Verification of the Utilization of Pigments Obtained from Red Mud and Converter Waste in Mural Painting

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Summary

The objective of the research was to verify the utilization of the pigments prepared using selected red mud from aluminia plant and the converter wastes and their comparison with industrial pigments when used in mural painting.
Two types of wastes were selected for the research. The criteria included the colour, availability and earlier research. The research focused on red mud generated by bauxite processing at the Birač Alumina Industry (BH) plant and converter sludge generated by steel production at Třinecké železárny a.s.
The testing of the materials under examination included their grinding and application in the restoration of a mural painting on a test panel, simulation of the aging process in a climatic chamber and a comparison with an industrial pigment commonly used in practice by means of a microscopic analysis, infrared and Raman spectrometry.

Keywords:waste utilization, pigments, mural painting, red mud Al, converter wastes, test panel

Characteristics of waste materials

The waste generated by bauxite processing at Birač Alumina Industry was red sludge (C.K.Birač), which had already been treated by bacterial leaching, calcination and grinding [1]. The intensive red colour following calcination was the main reason for choosing this material to be tested as a pigment. Based on a chemical analysis of its composition, the untreated sample contained predominantly the following oxidic forms: Fe_2O_3 (50.8%), Al_2O_3 (11.7%) and Na_2O (13%). An element analysis of the untreated sample and the treated sample showed an increase in Fe from 35.9% to 50.6%.

The waste generated by steel production at Třinecké železárny a.s. was converter sludge (K.K.Třinec), which had also been already treated by bacterial leaching, calcination and grinding [1]. Based on a chemical analysis of its composition, the untreated sample contained predominantly Fe_2O_3 (76.9%). An element analysis of the untreated sample and the treated sample showed an increase in Fe from 55.3% to 63.6%. The colour of the sample following calcination was dark brown.

Industrial pigments used

The comparative industrial pigment was selected on the basis of the following criteria – a colour similar to the pigments under examination, its quality and frequency of usage in practice.

Natural Sienna, Kremer (Sienna Kremer) – a natural pigment for artistic use, containing 50 – 70% of ferric oxide (Fe_2O_3) and a variable amount of manganese dioxide. It is bound with 0 – 200% of oil, creating a gel. The colour components of natural sienna are goethite and hematite. The pigment was used for a comparison with the pigments under examination, C.K.Birač and K.K.Třinec.

Grinding

To obtain the finest material, the C.K.Birač and K.K.Třinec samples were ground using two types of grinding machines. In the first case, in which the sample had been ground using the LAMOW–C–5×2 rotational vibrating mill at the AGH laboratory in Krakow, a relatively fine-grained material was obtained. Based on a laser analysis of particle sizes, 50% of the grains represented in the sample had a grain size of less than approx. 3 μm. The grinding process resulted in changes to the colour of the material. After three hours of grinding, the colour of the C.K.Birač sample corresponded to light iron oxide red. After three hours of grinding, the colour of the K.K.Třinec sample corresponded to Italian burnt sienna. Other grinding tests were performed using the Pulverisette 7 planetary mill at Precheza Přerov, a. s. at 300 rev/min for a period of one hour. In addition to the C.K.Birač and

K.K.Třinec samples under examination, the selected industrial pigment (having a similar colour) – natural sienna, Kremer (Sienna Kremer) was also ground. [2]

Application in mural painting

In order to imitate a natural support, which is characteristic of mural paintings, a test panel was made (a wooden frame with OSB at the bottom), which was filled with three layers of mortar material. A rough plaster was applied on the support in a ratio of 3:1 (aggregate : binder – sand : lime), subsequently a fine plaster in a ratio of 2:1 (aggregate : binder – sand : lime) and, as the final, surface layer, the intonaco – a fine-grained lime plaster with an addition of lime powder in a ratio of 1:1 (aggregate : binder – lime powder : lime). The binder was lime prepared using unslaked powder substrate from Vápenka Čertovy Schody, a.s. The aggregate was pit sand from the Hlučín sand pit. Before use, the sand was washed, dried and sieved in order to prevent contamination with salt.

The painting was designed in such a manner as to enable a comparison of the pigment obtained with the industrial pigment commonly used in practice. The painting on the panel was divided into two sections. The right section was painted using the pigment under examination; the left section was painted using the common industrial pigment. Another division was made based on the used binders, mixed with the pigment in the paint. A synthetic binder – the Primal SF 016 acrylic dispersion with a concentration of 1.5% was used in the upper part. A natural binder – an egg yolk emulsion – was used in the lower part of the panel.

Using the secco technique (secco – the paint is applied to a hardened plaster surface using pigments with a binder dissolved in water), a copy of the shape of the decorative ceiling painting located at the Litomyšl castle was painted on the test panel (see Figure 1). The Greek-style painting was created by D. Dvořák. Only the shape and position of the individual ornaments of the original painting were used for the test paintEng. A natural binder (egg yolk emulsion) and a synthetic (Primal SF 016) binder were used as the pigment binders.

Simulation of the aging process of a mural painting in a climatic chamber

To simulate the aging process, the test panel was placed in a climatic chamber. The climatic chamber

Fig. 1 Test panel – mural painting

Rys. 1. Test panelowy – malarstwo ścienne

was located at the Faculty of Civil Engineering of VŠB - TU Ostrava. It was a CTS C-40/1000/S climatic chamber; chamber volume: 1,000 litres, temperature range: - 40°C to +200°C, humidity range: 10 - 98%. The input values of the exposure process were set as follows: temperature: 5°C, humidity: 80%, duration: 20 days. These values were selected in such a manner as to ensure that they corresponded to the natural environment of mural paintings. The exposure took place in two cycles. During each cycle, the parameters and abrasion of the samples were monitored on a regular basis for the purpose of subsequent analyses. The paint on the right side of the test panel contained the pigment under examination while the paint on the left side contained the industrial pigment; a synthetic pigment binder was used in the top part and a natural pigment binder was used in the bottom part (see Figure 2).

At the AVU laboratories in Prague, polished sections of the samples were prepared for the purpose of a microscopic analysis (see Figure 3). The individual samples were placed in casting moulds. A day before this, the moulds were half filled with the REICHHOLD POLYLITE 32032-00 casting resin and left to harden. The samples taken, along with identification number labels, were placed in the moulds prepared in this manner and, again, filled with the same resin type. The hardening process took 24 hours. The samples were then taken out of the moulds and ground using the MTH KOMPAKT 1031 grinders, MATERIALS TESTING HRAZDIL, using carborundum abrasive paper of two grain sizes (a grain size of 80 for the actual grinding at 450 rev/min to work the shape of the sample in the casting and a grain size of 1,000 for polishing at 250 rev/min).

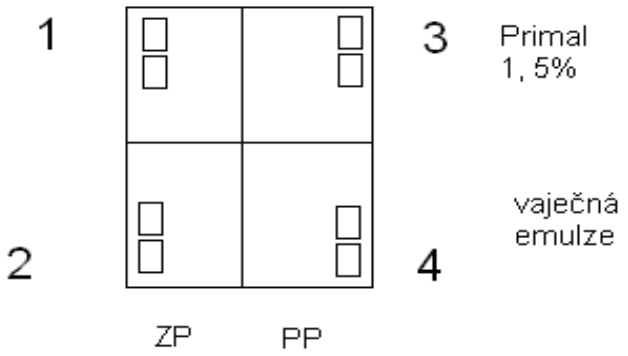


Fig. 2 Panel scheme – taking of samples following exposure in the climatic chamber

Rys. 2. Test panelowy – miejsca pobierania próbek przed komorą

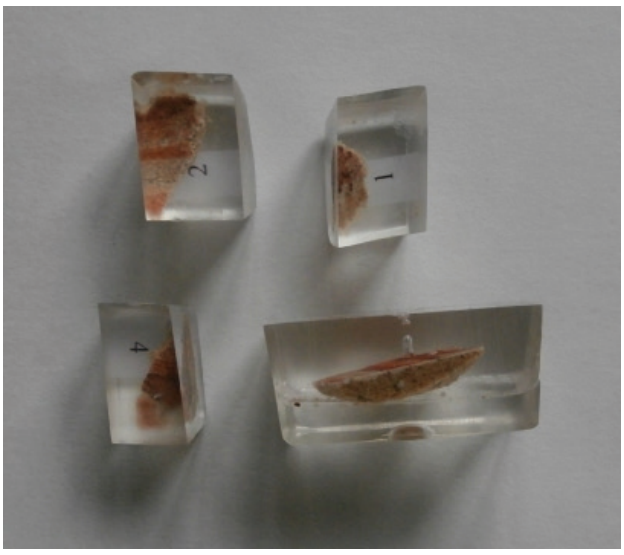


Fig.3 Polished sections of the samples.

Rys. 3 Szlif próbki

Microscopic analysis

Microscopic analyses were performed at the AVU laboratories in Prague using the LEICA DM LP material microscope, captured by the LEICA DFC 495 camera and processed using LAS software ver. 4.2. A digital photo was taken during each observation. The prepared sample in the casting (polished section) was placed on a laboratory glass, water was added to it and it was again covered with a laboratory glass. The samples were analysed in two types of light:

- VIS – the visible area – visible light – falling daylight,
- near-UV blue area, transmission cube – CUBE A, magnification: 10xPOL and 20x N PLAN.

The objective of the observation was to determine the stratigraphy of the colour layer for the purpose of confirming the ability of adhesion of the pigment to the ground layer. The scheme of the polished section for observation is explained in Figure 4.

The sample from polished section 1 contained the Sienna Kremer industrial pigment, bound by a natural binder – an egg yolk emulsion. Place on the panel from which the sample was taken – 4. The observation took place in VIS and in UV light (see Figures 5, 6).

The sample from polished section 2 contained the C.K.Birač pigment under examination, bound by a natural binder – an egg yolk emulsion. Place on the panel from which the sample was taken – 2. The observation took place in VIS and in UV light (see Figures 7, 8).

The sample from polished section 3 contained the Sienna Kremer industrial pigment, bound by a synthetic binder – Primal SF 016. Place on the panel from which the sample was taken – 3. The observation took place in VIS and in UV light (see Figures 9,10).

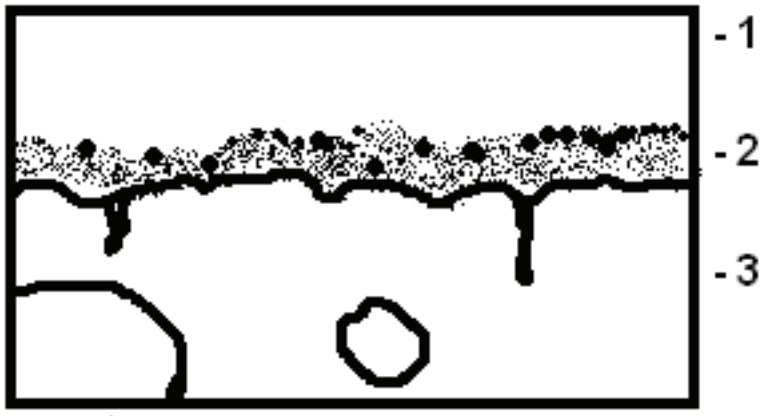
The sample from polished section 4 contained the pigment under examination, C.K.Birač and K.K.Třinec, bound by a synthetic binder – Primal SF 016. Place on the panel from which the sample was taken – 1. The observation took place in VIS and in UV light (see Figures 11, 12).

The ability of adhesion of the C.K.Birač and K.K.Třinec pigments under examination and the Sienna Kremer industrial pigment to the ground layer (the lime plaster) was confirmed.

In images taken in visible light, the filler (POLYLITE 32032) can be recognized in the top part; under this substance, it is possible to recognize the colour layer composed of a pigment mixed with the binder and the plaster substance can be recognized in the bottom part – see the scheme in Figure 4. The pigment under examination and the comparative industrial pigment were used in the colour surface layer. They were mixed with two binder types – a natural (egg yolk emulsion) and a synthetic binder (Primal SF 016).

Through observation in visible light, similarities in distribution, shape and adhesion of both the grains of the pigment under examination and the grains of the industrial segment were observed in all samples (see Figures 5, 7, 9 and 11). The types of the binder used cannot be identified through examination in visible light. UV light is used for these purposes. The synthetic binder fluoresces and shows as bright shining dots in the surface layer; a natural binder does not fluoresce. The pigment grains stay on the surface of the binder.

Observation in UV light confirmed the presence of a synthetic binder in the sample from polished section 3 of the Siena Kremer industrial pigment (see



1- filler
2- surface colour layer (pigment with the binder)
3- ground layer (lime plaster)

Fig. 4 Scheme of the polished section

Rys. 3 Schemat szlifu próbki

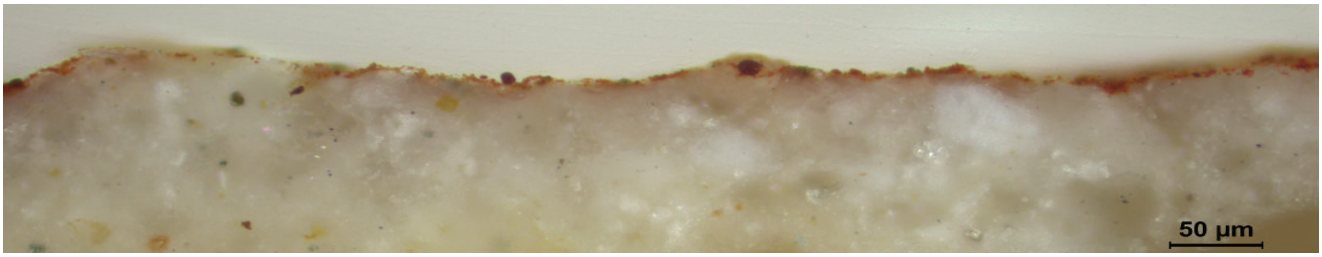


Figure 5: The industrial pigment Sienna Kremer, bound by a natural binder, observation in VIS

Rys. 5 Pigment przemysłowy Sienna Kremer, z naturalnym spoiwem, obserwacja w VIS

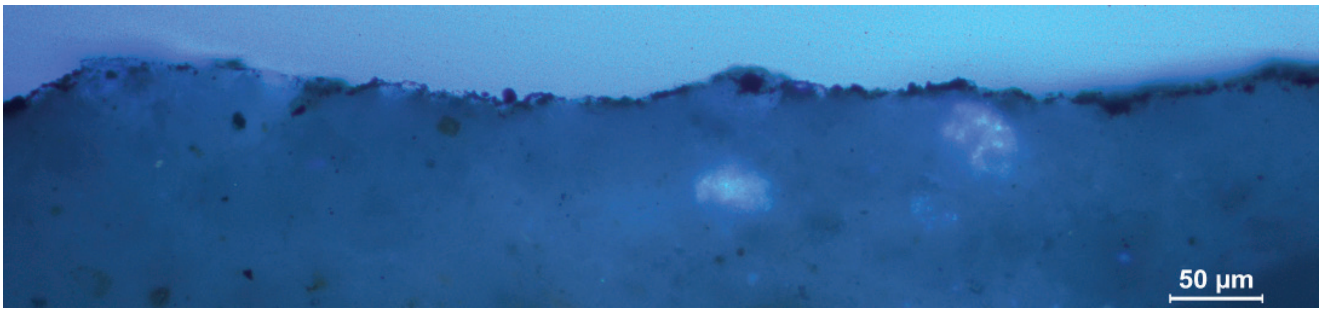


Fig. 6 The industrial pigment Sienna Kremer, bound by a natural binder, observation in UV

Rys. 6 Pigment przemysłowy Sienna Kremer, z naturalnym spoiwem, obserwacja w UV

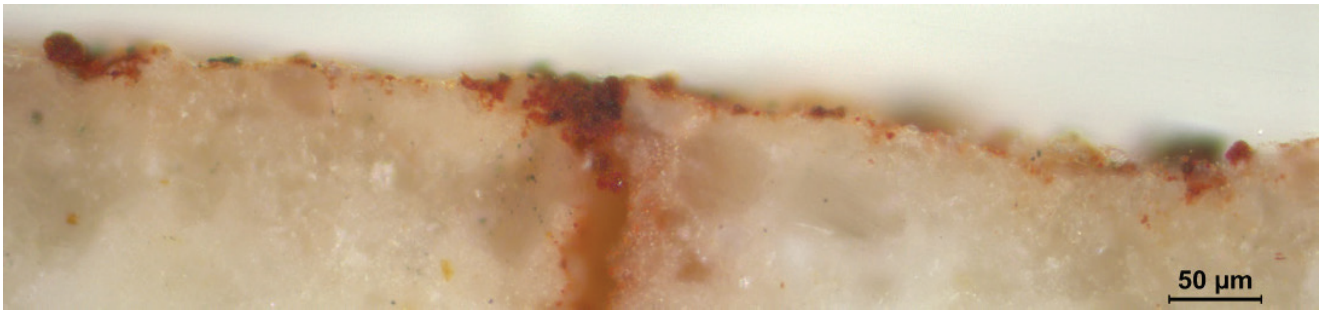


Fig. 7 The examined pigment C.K.Birač, bound by a natural binder, observation in VIS

Rys. 7 Badany pigment C.K.Birač, spoiwo naturalne, badanie w VIS

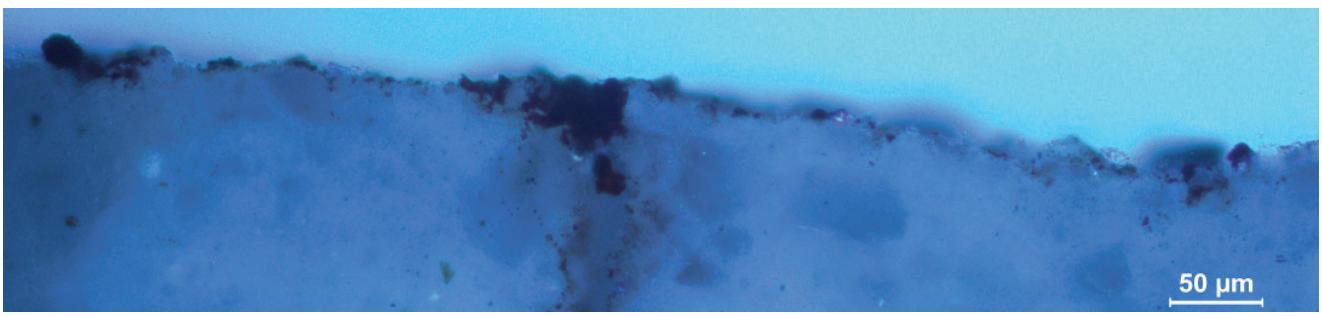


Fig. 8 The examined pigment C.K.Birač, bound by a natural binder, observation UV

Rys. 8 Badany pigment C.K.Birač, spoiwo naturalne, badanie w UV

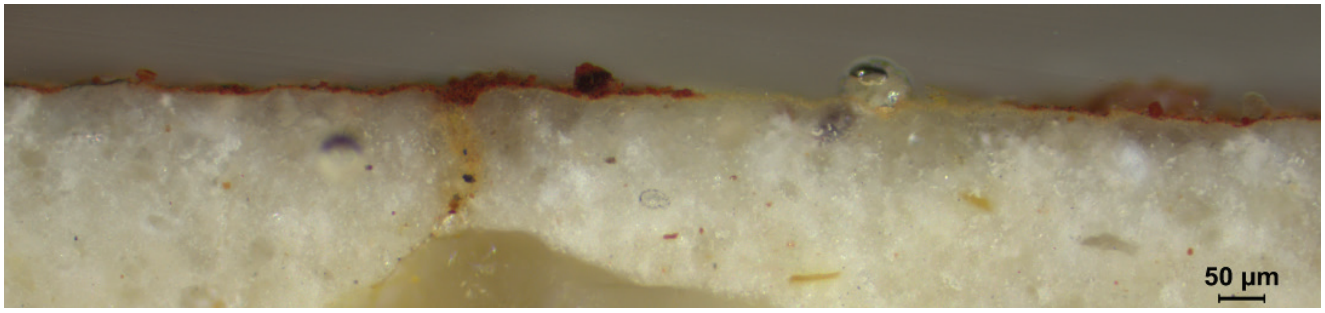


Fig. 9 The industrial pigment Sienna Kremer, bound by a synthetic binder, observation in VIS

Rys. 9 Pigment przemysłowy Sienna Kramer, spoiwo naturalne, badanie w VIS

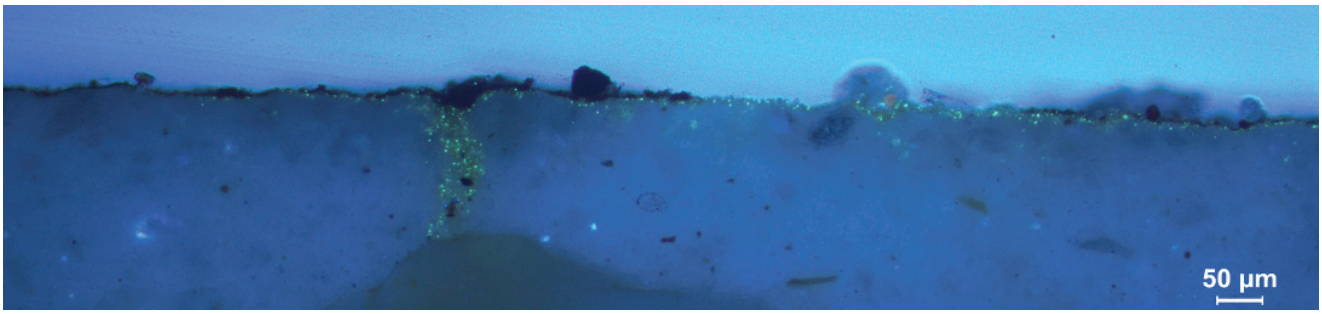


Fig. 10 The industrial pigment Sienna Kremer, bound by a synthetic binder, observation in UV

Rys. 10 Pigment przemysłowy Sienna Kramer, spoiwo naturalne, badanie w UV

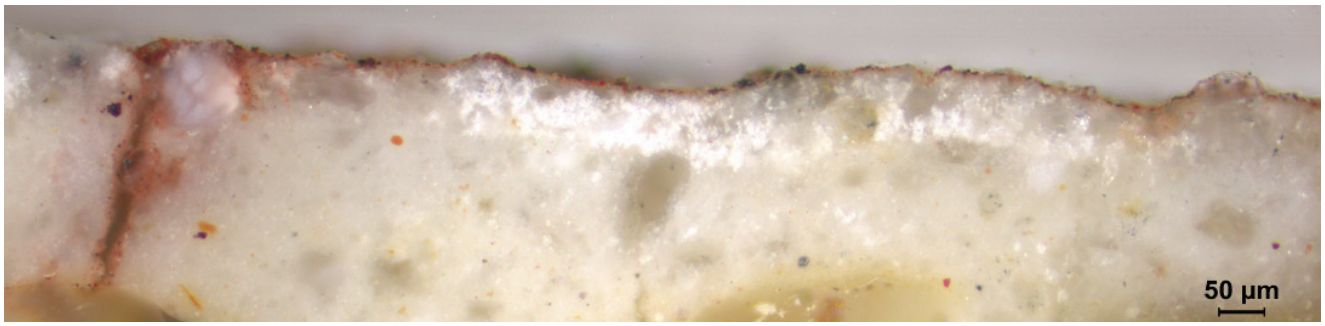


Fig.11 The examined pigments C.K.Birač, K.K.Třinec, bound by a synthetic binder, observation in VIS

Rys. 11 Badane pigmenty C.K.Birač, K.K.Třinec, spoiwo syntetyczne, badane w VIS

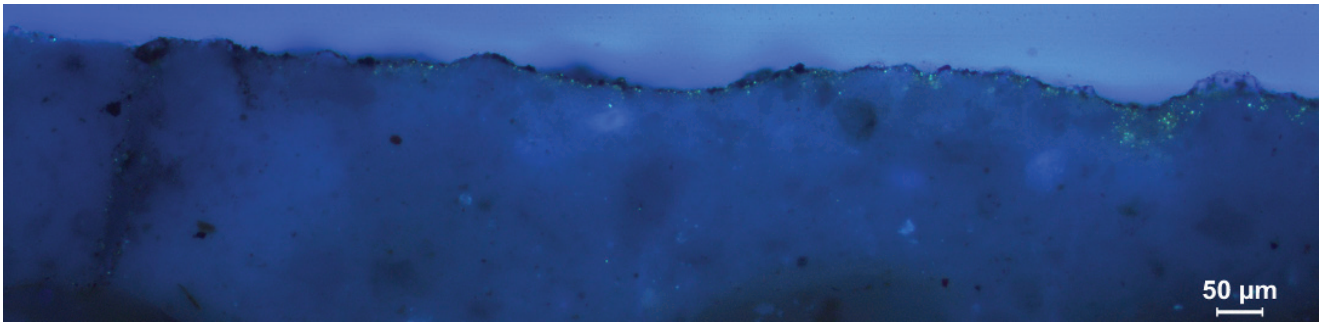


Fig. 12 The examined pigments C.K.Birač, K.K.Třinec, bound by a synthetic binder, observation in UV

Rys. 12 Badane pigmenty C.K.Birač, K.K.Třinec, spoiwo syntetyczne, badane w UV

Figure 10) and in the sample from polished section 4 of the C.K.Birač, K.K.Třinec pigments under examination (see Figure 12). The remaining samples did not fluoresce in UV light, which confirmed the presence of a natural binder.

Infrared and Raman spectroscopy

The analyses were conducted at the molecular spectrometry laboratories of the Prague Institute of Chemical Technology (VŠCHT). Red iron-based inorganic pigments were analysed. As regards the samples of pure pigments, the spectrums were measured using infrared spectroscopy and Raman spectroscopy. As regards the samples of the pigments used in the paint, the analysis focused on the stability of the pigment grains using Raman spectroscopy.

Infrared spectroscopy was performed using the Nicolet 6700 FTIR spectrometer (Thermo-Nicolet, USA) in connection with the GladiATR single-reflection diamond ATR accessory, reflectance measurement, DTGS detector, measurement parameters: spectrum range: 4000-400 cm^{-1}, resolution: 4 cm^{-1}, number of spectrum accumulations: 64, Happ-Genzel apodization.

Raman microspectroscopy was performed using the Nicolet DXR dispersion Raman microscope (Thermo Scientific, USA), equipped with the Olympus confocal microscope. A laser with a wavelength of 532 nm and an input power of 10 mW was used as the excitation source. The samples were measured at a 100% capacity of the laser, the duration of a pulse was 5 seconds and there was 1 spectrum accumulation. These parameters prevent the sample from suffering thermic damage. A dispersion grating with 900 grooves/mm and a 50µm pinhole was used. A multichannel air-cooled CCD camera served as the detector. A microscope objective with 50x magnification and a long working distance was used for the measurement.

The spectrums were computer processed using Omnic 8.0 (Nicolet Instruments Co., USA) and identified using the spectrum library of VŠCHT Prague.

Analyses of powder preparations of the pure pigments

Samples of pure powder preparations of the pigments were analysed before their application in the paint on the lime ground.

Sample 051112/2 Kremer natural sienna – this was an industrial powder pigment (Sienna Kremer) that was used for a comparison with the pigments under examination, i.e. C.K.Birač (red sludge generated by bauxite processing) and K.K.Třinec (converter sludge from Třinec) before its subsequent application in the paint on a lime ground.

Sample 051112/5 C.K.Birač – this was a powder preparation of the pigment under examination (C.K.Birač – red sludge generated by bauxite processing) that was used for a comparison with the Sienna Kremer industrial pigment before its subsequent application in the paint on a lime ground.

Sample 051112/6 K.K.O.Třinec – this was a powder preparation of the pigment under examination (K.K.Třinec – converter sludge from Třinec) that was used for a comparison with the Sienna Kremer industrial pigment before its subsequent application in the paint on a lime ground.

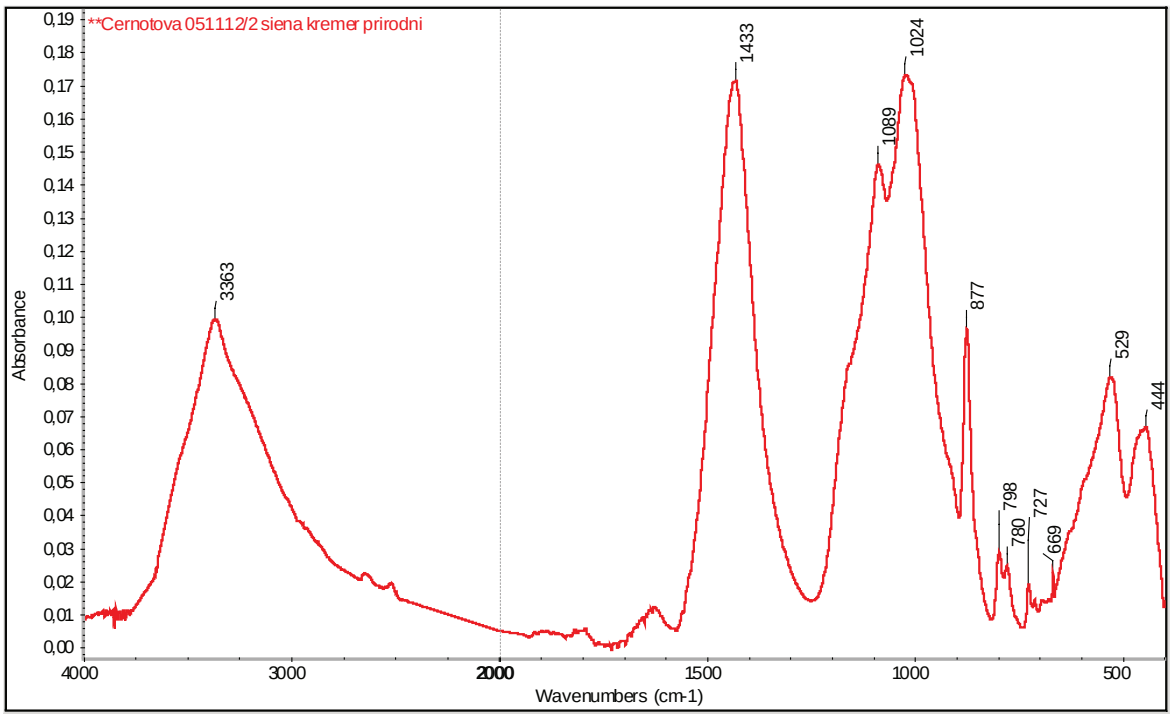
The results of analyses for the individual samples of the pure powder pigments before their application in the paint on the test panel with a lime plaster are shown in the following Graphs 1 - 6.

- 051112/2 Kremer natural sienna – the pigment sample is composed of hydrated aluminosilicate (3363, 1089 cm-1), silicon dioxide (1024, 798, 780 cm-1) and calcium carbonate. The characteristic spectrums are shown in Graphs 1 and 2.
- 051112/5 C.K.Birač – based on the analyses performed, the presence of aluminosilicate and hematite was identified in the sample. The characteristic spectrums of the sample resulting from the measurements are shown in Graphs 3 and 4.
- 051112/6 K.K.O.Třinec - the presence of calcium sulphate dihydrate mixed with aluminosilicate was identified in the sample using infrared spectroscopy. Raman spectroscopy identified the presence of hematite in the sample. The spectrums resulting from the measurement are shown in Graphs 5 and 6.

The industrial pigment designated as Sienna Kremer is composed of hydrated aluminosilicate, silicon dioxide and calcium carbonate. Based on an analysis of red iron-based inorganic pigments, the presence of hematite was identified in the pigments under examination before their use in the paint. Analyses of the pigment under examination designated as C.K.Birač (red sludge generated by bauxite processing) identified the presence of aluminosilicate and hematite in the sample. Hematite and calcium sulphate dehydrate mixed with aluminosilicate were also identified in the pigment sample under examination designated as K.K.Třinec (converter sludge).

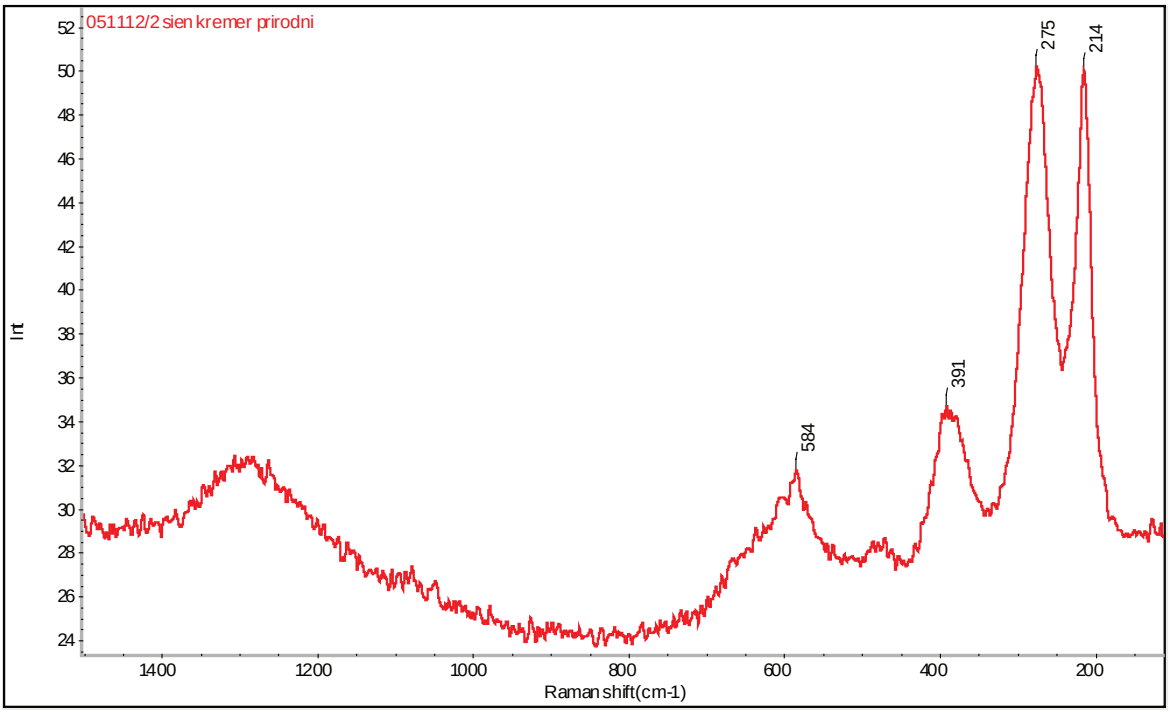
Analyses of samples of the pigments used in the paint

Samples of the pigments used in the secco paint were analysed; they contained a colour layer and a ground layer. Sample 1 contained the examined pigment bound with a synthetic binder from the test panel



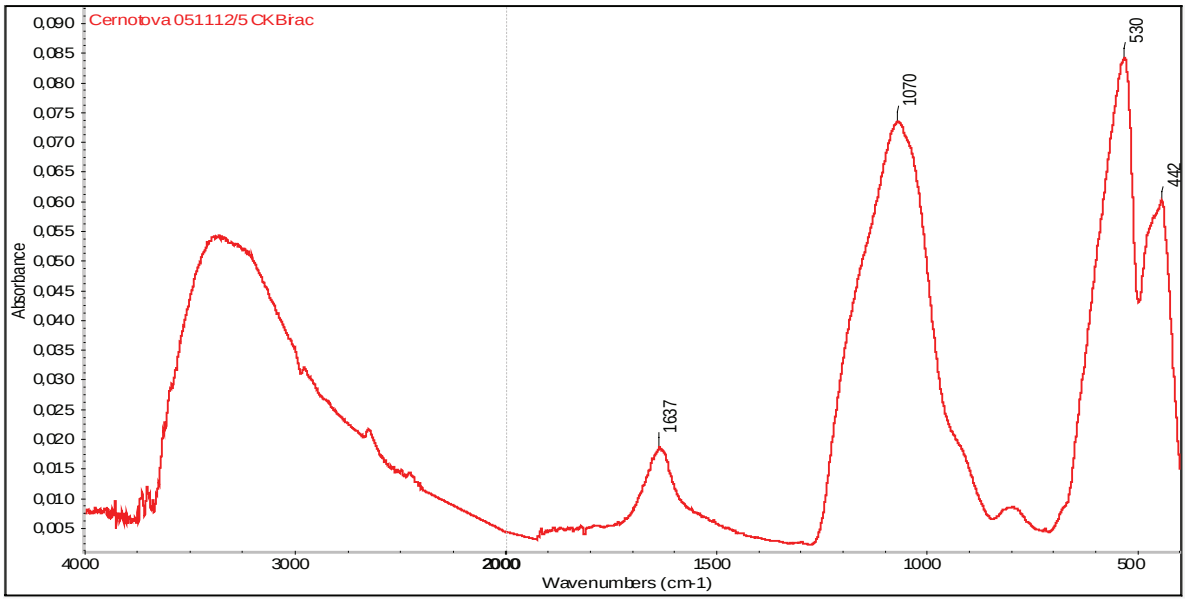
Graph 1 IR spectrum of the sample 051112/2 Kremer natural sienna

Graf. 1 Spektroskopia IR, próbka 051112/2 Kremer siena naturalna



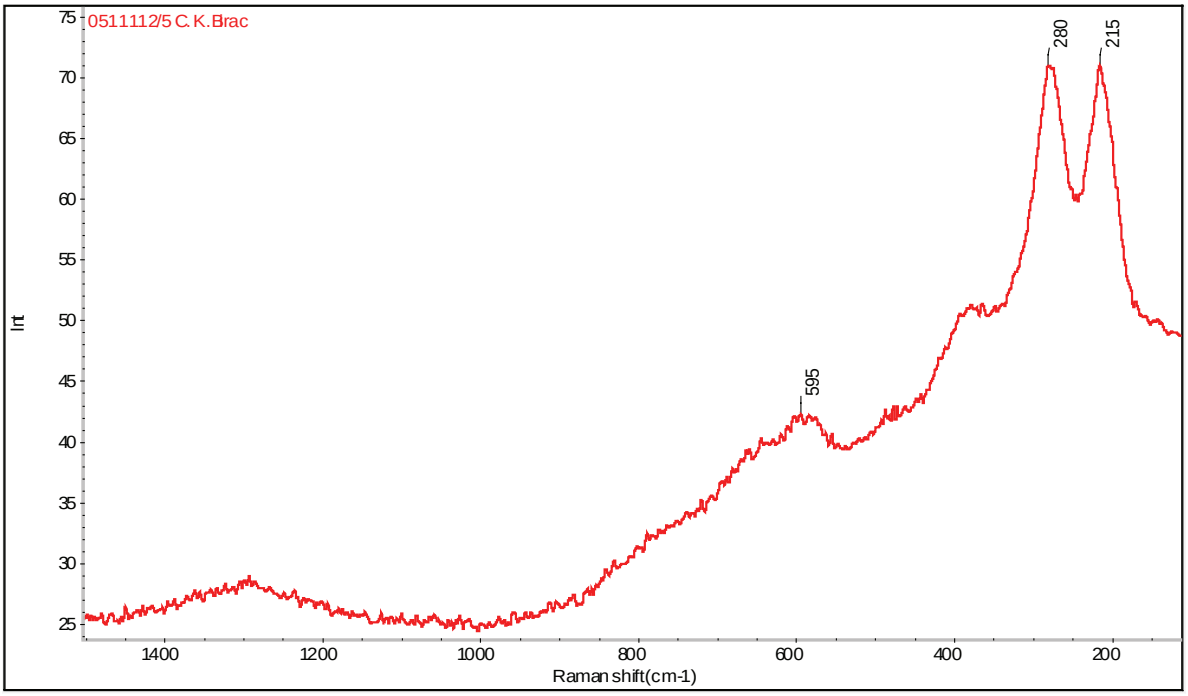
Graph 2 The Raman spectrum of the sample 051112/2 Kremer natural sienna

Graf. 2 Spektroskopia ramana, próbka 051112/2 Kremer siena naturalna



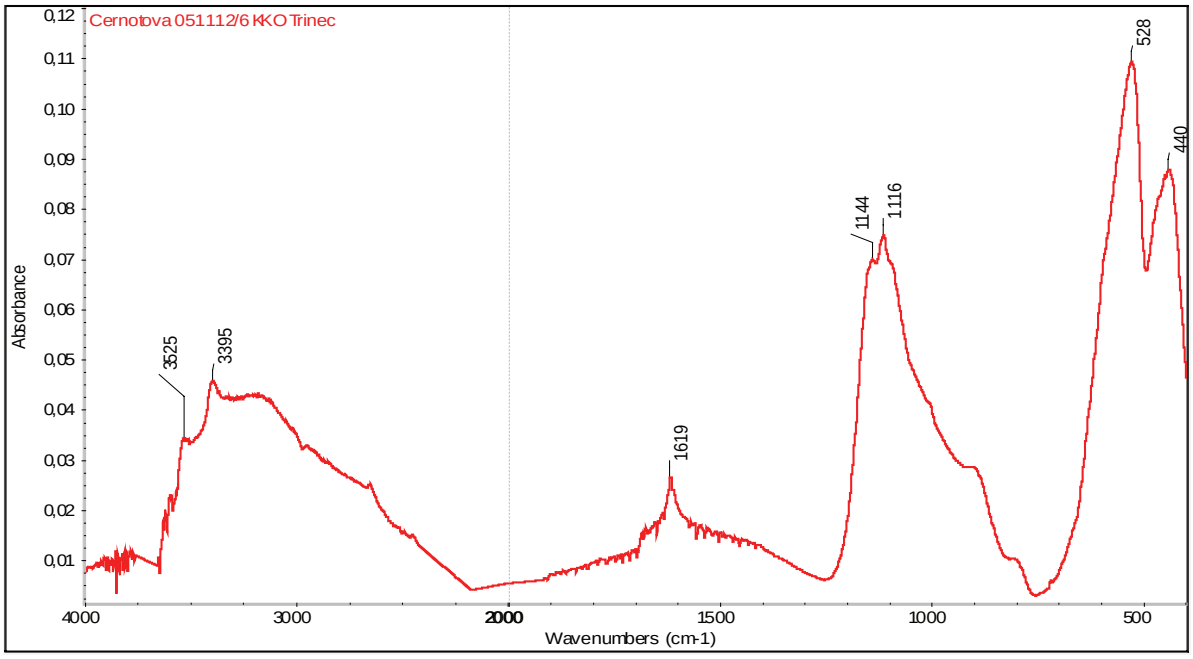
Graph 3 IR spectrum of the sample 051112/5 C.K.Birač

Graf. 3 Spektroskopia IR, próbka 051112/5 C.K.Birač



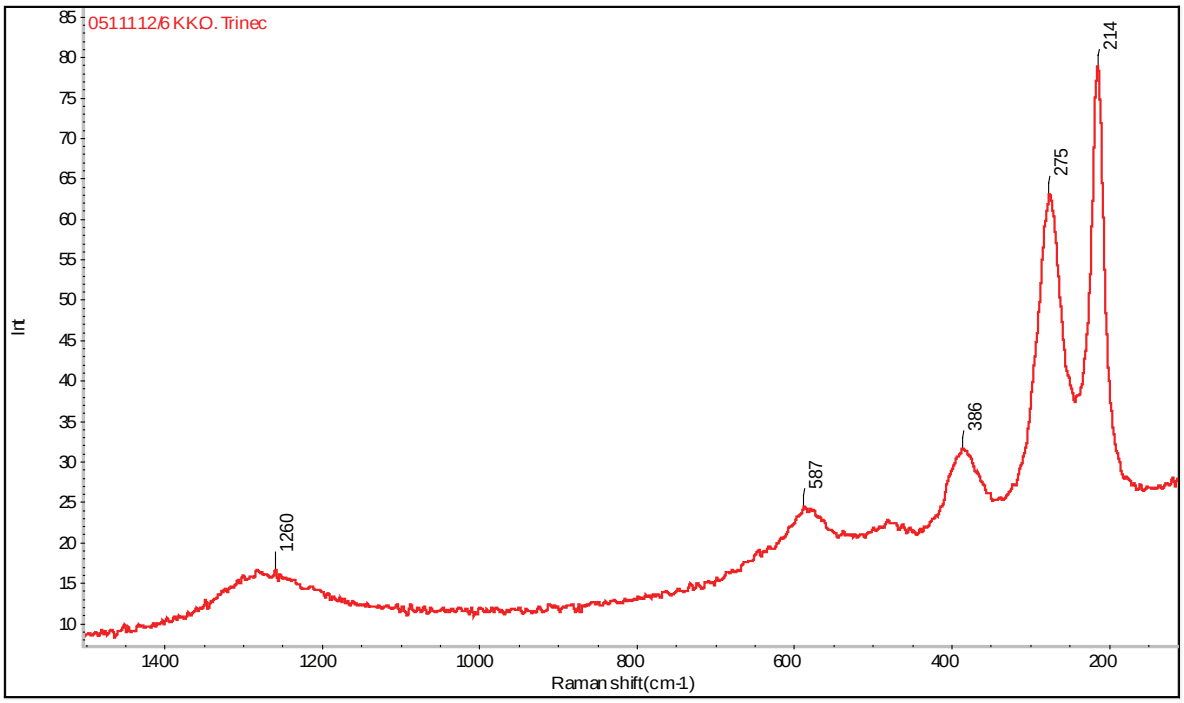
Graph 4 The Raman spectrum of the sample 051112/5 C.K.Birač

Graf. 4 Spektoskopia Ramana próbka 051112/5 C.K.Birač



Graph 5 IR spectrum of the sample 051112/6 K.K.O.Třinec

Graf. 5 Spektroskopia IR próbki 051112/6 K.K.O.Třinec



Graph 6 The Raman spectrum of the sample 051112/6 K.K.O.Třinec

Graf. 6 Spektroskopia Ramana próbki 051112/6 K.K.O.Třinec

(place from which the sample was taken: 1). Sample 2 contained the examined pigment bound with a natural binder from the test panel (place from which the sample was taken: 2). Sample 3 contained the industrial pigment bound with a synthetic binder from the test panel (place from which the sample was taken: 3). Sample 4 contained the industrial pigment bound with a natural binder from the test panel (place from which the sample was taken: 4).

The samples of the pigments used in the paint were measured using Raman spectroscopy. The general trivial designation of the shade spectrum of the pigment samples for the analyses performed using Raman spectroscopy is explained in the following Table 1.

The Raman spectrum of the dark brown shade for samples 051112/2 Kremer natural sienna and 051112/6 K.K.O.Třinec, bound with a synthetic or natural binder and used in the paint on a lime ground, is shown in Graph 7. The legend for Graph 7 is contained in the following Table 2.

The Raman spectrum of the bole shade for samples 051112/2 Kremer natural sienna and 051112/5 C.K.Birač, bound with a synthetic or natural binder and used in the paint on a lime ground, is shown in Graph 8. The legend for Graph 8 is contained in the following Table 3.

The standard Raman spectrum of hematite is shown in Graph 9 and the standard Raman spectrum of calcite is shown in Graph 10. The samples might have contained further components whose concentration was below the detection threshold of the selected method or whose absorption bands are situated beyond the selected spectrum range of the analysis (e.g., oxides, sulphides, halides, etc.)

The analysis of the pigments used in the paint focused on particles corresponding to the red pigments used in the individual colour shades that were designated as dark brown and bole in the general trivial designation of the shade spectrum of the samples of pure pigments. All of the pigments under examination contained Fe_2O_3 in the form of hematite. A comparison of the individual shades in terms of aging or the binder used showed that there had not been any significant spectrum changes of the pigments following their use in the paint. It can be inferred from the spec-

Tab. 1 The general trivial designation of the shade spectrum of the pigment samples

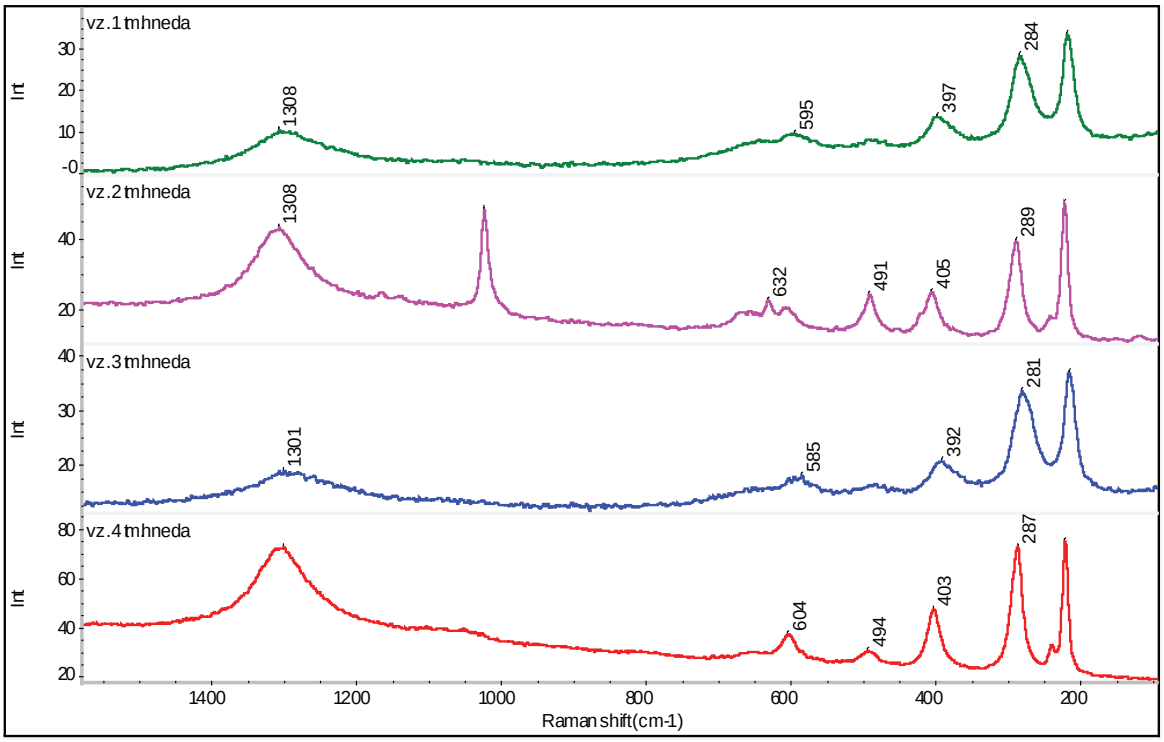
Tab. 1 Oznaczenie widma próbek pigment

Trivial designation of the shade	Description	Industrial pigment	Examined pigment
dark brown	samples of dark brown	051112/2 Kremer natural sienna	051112/5 C.K.Birač, 051112/6 K.K.O.Třinec
bole	samples of dark red	051112/2 Kremer natural sienna	051112/5 C.K.Birač

Tab. 2 Legend for Graph 7 of the Raman spectrums of the shade of the samples – dark brown

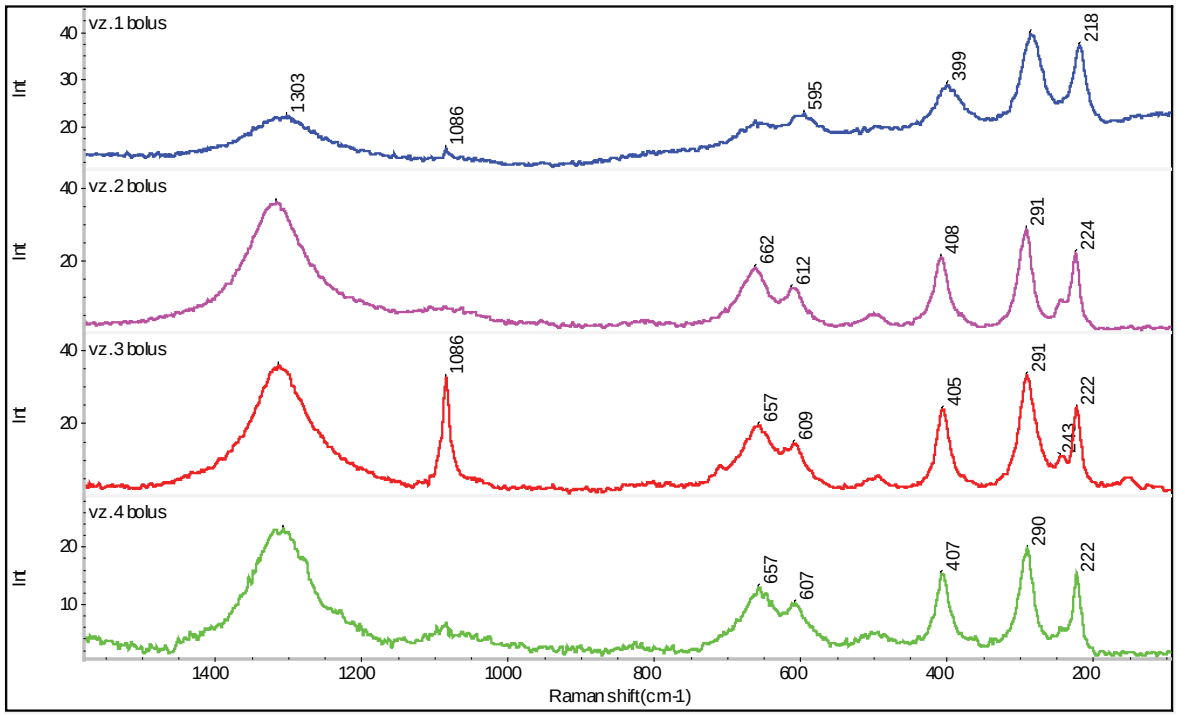
Tab. 2 Legenda na wykresie 7 z widm Ramana - ciemny brąz

Designation of the sample	Industrial pigment	Examined pigment	Synthetic binder	Natural binder
s.1 dark brown		051112/6 K.K.O.Třinec	✓	
s.2 dark brown		051112/6 K.K.O.Třinec		✓
s.3 dark brown	051112/2 Kremer natural sienna		✓	
s.4 dark brown	051112/2 Kremer natural sienna			✓



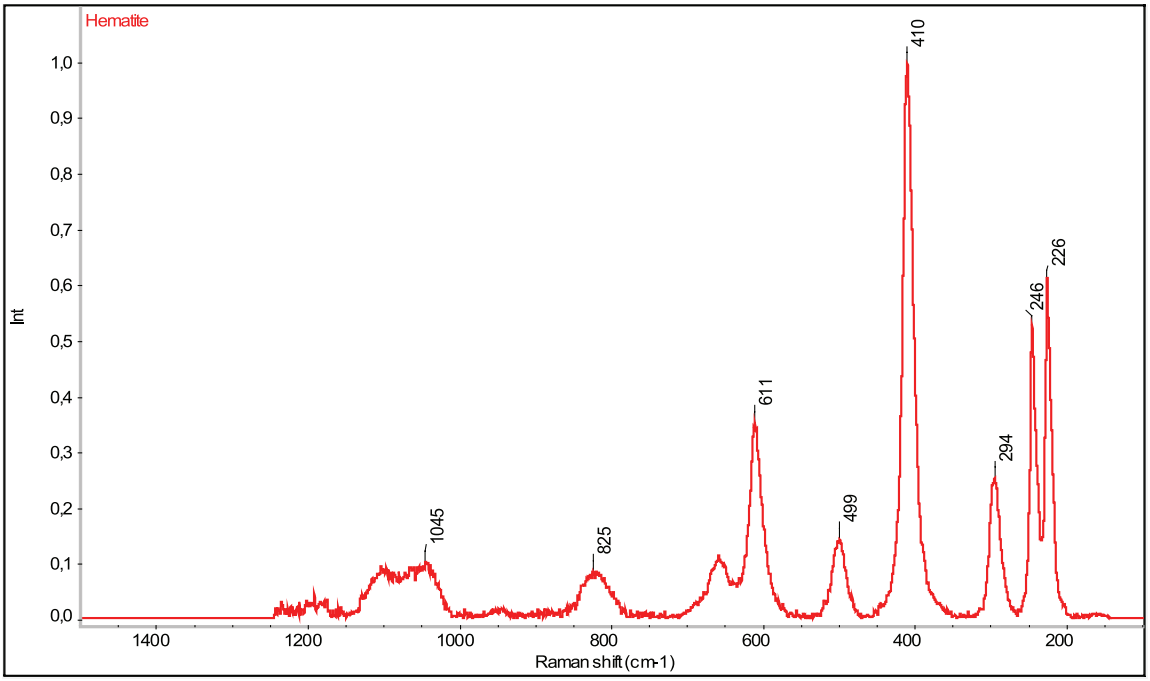
Graph 7 The Raman spectrums of the shade of the samples – dark brown

Graf. 7 Spektrum Ramana widma próbki – ciemno brązowy



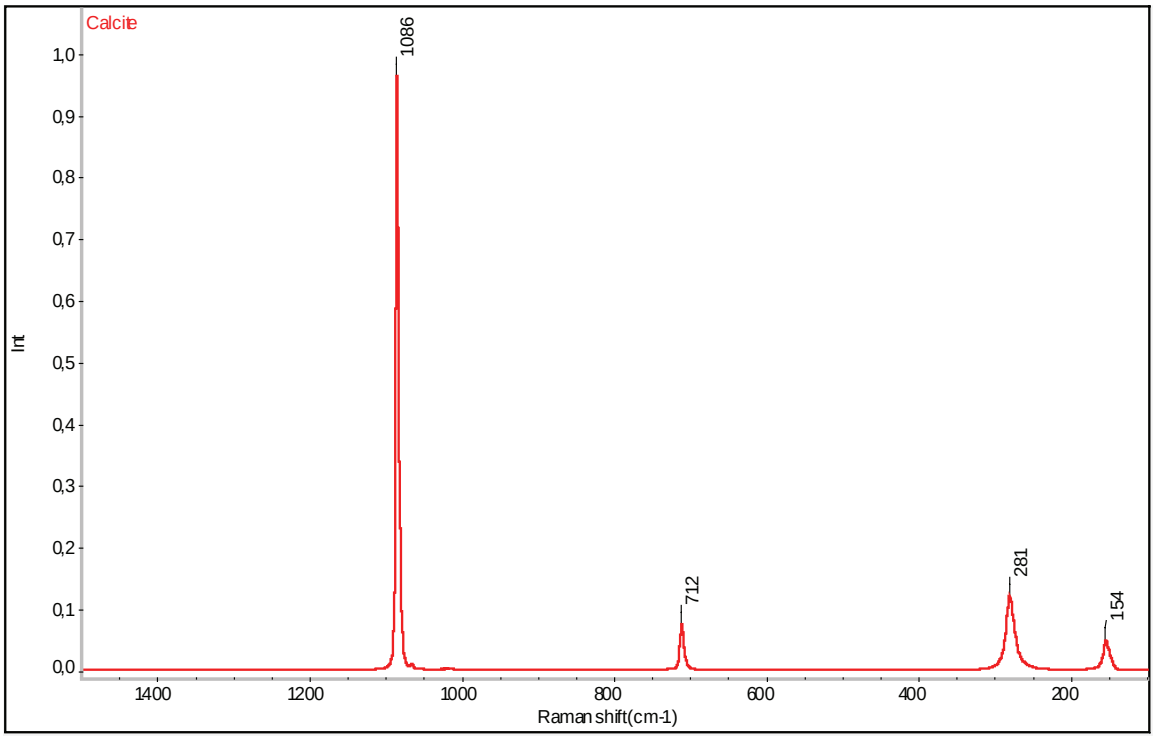
Graph 8 The Raman spectrums of the shade of the samples – bole

Graf. 8 Widmo ramanowskie szlifu próbki



Graph 9 The standard Raman spectrum of hematite

Graf. 9 Widmo ramanowskie próbki hematytu



Graph 10 The standard Raman spectrum of calcite

Graf. 10 Widmo ramanowskie szlifu próbki kalcytu

Tab. 3 Legend for Graph 8 of the Raman spectrums of the shade of the samples – bole

Tab. 3 Legenda na wykresie 8 widm Ramana - bole

Designation of the sample	Industrial pigment	Examined pigment	Synthetic binder	Natural binder
s.1 bole		051112/5 C.K.Birač	✓	
s.2 bole		051112/5 C.K.Birač		✓
s.3 bole	051112/2 Kremer natural sienna		✓	
s.4 bole	051112/2 Kremer natural sienna			✓

trums resulting from the measurements that neither a different environment nor aging has any influence on the pigment particles.

The above analyses of changes in the physical and chemical properties of the pigments under examination, namely the pigments from red sludge (C.K.Birač) and converter sludge (K.K.Třinec), following their application on a test panel, have confirmed that these pigments can be used for artistic purposes. It has been confirmed that these pigments are able to compete with industrial pigments and also that these secondary raw materials can be utilized and recycled.

Literatura - References

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Streszczenie

Celem badań jestsprawdzenie mozliwości wykorzystania wybranych odpadów – czerwonego szlamu i odpadów konwertorowych jako pigmentu oraz porównanie pigmentów z pigmentami handlowymi.

Dwa rodzaje odpadów zostały wytypowane do badań. Kryterium było uzyskanie koloru, dostepność wykazane we wcześniejszych badaniach. Badania obejmowały czerwony szlam pochodzacy z zakładu Birač Alumina Industry (BH) i szlam konwertorowy z huty Třinecké železárny a.s.

Badnia obejmowały badanie efektywności rozdrobnienia pigmentu i jego zastosowanie w malarstwie ściennym na testowym panelu, badanie w komorze starzenia , porównanie z pigmentem handlowym w wykorzystaniem mikroskopii skaningowej, spekrtometrii w podczerwieni oraz ramanowskiej.

Słowa kluczowe: utylizacja odpadów, malarstwo ścienne, pigmenty, czerwony szlam Al, odpady konwertorowe, panel testowy