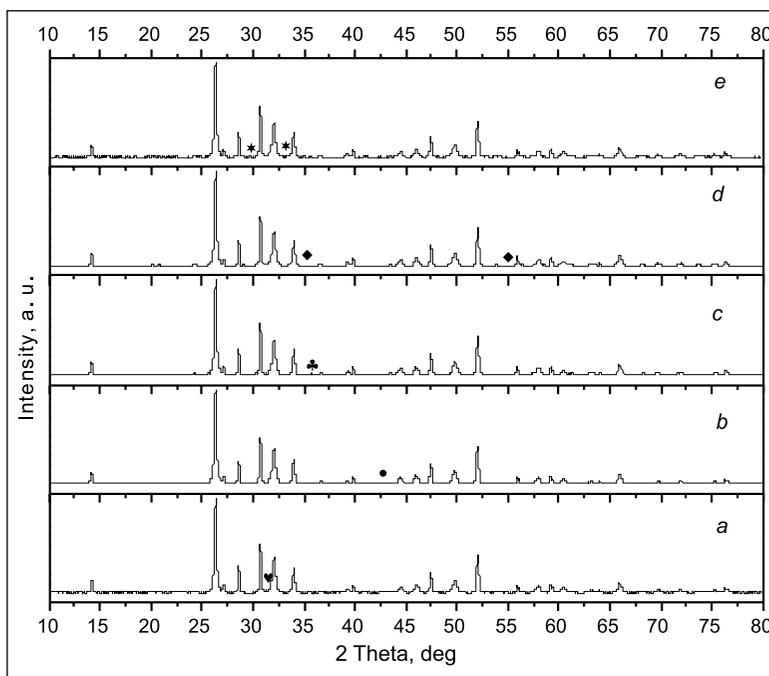


Fig. 5. XRD patterns of glaze mixtures prepared with the green pigments: malachite (a), cobalt green (b), cobalt bottle green (c), chrome oxide green (d) and Victoria green (e). The phases are marked: ♥ – $\text{Cu}_2(\text{OH})_2\text{CO}_3$; ● – NiZnTiO_4 ; ♣ – CoCr_2O_4 ; ♦ – Cr_2O_3 and * – $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$

green (Fig. 5e) pigment in their glazes can be distinguished very roughly. As it is seen from Fig. 5, all characteristic diffraction peaks of pigments are very weak. Nevertheless, these green pigments also could be determined by the XRD method in their glazes. Finally, no specific signals from pigments were detected in the XRD patterns of glazes prepared with Egyptian green (Fig. 6a), Florentine green (Fig. 6b) and green jasper (Fig. 6c). All these XRD patterns are identical to the XRD patterns of an individual lead-based glaze

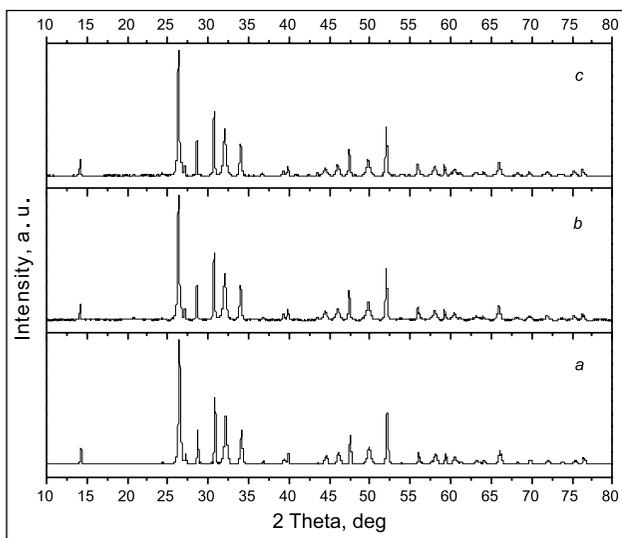


Fig. 6. XRD patterns of glaze mixtures with the green pigments: Egyptian green (a), Florentine green (b) and green jasper (c)

mixture without pigments. Consequently, Egyptian green, Florentine green and green jasper pigments could be hardly determined by XRD in their lead-based glazes, except the concentration of pigment would be unusually very high.

FTIR characterisation of individual pigments and their glaze mixtures

Additionally infrared spectroscopy was applied to test the possibility of determination of historical green pigments. Characterisation of individual pigments revealed that the FTIR spectra of malachite and verdigris (Fig. 7) contain absorption bands attributable to the carbon-oxygen vibration in the double bond containing functional groups. Besides, the transmittance mode of both malachite and verdigris spectra shows the presence of bands of the O–H vibrations at 3 402 and 3 311 cm^{-1} for malachite [20–22] and $\sim 3\ 468$, 3 365 and 3 266 cm^{-1}

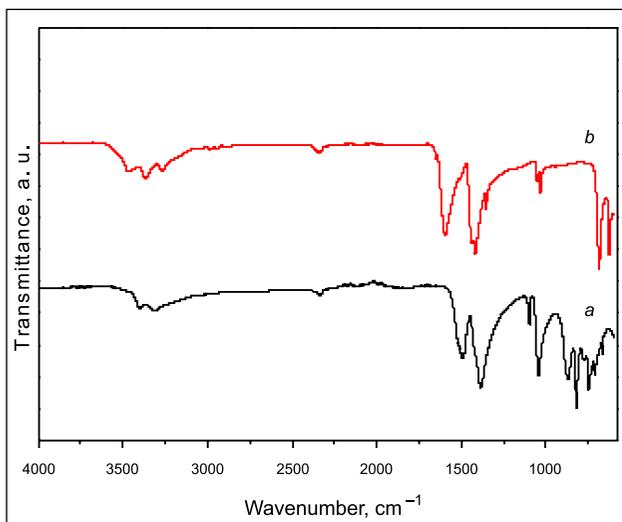


Fig. 7. FTIR spectra of the C–O bond containing the pigments: malachite (a) and verdigris (b)

for verdigris [23, 24]. The absorption bands for malachite at 1 490 and $\sim 1\ 386\ \text{cm}^{-1}$ correspond to the ν_3 asymmetric stretching mode [22, 23, 25, 26] and the ν_1 symmetric stretching mode at 1 096 cm^{-1} [23, 26] of the CO_3^{2-} group. For verdigris, the bands at $\sim 1\ 595$ and 1 418 cm^{-1} are due to the presence of the COO^- group and correspond to the asymmetric stretching and symmetric stretching vibrations of the C–O bond in the acetate group, respectively [23]. The band for malachite at 1 045 cm^{-1} coincides with the δOH bending mode [23, 26]. Bending modes of the C–H bond in verdigris are observed at 1 048 and 1 032 cm^{-1} [23]. For malachite two ν_2 bending modes at ~ 870 and 817 cm^{-1} of the CO_3^{2-} group are also visible [26].

FTIR spectra of green oxide pigments are given in Fig. 8. All three spectra are very similar containing a sharp peak at 668 cm^{-1} , which can be assigned to metal–oxygen (M–O) stretching vibrations [27–30]. This band, only sharper and more intense, is also seen at the same wavenumber (668 cm^{-1}) in the FTIR spectra of green silica pigments (Fig. 9). But in

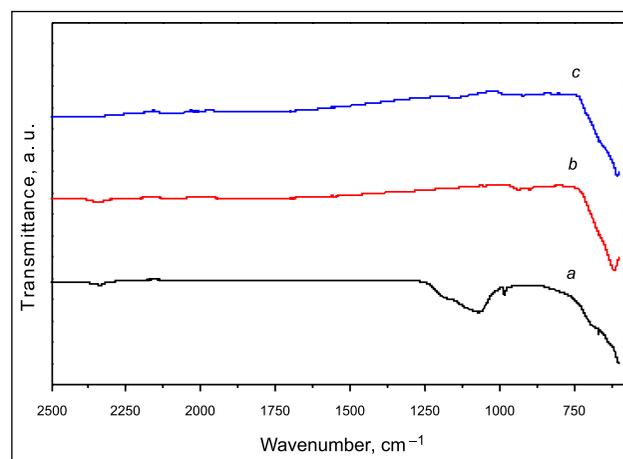


Fig. 8. FTIR spectra of the green oxide pigments: cobalt green (a), cobalt bottle green (b) and chrome oxide green (c)

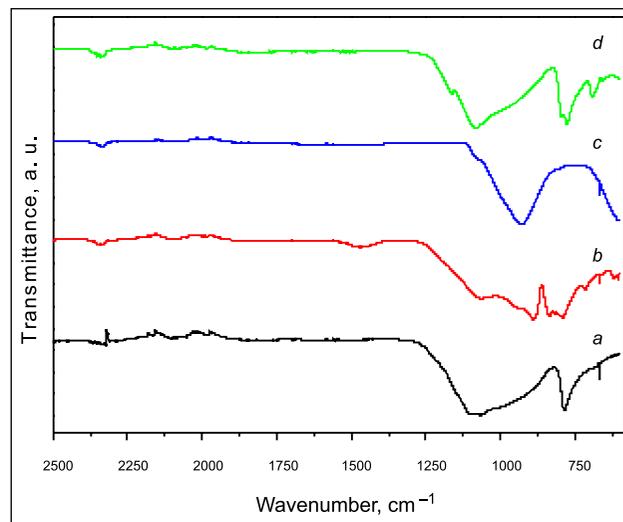


Fig. 9. FTIR spectra of the green silica pigments: Egyptian green (a), Victoria green (b), Florentine green (c) and green jasper (d)

this case these bands along with intensive bands located in the region of $\sim 1\,100\text{--}950\text{ cm}^{-1}$ could be attributed to Si–O vibrations [31].

FTIR results of the characterisation of glazes revealed that the qualitative identification of the inorganic pigments in such range of wavenumbers was possible only for green pigments malachite (Fig. 10a) and verdigris (Fig. 10b). The spectra show that their characteristic vibrations are very well resolved. All vibration bands are slightly shifted to a higher wavenumber region. Weak absorption peaks at $\sim 1\,505\text{ cm}^{-1}$ and $886, 820\text{ cm}^{-1}$ for malachite in the glaze mixture coincide with an asymmetric stretching of $\nu_3\text{CO}_3^{2-}$ and bending modes of $\nu_2\text{CO}_3^{2-}$ vibrations, respectively.

A weak peak at $1\,051\text{ cm}^{-1}$ is ascribed to δOH and a broad doublet at $3\,399$ and $\sim 3\,257\text{ cm}^{-1}$ is due to O–H stretching vibrations. A weak absorption peak at $\sim 1\,609\text{ cm}^{-1}$ in the FTIR spectrum of the glaze mixture with verdigris pigment corresponds to an asymmetric stretching vibration of the C–O bond in the acetate group and the broad band at $\sim 3\,254\text{ cm}^{-1}$ corresponds to the stretching mode in the hydroxide group.

CONCLUSIONS

Historical green pigments of different chemical composition and their glazes were characterised by the XRD analysis and FTIR spectroscopy. The XRD method has clearly shown

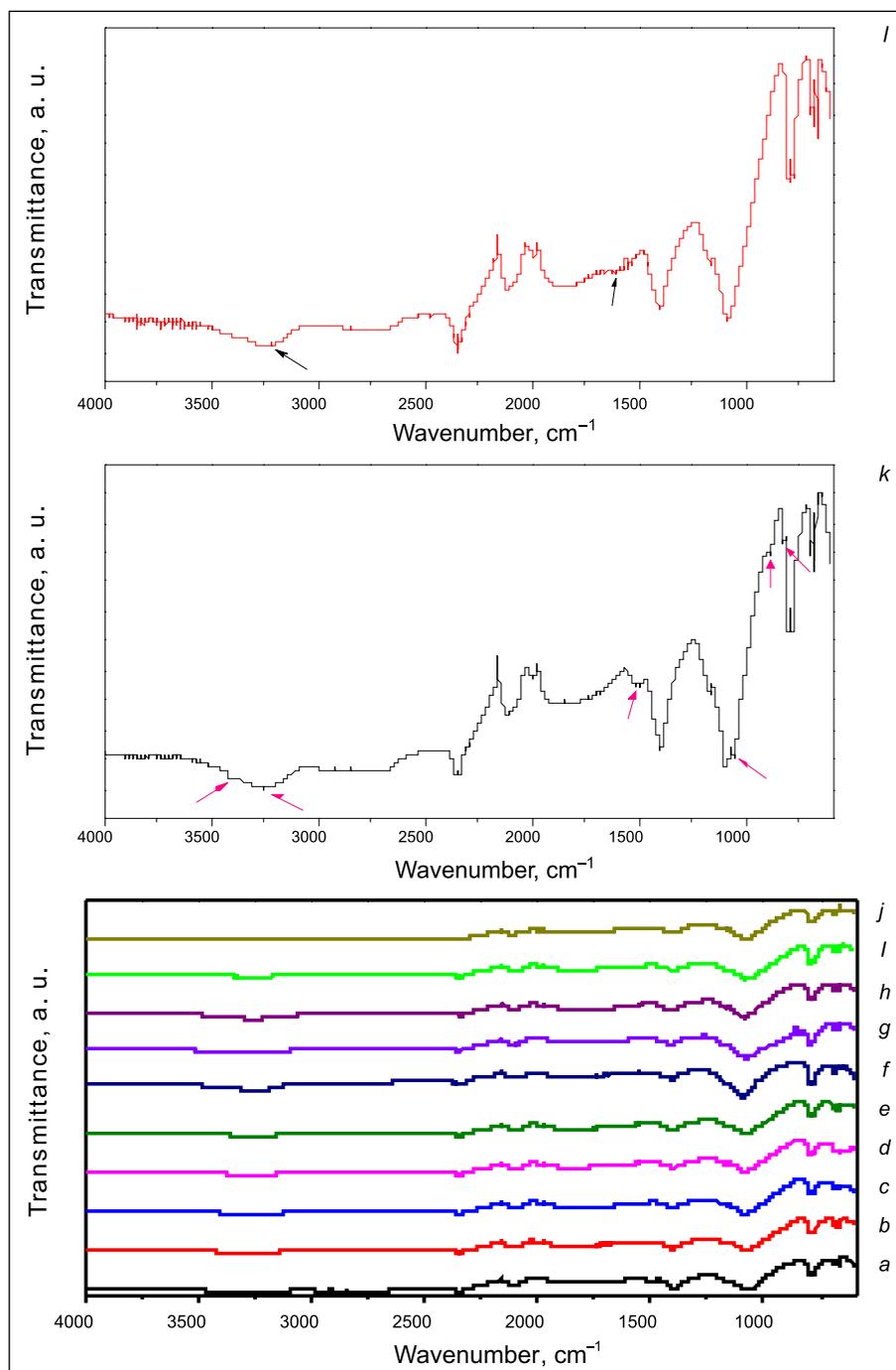


Fig. 10. FTIR spectra of glaze mixtures with the green pigments: malachite (a), verdigris (b), cobalt green (c), cobalt bottle green (d), chrome oxide green (e), Egyptian green (f), Victoria green (g), Florentine green (h), green jasper (i) and glaze mixture itself (j). The close up of malachite in a glaze mixture (k) and close up of verdigris in a glaze mixture (l)

that the chemical composition of three purchased pigments (malachite, cobalt bottle green and chrome oxide green) corresponds to the one given in the Kremer Pigmente catalogue. However, the chemical composition of several pigments has been slightly specified. It appeared that verdigris is copper(II) acetate monohydrate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ rather than basic copper(II) acetate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$. Victoria green pigment contains not only calcium-chromium silicate $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ as the main phase but also silicon oxide SiO_2 as the secondary phase. The XRD results revealed the chemical compositions of pigments with an unclear constitution (cobalt green and Egyptian green). Unfortunately, not all compositions were determined – green earth pigments (Florentine green and green jasper) stayed unclear. It was also demonstrated that only verdigris could be easily characterised in its glaze. Malachite, cobalt green, cobalt bottle green, chrome oxide green and Victoria green could be hardly distinguished whereas Egyptian green, Florentine green and green jasper would be completely undetectable. Moreover, it was demonstrated that the FTIR analysis of green inorganic pigments was imperfect in the range of $4\,000\text{--}600\text{ cm}^{-1}$. Investigation of pigments in glaze mixtures at this range is possible if pigments contain carboxylate or carbonate functional groups (malachite and verdigris). In conclusion, XRD as well as FTIR can detect malachite and verdigris best of all analysed pigments. For the rest of them these methods are not sensitive enough.

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Jūratė Senvaitienė, Aivaras Kareiva

ISTORINIŲ ŽALIŲJŲ PIGMENTŲ IR JŲ ŠVININIŲ GLAZŪRŲ APIBŪDINIMAS RSDA IR FTIR METODAIS

Santrauka

Neorganiniai istoriniai žalieji pigmentai (*Kremer Pigmente*) ir jų glazūros buvo tiriami rentgeno spindulių difrakcinės analizės (RSDA) ir infraraudonosios spektroskopijos (FTIR) metodais. Tiriant pigmentus RSDA metodu nustatyta, kad ne visų pigmentų cheminė sudėtis atitinka nurodytą gamintojo kataloge. Tiriant švinines glazūras įrodyta, kad lengviausia tokiose glazūrose nustatyti žaliąjį pigmentą verdigrį, kiek sunkiau – malachitą, kobalto žaliąjį, kobalto žaliąjį tamsųjį, chromo oksidą ir Viktorijos žaliąjį, o Egipto žaliojo, Florencijos žaliojo ir žaliojo jaspio pigmentų glazūrose nustatyti nepavyko. Taip pat įvertinta, kad FTIR metodas tiriant švinines glazūras geriausiai tinka pigmentams, turintiems C–O jungtį (malachitui ir verdigriui).