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Investigation of the technique of painting on a tin alloy plate

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A detailed investigation of a rare painting, *Madonna with Child*, preserved at the Lithuanian National M. K. Čiurlionis Museum of Art has been performed. By combining the analytical methods, the pigments, binding media, components of varnish, the metal plate alloy were identified. By the FAAS method it has been determined that the painting support is made of a tin (92.75%) alloy containing a small amount of lead (5.22%). On the basis of FTIR and SEM / EDX analysis results, we determined the pigment and the binding medium of the painting ground and described the composition of the greenish brown and red paints. The lead white, cinnabar, azurite and smalt pigments were identified. The optical microscopic examination of painting cross-section showed that the reason for the viridescence and rustiness of the layer of blue paint, observed visually, is mainly the yellowing of the binder and varnish layers. The structure of the painting provided an important information on the technological features of painting on a tin alloy plate.

Key words: painting, metal support, pigment, FTIR, optical microscopy, SEM / EDX

INTRODUCTION

This paper presents results of the analysis of a rare painting, *Madonna with Child* (Mt-1506, 36.4 × 29 cm), on a tin plate, preserved at the Lithuanian National M. K. Čiurlionis Museum of Art (Fig. 1). This painting was created by an unknown seventeenth-century (?) painter. From the literature sources [1–4] it is known that small-size paintings on metal appeared in the middle of the 16th century and soon became popular in the entire Europe. Paintings of a larger size appeared only at the end of the 16th century when rolls came into use. They depicted different genre scenes, portraits, religious and mythological subjects on a landscape background. In the 19th century, this painting technique became very rare. Usually, painters used copper and iron, sometimes silver or golden supports. For painting, tin as well as a tin and lead alloy were rarely used. This study is a pioneering work designed to enhance our knowledge of the technological features of painting on tin alloy supports.

The methods of atomic absorption spectroscopy (AAS) [5, 6], infrared spectroscopy (FTIR) [7–9], optical microscopy and scanning electron microscopy (SEM), coupled with an energy dispersive X-ray spectrometer (EDX) [10–12] were used to determine the technological features of the painting on a tin plate, as well as the reasons for changes of the painting's blue colour.

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EXPERIMENTAL

In order to characterize the composition of the metal support, a flame atomic absorption analysis (FAAS) was performed. The pigments of the ground and the paint layers were characterised by preliminary microchemical spot tests, FTIR, and a stratigraphic analysis using an optical microscope, and the energy-dispersive X-ray analysis with a system integrated into the SEM.

The quantative analysis of the metal alloy of the support plate was performed by the FAAS method. For this purpose, the Hitachi 170–50 atomic absorption spectrometer was used. The FAAS analysis of each metal was performed under optimal detection conditions (Table 1).

For the analysis, 0.0200 g of the alloy was dissolved by heating it in a concentrated mixture of nitric and hydrochloric (1 : 3) acids, evaporated to the wet state of the salt which was then dissolved by adding 10 ml of concentrated hydrochloric acid. The resulting solution was boiled to a half of its volume and diluted with bidistilled water to 25 ml. Then, the atomic absorption of metals was measured and the amount

Fig. 1. Unknown painter. *Madonna with Child.* 17th century (?). Lithuanian National M. K. Čiurlionis Museum of Art. Metal plate, oil, 36.4 × 29 cm, Mt-1506

Table 1. **Conditions of metal determination by the FAAS method**

Conditions of metal determination						
Metal	**Wavelength, nm**	**Current strength, mA**	**Gas**	**Gas pressure, Pa · 10^{-4}**	**Linearity interval, µg/ml**	**Detection limit, µg/ml**
Pb	283.3	10	$C_3H_8 + C_4H_{10}$	0.98	0.1–4.0	0.03
Sn	224.6	15	C_2H_2	3.43	1.0–10.0	0.25
Sb	217.6	15	C_2H_2	3.43	1.0–10.0	0.35
Cu	324.8	10	$C_3H_8 + C_4H_{10}$	0.98	0.05–2.5	0.01
Ni	232	10	C_2H_2	3.43	0.25–4.0	0.09
Fe	248.3	15	$C_3H_8 + C_4H_{10}$	0.98	0.2–4.0	0.07

of a respective metal in the alloy was calculated using calibrating curves.

Infrared spectra of the samples of the painting ground, paint layers and the standards of pigments (Kremer Pigmente GmbH & Co. KG, Germany) were recorded using the FT-IR-8400S spectrophotometer (SHhimadzu) connected to the IR AIM-8800 microscope and a detector MCT. Different spectra were registered under the following conditions:

- a sample mixed with KBr and pressed into a pellet, using the MHP-1 manual minipress: the spectrum interval ranged from 4000 to 400 cm^{-1}, 100 scans in total, 4 cm^{-1} resolution;
- a sample pressed under a P / N0045-434 diamond cell: the spectrum interval ranged from 4000 to 720 cm^{-1}, 200 scans in total, 4 cm^{-1} resolution.

Samples were prepared under the microscope. The ground was separated from the paint layer mechanically.

The components of greenish brown and red paint layers were analysed by performing a stratigraphic analysis of a sample, using an optical microscope (visible and UV light) and the SEM / EDX method. Small samples of paints were fixed in epoxy resin and polished across the paint layers. The following equipment was used for the analysis of paint samples:

– the XL 30 CP (Philips) scanning electron microscope connected to SEM and EDX detectors and the voltage ranging from 1 to 30 keV;

– the Olympus BX40 optical microscope.

RESULTS AND DISCUSSION

FAAS analysis

Results of analysis of the metal alloy of the painting support are presented in Table 2. According to the data obtained, the painting support is made of a tin (92.75%) alloy containing a small amount of lead (5.22%). The thickness of the painting support is uneven and fluctuates between 1.5 and 2.7 mm. It is known [1, 13] that soft alloy supports used to be molded on the surface of a polished stone by spreading it to the desired format and thickness. The composition of such alloys used for painting supports can be very different; however, usually lead makes up to 30% of the whole alloy. From this point of view, the painting under consideration is quite unique.

Table 2. **Results of metal determination in the painting support alloy by the FAAS method**

Metal	Metal, %
Pb	5.22
Sn	92.75
Sb	0.75
Fe	0.21
Cu	0.042
Ni	0.035

FTIR spectroscopy

The painting ground, the greenish brown paint (from the mantle of Madonna's right arm) as well as the red paint (from the drapery of Madonna's red cloak) were examined using FTIR analysis. The IR spectra of the painting ground and of the standard lead white ($2PbCO_3 \cdot Pb(OH)_2$) pigment are presented in Fig. 2. Sharp absorption bands in both spectra at 3538 cm^{-1} (O–H bond vibrations), at 1431 cm^{-1} (C–O stretching vibrations) and at 839 cm^{-1} (C–O deformation vibrations) [14] are clearly present and coincide well enough. Thus, it can be concluded that the painting ground contains the lead white pigment. The IR spectrum of the painting ground shows rather intensive absorption bands at 2923 cm^{-1} and at 2850 cm^{-1}, characteristic of C–H stretching vibrations, as well as absorption bands at 1722 cm^{-1} characteristic of the ester carbonyl C = O stretching vibrations. These absorption bands are attributable to the vibrations of the oil functional group of the ground binding medium. Other characteristic absorption bands assigned to the oils in the areas of lower frequencies (1653, 1460, 1238, 1163, 1099, 726 cm^{-1}) are overlapped by the absorption bands of stretching and deformational vibrations characteristic of the functional groups of the white lead pigment.

On the basis of these FTIR analysis results, we conclude that the pigment of the painting ground is lead white, whereas the binding medium is oil.

The IR spectra of the greenish brown paint, standard azurite ($2CuCO_3 \cdot Cu(OH)_2$) and standard smalt ($CoO \cdot K_2SiO_3$) pigments are presented in Fig. 3. The IR spectrum of the greenish brown paint clearly demonstrates the main sharp absorption bands and peaks that coincide with the absorption bands of standard azurite and smalt pigments provided for comparison. The intensive sharp-shaped absorption band at 3425 cm^{-1} coincides completely with the characteristic absorption band of azurite (belonging to the hydroxylic group) in this area, both by its shape and intensity. Moreover,

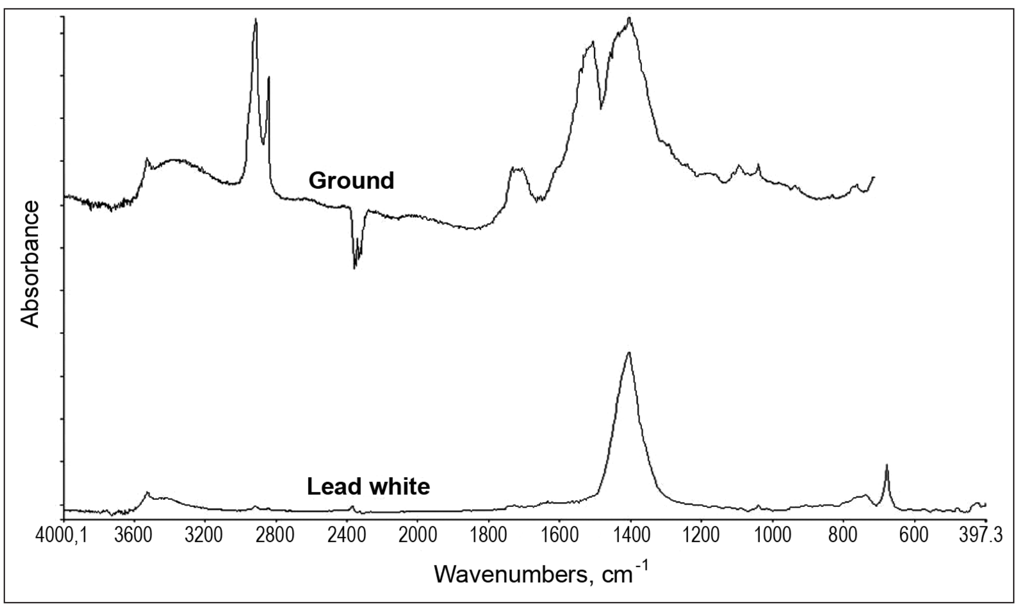

Fig. 2. FTIR spectra of the painting ground sample and the standard lead white pigment

the rather intensive absorption band with its maximum at 1415 cm^{-1} corresponds to C–O stretching vibrations of azurite, whereas the sharp peak at 835 cm^{-1} corresponds to C–O deformational vibrations of azurite. Besides, the spectrum contains a sharp absorption band of O–H deformational vibrations at 952 cm^{-1}, which is characteristic of hydrated carbonates. In the IR spectrum of the greenish brown paint, a rather wide and intensive absorption band at 1077 cm^{-1} can be attributed to Si–O stretching vibrations of smalt, despite the fact that azurite has a low intensity peak at 1090 cm^{-1} assigned to the carbonaceous group. The characteristic bands of the lead white pigment, identified by the microchemical analysis of the greenish brown paint, are not highlighted at 1431, 839, and 678 cm^{-1} [15] since they are overlapped by the absorption bands and peaks of azurite and smalt. Also, based on the minor doublet absorption band between 2922 and 2848 cm^{-1} as well as the asymmetric absorption band at 1709 cm^{-1}, it can be assumed that the binding medium of paint is oil.

When identifying the blue azurite ($2CuCO_3 \cdot Cu(OH)_2$) and green malachite ($CuCO_3 \cdot Cu(OH)_2$) pigments that have a similar chemical composition, it is very important to observe the longer waves of the IR spectrum exceeding 600 cm^{-1}. In such areas, absorption bands characteristic of Cu–O stretching and deformational vibrations can be observed. These bands differ depending on the pigment's composition [16]. The IR spectrum of the greenish brown paint shows Cu–O stretching vibrations characteristic of azurite at 493 cm^{-1} and 453 cm^{-1}.

Based on the FTIR analysis results, it can be concluded that the greenish brown paint contains azurite and smalt pigments; however, the presence of the lead white pigment identified by the microchemical analysis is not reflected at all.

A red paint sample was prepared in order to obtain the IR spectrum of the red organic pigment included in the translucent layer. However, it was impossible to separate mechanically a very thin translucent layer of paint from the covering layer of varnish. Therefore, the obtained IR spectrum of the paint layer, recorded by pressing the sample with a diamond cell, was compared to the IR spectra of possible materials in the varnish layer (dammar, mastic, rosin, shellac, gum arabic and other). The IR spectra of the red paint and its analogue standard rosin and gum arabic are presented in Fig. 4. The absorption bands and peaks found in the IR spectrum of the red paint are attributable to varnish materials. These materials include natural rosin (the characteristic absorption band at 1710 cm^{-1}, carboxylic C = O stretching vibrations) and natural gum arabic (the characteristic absorption band between 2965–2880 cm^{-1} and 1415–1380 cm^{-1}, CH_3 and CH_2 vibrations) which by its chemical composition is similar to other natural hydrocarbons such as plum, cherry and other gums. Based on the data obtained, the authentic varnish cannot be exactly specified. Because in the 18th century for the restoration of paintings a varnish compound of rosin and natural hydrocarbons was used [4], it is quite possible that it is a restoration varnish. The characteristic bands of the lead white pigment identified by the microchemical analysis of the red paint are not highlighted at 1431, 839 and 678 cm^{-1}, since they are overlapped by the absorption bands and peaks of rosin and gum arabic.

However, in the IR spectrum of the red paint, the red pigment cinnabar (HgS) which was initially identified by the microchemical method is not reflected at all. This can be explained by the fact that the IR spectrum of cinnabar does not have any characteristic absorption bands in the range of 4000–400 cm^{-1}. Moreover, based on the IR spectrum, it was impossible to identify the absorption bands of the red organic pigment included in the translucent layer.

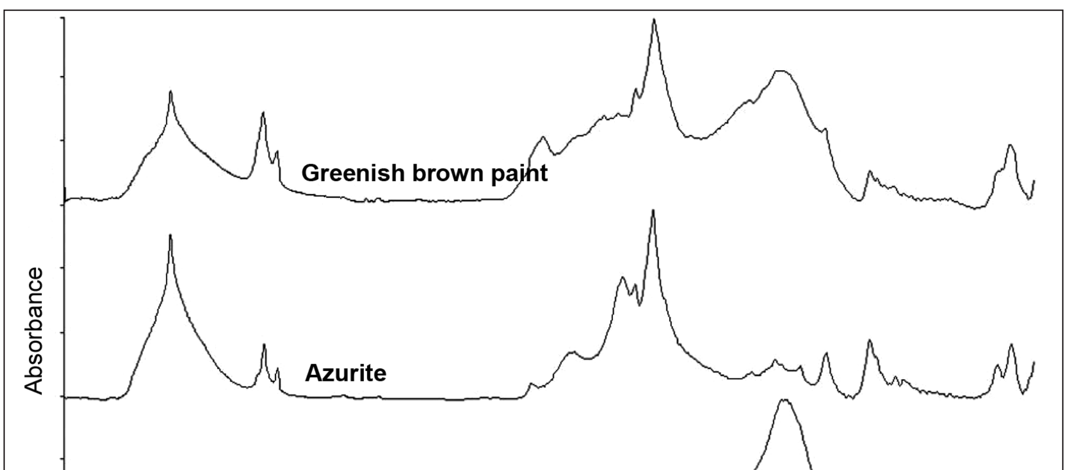

Fig. 3. FTIR spectra of the greenish brown paint, standard azurite and smalt pigments

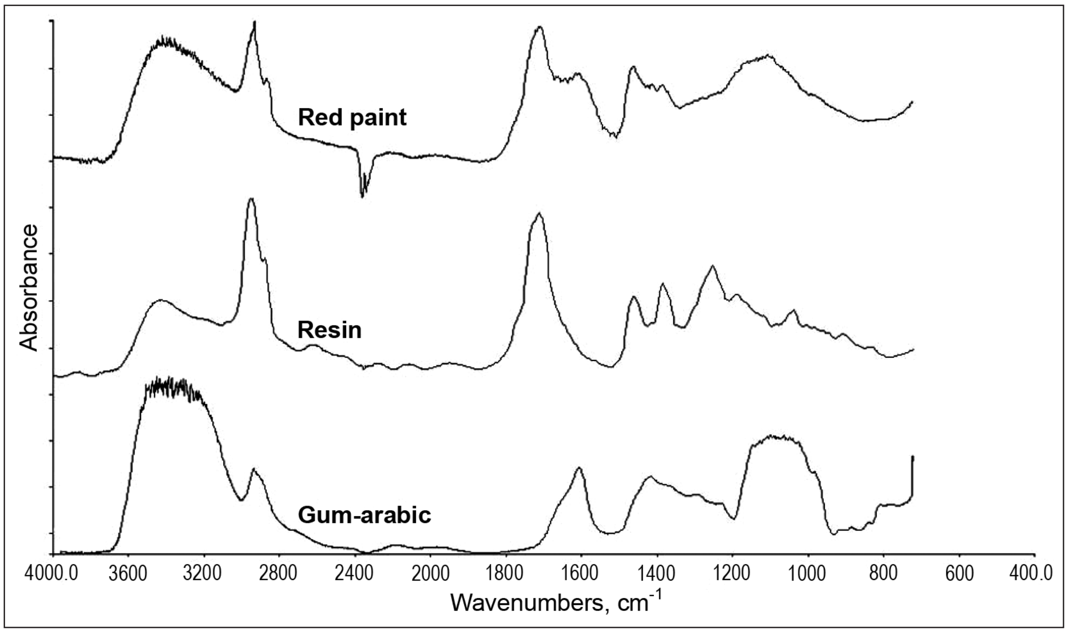

Fig. 4. FTIR spectra of the red paint, rosin and gum arabic standards

Optical microscopy and SEM / EDX analysis

The stratigraphic view of the greenish brown paint sample in visible and UV light is shown in Fig. 5. Information on the sequence of the main painting layers and the distribution of pigments was obtained. This kind of research provides information on the structure of paint, the size of pigment specks, their colour and distribution in a paint, as well as information on the layers of varnish and the binding media of the ground and paints [1, 10, 17]. In the picture taken with the optical microscope in visible light (Fig. 5 a), one can see that the painting sample consists of five layers. The following layers can be clearly identified: a relatively thin layer of white ground, two different layers of bluish brown paint of uneven thickness, and two layers of varnish. Moreover, the picture taken in UV light (Fig. 5 b) enables us to extend this stratigraphic description of the sample. The UV light emphasizes a clear boundary between the two layers of paint (2nd and 3rd) and the painting varnish. One can also see that the 2nd layer consists of bluish, glassy particles of some pigment (smalt), whereas the visually observed brownish colour was formed due to the browning / yellowing of the binding medium. Smalt is easily distinguished from azurite by its colour and by its elongated sharp particles with visible fractured edges. Also, the binding media of the 2nd and 3rd layers of paint are different since they have different fluorescence. The layers of varnish (4th and 5th) were also coated on the painting at different times because the intensity of their fluorescence is different. The SEM / EDX analysis results of paint samples (greenish brown and red) are provided in Table 3.

The description of the stratigraphic view of the greenish brown paint sample is based on the SEM / EDX analysis results:

I. The ground layer, dominated by the lead white pigment ($2PbCO_3 \cdot Pb(OH)_2$).

II. A paint layer composed of pigments containing smalt ($CoO \cdot K_2SiO_3$), lead white and copper based pigments as well as a small amount of chalk.

III. A paint layer composed of azurite ($2CuCO_3 \cdot Cu(OH)_2$), lead white pigments as well as small amounts of chalk and ochre (?).

IV–V. Varnish layers.

By the SEM / EDX method it has been determined that the layer of paint, which was visually estimated as greenish brown, actually includes two layers of a blue paint characterized by a different chemical composition. The lower layer of the blue paint (Fig. 5 a, 2nd layer) is dominated by faded smalt, whereas the upper blue layer (Fig. 5 a, 3rd layer) is dominated by the particles of a bright blue, roughly grinded azurite pigment. The FTIR and SEM / EDX analyses of the

Table 3. **SEM / EDX elemental composition of greenish brown and red paint samples (wt %)**

Samples		Si	S	Ca	Cu	Pb	Al	Cl	K	Fe	Co	As	Hg
Greenish brown paint (Fig. 5 a)	Layer 1	2.66	0.44	1.80	2.74	92.37	–	–	–	–	–	–	–
	Layer 2	47.95	0.31	3.11	2.85	29.68	1.78	0.78	7.49	2.84	2.80	0.42	–
	Layer 3	5.93	–	1.98	73.25	13.88	1.79	1.45	1.45	0.79	0.71	0.62	–
Red paint (Fig. 6 a)	Layer 1	–	–	–	–	100	–	–	–	–	–	–	–
	Layer 2	0.53	17.55	3.71	–	45.46	4.39	–	–	–	–	–	66.42
	Layer 3	–	39.67	0.53	–	–	58.11	–	1.69	–	–	–	–

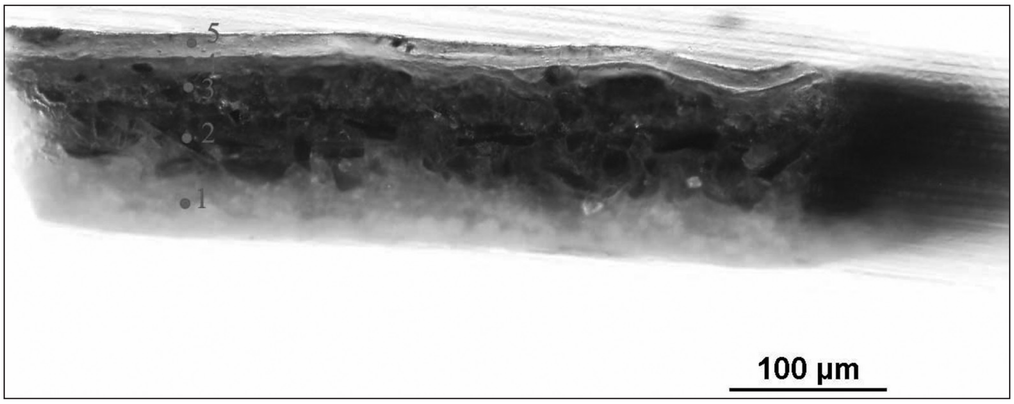

Fig. 5a. Stratigraphic view of paint sample with layers of greenish brown paint, 320× magnification: a – visible light, b – UV light

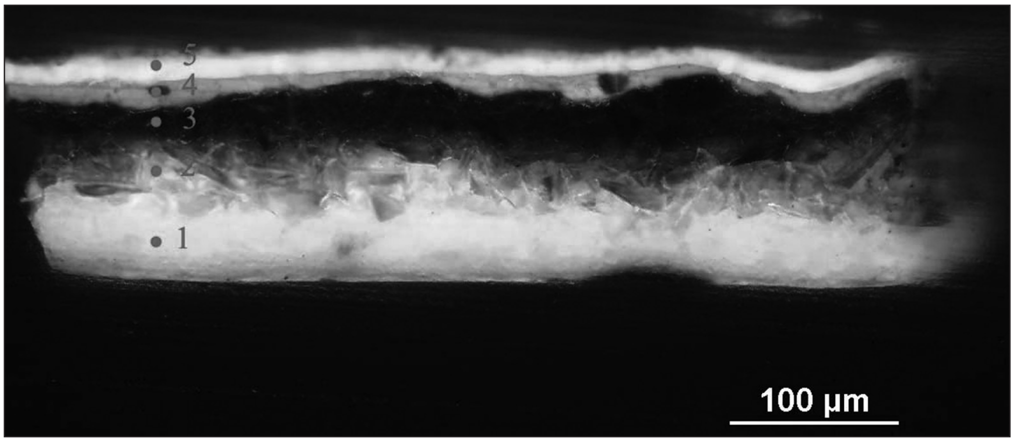

Fig. 5b. Stratigraphic view of paint sample with layers of red paint, 320× magnification, UV light

greenish brown paint leave no doubt that the paint contains blue copper carbonate (azurite) and smalt pigments.

The composition of the two layers of blue paint for paintings was described in treatises of the 16th century. This reveals the specific features of the painting technology used at that time, which was partly determined by the prevalent economic conditions. It is known from written sources that lazurite and azurite were difficult to import to Europe due to the wars in Turkey; therefore, the usage of smalt became more widespread [1, 16, 17]. At that time, it was already known that the inexpensive pigment smalt was a melt of shredded quartz sand, potash and cobalt compounds. Moreover, it had a tendency to fade and become grey, especially, if it was ground too much or produced in a technologically faulty way by adding too much potash into the melted compound [18]. Therefore, smalt was mixed with other bright blue yet much more expensive pigments, lazurite and azurite. The underpaint included compounds of blue pigments containing a greater portion of smalt, whereas such compounds with a smaller amount of smalt were used for upper paint layers.

In the painting *Madonna with Child*, the viridescence and rustiness of the layer of blue paint can be observed visually, which was mainly determined by the yellowing of the binding media and the varnish layers.

The stratigraphic view of the red paint sample in visible and UV light is shown in Fig. 6. In the photo taken through the optical microscope in visible light (Fig. 6 a), one can see that the paint sample consists of four layers. The following layers can be clearly identified: a white ground layer, a brownish layer with unevenly dispersed smaller and larger particles of a red pigment, as well as two layers of varnish. Moreover, the picture taken in UV light (Fig. 6 b) enables us to extend this stratigraphic description of the sample. UV light emphasizes clear boundaries among all the four layers of painting. In the UV picture, a chaotic distribution of the pigment particles in the second layer and the uneven thickness of the second layer can be seen. Also, the structure of the third layer can be examined; here, the orange particles of the pigment indicate the presence of some organic (most probably madder lake) pigment.

The stratigraphic description of the red paint sample, based on the results of the SEM/EDX:

I. The ground layer, dominated by the lead white pigment ($2PbCO_3 \cdot Pb(OH)_2$).

II. A paint layer containing cinnabar and lead white pigments.

III. A paint layer containing cinnabar and red organic pigments.

IV. A varnish layer.

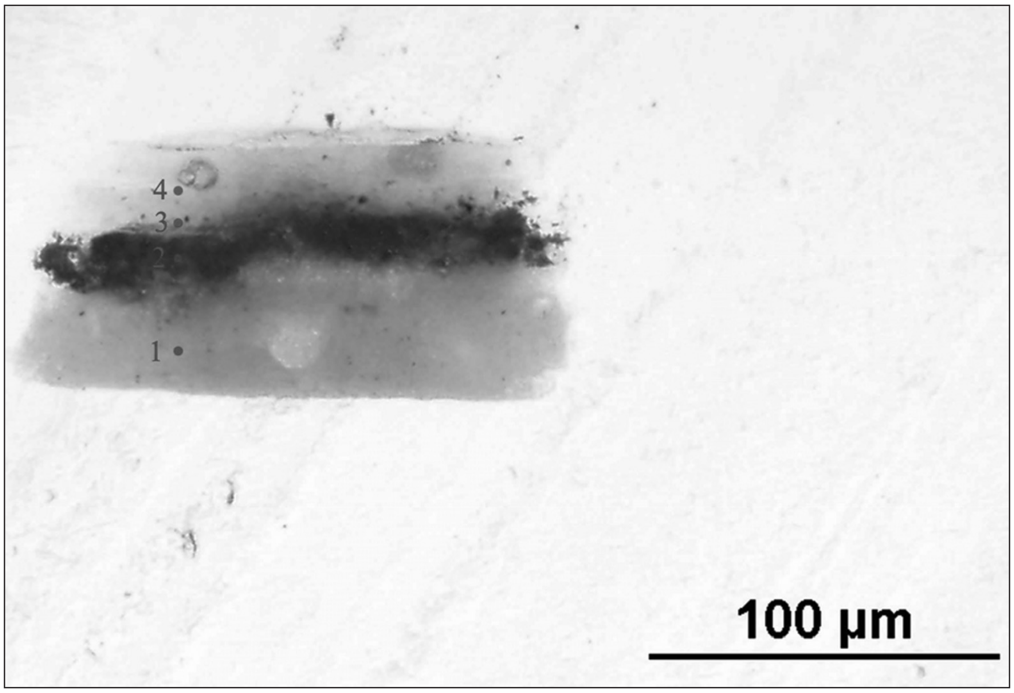

Fig. 6a. Stratigraphic view of paint sample with layers of red paint, 320× magnification, visible light

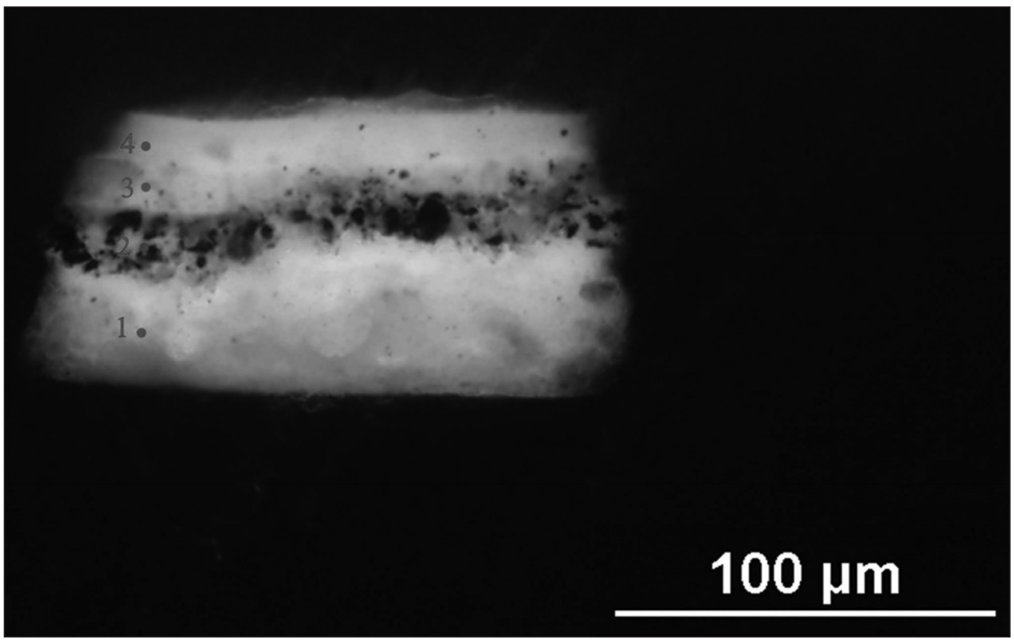

Fig. 6b. Stratigraphic view of paint sample with layers of red paint, 320× magnification, UV light

The SEM / EDX analysis results allow determining the specific technological characteristics of a fragment of the red paint. In order to make the red colour 'deeper' and darker, the areas painted with carmine-red paint made of a compound of cinnabar and lead white pigments were covered with a glazing of transparent paint with a red organic pigment. Using glazings, painters were able to produce masterful transitions among brighter and darker, as well as contrasting, colours. It is known [19] that glazings were produced using either red varnish containing some organic pigment, or cinnabar which was blended with red varnish.

The stratigraphic view of both painting samples has clearly demonstrated that the cohesion of the painting ground and different kinds of paint is appropriate. In some areas of the painting, where the folds of the red cloak and Mary's greenish brown cloth were painted in a thicker layer of paint, small painting crumbs can be observed. Such decay is a possible result of mechanical damage.

CONCLUSIONS

A detailed investigation of a rare painting *Madonna with Child*, preserved at the Lithuanian National M. K. Čiurlionis Museum of Art has been performed. By combining the analytical methods, its pigments, binding media, components of varnish, the metal plate alloy were identified. By the FAAS method it has been determined that the painting support is made of a tin alloy including a small amount of lead. On the basis of FTIR, SEM / EDX analysis results, we determined the pigments of the painting ground and binding media, also described the composition of greenish brown and red paints. The palette of the pigments is fairly limited. The lead white, cinnabar, azurite and smalt pigments were identified.

The analysis of the painting has shown that the viridescence and rustiness of the blue paint layer can be observed visually and was mainly determined by the yellowing of the binding media and the varnish layers.

The structure of the painting provided an important information on the technological features of painting on a tin alloy plate. It was a skillful and technologically sound work, therefore, it has been preserved in a satisfactory state.

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TAPYBOS TECHNIKOS ANT ALAVO PLOKŠTĖS TYRIMAS

Santrauka

Atliktas išsamus nežinomo autoriaus ant alavo plokštės tapyto paveikslo *Madona su kūdikiu* (Nacionalinio M. K. Čiurlionio dailės muziejaus rinkiniai, Mt –1506, 36,4 × 29 cm) tyrimas. Derinant kelis analitinius metodus nustatyta metalinio tapybos pagrindo lydinio sudėtis, pigmentai, rišamosios medžiagos bei lako komponentai. Taikant FAAS metodą nustatytas paveikslo pagrindas, kuris yra padarytas iš alavo lydinio su nedaug švino. Remiantis FTIR ir SEM / EDS analizės rezultatais identifikuoti pigmentai bei rišamosios medžiagos, sudarančios tapybos gruntą, žalsvai rudus bei raudonus dažus. Tyrimų metu nustatyti švino baltojo, cinoberio, azurito ir smaltos pigmentai. Tapybos stratigrafinės analizės rezultatai parodė, kad mėlynų dažų sluoksnio vizualiai matomo pažaliavimo (parudavimo) priežastis yra mėlynų dažų rišamosios medžiagos bei dengiančio lako sluoksnio pageltimas. Paveikslo struktūros tyrimu gauta svarbios informacijos apie tapybos ant alavo plokštės techniką.