VILNIUS UNIVERSITY

Jurga Bagdzevičienė

INVESTIGATION AND DESCRIPTION OF ANCIENT PIGMENTS IN PAINTINGS AND ARCHAEOLOGICAL GLASS FINDS

Summary of Doctoral Dissertation

Physical Sciences, Chemistry – 03P

Vilnius, 2012

This dissertation was carried out in Vilnius University in the period 2006 – 2012

Scientific supervisors:

prof. dr. Stasys Tautkus (Vilnius University, Physical Sciences, Chemistry – 03P).

Evaluation board:

Chairman:

prof. habil. dr. Audrius Padarauskas (Vilnius University, Physical Sciences, Chemistry – 03 P).

Members:

dr. Sigita Jurkonienė (Nature Research Centre, Institute of Botany, Biomedical Sciences, Biology – 01B);

dr. Galina Lujanienė (Center for Physical Sciences and Technology, Institute of Physics, Physical Sciences, Chemistry – 03 P);

prof. habil. dr. Eugenijus Norkus (Center for Physical Sciences and Technology, Institute of Chemistry, Physical Sciences, Chemistry – 03 P);

prof. dr. Vida Vičkačkaitė (Vilnius University, Physical Sciences, Chemistry – 03 P).

Official opponents:

prof. habil. dr. Aivaras Kareiva (Vilnius University, Physical Sciences, Chemistry – 03 P);

dr. Benedikta Lukšienė (Center for Physical Sciences and Technology, Institute of Physics, Physical Sciences, Chemistry – 03 P).

The official discussion will be held on 2 p.m. 1 June 2012 at the meeting of the Evaluation Board at the Auditorium of Inorganic Chemistry of the Faculty of Chemistry of Vilnius university. Address: Naugarduko 24, LT-03225 Vilnius, Lithuania. Tel. 2193108. Fax:2330987.

The summary of the doctoral dissertation was distributed on 30 April 2012.

A copy of the doctoral dissertation is available for review at the Library of Vilnius University and at the Library of Institute of Chemistry.

VILNIAUS UNIVERSITETAS

Jurga Bagdzevičienė

SENOVINIŲ PIGMENTŲ TAPYBOS KŪRINIUOSE IR ARCHEOLOGINIO STIKLO RADINIUOSE TYRIMAS IR APIBŪDINIMAS

Daktaro disertacijos santrauka

Fiziniai mokslai, chemija (03P)

Vilnius, 2012

Disertacija rengta 2006 – 2012 metais Vilniaus universitete

Mokslinis vadovas:

prof. dr. Stasys Tautkus (Vilniaus universitetas, fiziniai mokslai, chemija – 03 P).

Disertacija ginama Vilniaus universiteto chemijos mokslo krypties taryboje:
Pirmininkas:

prof. habil. dr. Audrius Padarauskas (Vilniaus universitetas, fiziniai mokslai,
 chemija – 03 P).

Nariai:

dr. Sigita Jurkonienė (Gamtos tyrimų centro Botanikos institutas, biomedicinos mokslai, biologija– 01 B);

dr. Galina Lujanienė (Fizinių ir technologijos mokslų centro Fizikos institutas, fiziniai mokslai, chemija – 03 P);

prof. habil. dr. Eugenijus Norkus (Fizinių ir technologijos mokslų centro Chemijos institutas, fiziniai mokslai, chemija – 03 P);

prof. dr. Vida Vičkačkaitė (Vilniaus universitetas, fiziniai mokslai, chemija – 03 P);

Oponentai:

prof. habil. dr. Aivaras Kareiva (Vilniaus universitetas, fiziniai mokslai,
chemija – 03 P);

dr. Benedikta Lukšienė (Fizinių ir technologijos mokslų centro Fizikos institutas, fiziniai mokslai, chemija – 03 P).

Disertacija bus ginama viešame Chemijos mokslo krypties tarybos posėdyje 2012 birželio 1 d. 14 val. Vilniaus universiteto Chemijos fakulteto Neorganinės chemijos auditorijoje. Adresas: Naugarduko 24, LT-03225 Vilnius, Lietuva. Tel.: 2193108. Faksas: 2330987.

Disertacijos santrauka išsiuntinėta 2012 balandžio 30 d.

Disertaciją galima peržiūrėti Vilniaus universiteto ir FTMC Chemijos instituto bibliotekose.

1. INTRODUCTION

There are a lot of unique archaeological finds, historical valuables and works of art in the collections of Lithuanian museums. It's all allows us better understand and comprehend the history of our state, traditions and culture. The success of restoration of cultural heritage depends to a large extent on the exactness and reliability of research results concerning the technology of a work of art. These results allows a proper characterization of its composition and structure. Based on these results, it is possible to determine the condition of a cultural object as well as to identify efficient conservation and restoration technologies eliminating chemical reactions between the object and conserving agents. Academically based results could be obtained only by application of various analytical methods for investigation of all components of artefact (support, ground, binding media, varnish layers). Especially valuable are the results of the pigments research. Analysis of the pigment's chemical composition, colour, characteristics and their changes in time gives opportunity to identify not only individual pigments and dyes, but also all the palette of the work of art which highlight particularity of it and allows to attribute works of art to authors according to their typical and favourite painting material and techniques too. Interpretation of the research results also reveals technological particularities of the pigments and dyes manufacturing, their degradation processes, ways of applying in the work of art. Though indirectly, all this information enlarge a whole data which reliably describe authenticity of the work of art.

Possibility of comparison is very important when examination of the works of art is carried out. In this case data bases of research results are very important and necessary. Such bases allows comparing research results with the accumulated information, the main part of which is collected data about known authors'works of art materials and technique. Unlike in other countries, in Lithuania, such data base has been started to collect only several decades ago. Today, the biggest part of collected data contain the information about pigments in the paint layers of paintings and polychromic sculpture. Unfortunately, most of this data was gathered using only microchemical qualitative and stratigraphic analyses results.

Importance of scientific novelty and topicality of the dissertation as follows: for the first time combining the methods of optical microscopy, SEM/EDX, XRD, µXRD, FTIR and micro-Raman were examined seven works of art and archaeological finds of glass, important to history and culture of Lithuania and obtained comprehensive and reliable data which allows to compare techniques of the old masters. All obtained data was used for practical restoration purposes – to choose the methods for conservation and restoration of cultural heritage. It is possible at the maximum to avoid accidental and sometimes systematic mistakes if instrumental research methods are combined.

Aforementioned complex examination of the cultural heritage and interpretation of the results were established in the everyday practice of the P. Gudynas Restoration Centre. Accumulated base of technical data constantly is complemented with new data obtained from the instrumental research methods. This base gives opportunity to Lithuanian specialist to cooperate with the centres of scientific research of European countries, which already have such data bases, to implement programs of the research, comparing and safety of the cultural heritage, to share experience and knowledge.

The main aim of this work was to investigate and evaluate different methods of instrumental capabilities and effectiveness in identifying and describing the pigment's elemental and phase compositions in paintings and archaeological finds of glass; to use the results of the research for describing of historical and artistic value-selected works.

For this reason there were formulated tasks as follows:
1. Comprehensively to describe the technology of selected paintings and archaeological finds of glass;
2. To describe the structure of the samples of painting and archaeological glass applying optical microscopy;
3. To establish the possibilities of FTIR method in characterizing ancient pigments and destruction products in archaeological glass;
4. To explore the possibilities of SEM/EDX method in determining pigment's elemental composition;
5. To identify the studied objects pigments by XRD, µXRD analysis; and to reveal the strengths and weaknesses of use of this method;
6. To identify the pigments of archaeological glass by micro-Raman spectroscopy.

Statements for defence:

1. Only a complex instrumental methods of analysis allow to obtain comprehensively accurate and reliable data about the structure of the paintings and archaeological glass and the materials used also;

2. Optical microscopy in visible and UV light is a first step to investigate samples of paintings and archaeological finds of glass. The stratigraphic view of the samples provides for information on the structure of painting, the size of pigment specks, their color and distribution in paint, as well as for information on the layer (-s) of varnish and possible underpaints made in different periods;

3. The Infrared spectroscopy enables rapid and reliable identification of some pigments or their mixtures in painting's ground, paint layers, and destruction products in archaeological glass, and binders in some cases;

4. SEM/EDX analysis is fast, reliable and perfectly suitable for establishing the basic elemental composition of painting paint and archaeological glass. SEM provides a possibility to explore the peculiarities of morphological features of archaeological glass;

5. Multiphase materials – paint and archaeological glass – can be successfully identified by XRD, μXRD and micro-Raman spectroscopy methods.

2. EXPERIMENTAL

2.1. *Materials and reagents*

Analytical grade reagents were used for the microchemical qualitative and the flame atomic absorption spectroscopic analysis (FAAS). Twenty reference standards pigments (*Kremer Pigmente, Lukas Pigment*) and binding media were used for the determination of pigments of paintings and archaeological glass samples by microchemical qualitative and IR spectroscopy analysis: white pigments – $CaCO_3$ (chalk), $2PbCO_3 \cdot Pb(OH)_2$ (lead white), $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (kaolin), $CaSO_4 \cdot 2H_2O$ (gypsum), SiO_2 (~98% quarc); red pigments – $F_2O_3 \cdot nH_2O$ (red ochre), HgS (cinnabar); yellow pigments – $FeO(OH)$ (yellow ochre), Pb_2SnO_4 (lead tin yellow type I), $PbSnO_3$ (lead tin yellow type II); blue pigments – $2CuCO_3 \cdot Cu(OH)_2$ (natural and synthetic azurite), $CoO \cdot K_2SiO_3$ (smalt), $CaCuSi_4O_{10}$ (Egyptian blue), $Fe_4[Fe(CN)_6]_3$ (Prussian

blue); green pigments – green ochre, $Cu(CH_3COO)_2 \cdot H_2O$ (verdigris), copper resinate; binding media – gelatine, skin glue, flour glue, linseed oil, rosin, mastic, damar, bees wax, gum arabic.

2.2. *Characterization techniques*

The painting support, the pigments of the ground, the paint layers and archaeological glass samples were characterised by microchemical qualitative analysis. The reactions performed in reflected light using the microscope *Nikon SMZ–1/ SMZ–1ESD* (magnification from 7 to 30). The quantative analysis of the metal alloy of the support plate was performed using the atomic absorption spectrometer *Hitachi 170–50*. The FAAS analysis of every metal was performed under optimal detection conditions. Infrared spectra of the samples of the painting ground, paint layers and the standards of pigments were recorded using the spectrophotometer *FT-IR–8400S* (SHIMADZU) connected to the IR microscope *AIM–8800* and *MCT* detector. Spectra were registered under the following conditions: 1) the sample was mixed with KBr and pressed into a pellet using the manual minipress *MHP-1*, the spectrum interval ranges from 4000 to 400 cm^{-1}, 100 scans in total, 4 cm^{-1} resolution; 2) the sample pressed under a diamond cell *P/N0045-434*, the spectrum interval ranges from 4000 to 720 cm^{-1}, 200 scans in total, 4 cm^{-1} resolution. Infrared spectra of the samples of the glass were recorded using the spectrophotometer *ALPHA* (Brucker Optics). Optical microscopy (*Olympus BX-60* in reflected visible light and UV light in the wavelength range of 330-380nm, *OLYMPUS SZX16, Micros*), and scanning electron microscopy (*Philips XL-30 CP*, *Hitachi S-3500N* (Ibaraki, Japan), *Hitachi TM–3000* (Tokyo, Japan)) coupled with an energy dispersive X-ray spectrometer were used to describe the layer stratigraphy and elemental composition of various colours paint and archealogical glass samples. X-ray diffraction analysis was used for the phase (mineral) analysis and was carried out in several instruments. Archaeological glass samples were performed on the Bruker *AXE D8 Focus* and *STOE X-ray* diffractometers. Micro-X-ray diffractometer *X'PertPro* (PANalytical) with 0.15 mm diameter of the primary beam was used for the phase analysis of paint cross-sections. Micro-Raman spectroscopy was applied for characterization of yellow pigments in archaeological glass. Raman spectra were

recorded with the *Horiba Jobin Yvon* spectrometer *LabRam HR800* equipped with 600 groove/mm grating. The 632.8 nm emission of a He-Ne laser was used to excite the spectra.

3. RESULTS AND DISCUSSION

3.1. Investigation of the technique of paintings and characterization of pigments

To identify the painting's pigments and describe its structure were choosen artworks of paintings and polychromy of various periods:

1) Unknown painter, *Madonna with Child*, XVII century, metal plate, oil, 36,4 x 29 cm, Lithuanian National M. K. Čiurlionis Museum of Art, Mt – 1506;

2) Johann Berchhoff, *St. Bruno. A Miracle in the Church*, 1674, oil on canvas, 283 x 281.5 cm, Lithuanian Art Museum, Ap. 9152, T10117;

1) Unknown Lithuanian painter, *St. Mary and St. Anthony with Child,* 1746, oil on canvas, 130 x 90 cm, Lithuanian Folk Museum, Aps. 38779;

2) Sarcophagus of a singer of God Amon, Ancient Egypt, Thebes, 11th–9th century BC, Ficus sycomorus wood, polychromy, 27 x 192 x 50 cm, National M. K. Čiurlionis Art Museum.

3.1.1. Painting *Madonna with Child:* Investigation of the technique of painting and characterization of pigments

A detailed investigation of the rare painting *Madonna with Child* stored in Lithuanian National M. K. Čiurlionis Museum of Art has been performed. By combining the analytical methods (microchemical, optical microscopy, FAAS, FTIR and SEM/EDX) the ground, pigments, binding media, components of varnish, the metal plate alloy were identified. The structure of painted layers was also described and the changes of the painting's blue color explained.

FAAS analysis

According to the data obtained the painting support is made of a tin 92.75% alloy including a small amount of lead 5.22%. Results of analysis by FAAS of the metal alloy of the painting support are presented in Table 1.

The tin alloy plate is covered with a thin, white one-layer ground, which consists mainly of lead white pigment. The lead white, cinnabar, azurite and smalt, carbon pigments were identified. The binding material of both the painting ground and the paint layer is oil. The surface of the painting is covered with a layer of medium thickness of a yellowish varnish.

Table 1. The results of metal determination in the alloy of painting support by FAAS method

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

FTIR spectroscopy

This part presents the results of identification of pigments in painting ground, greenish brown and red paint samples using FTIR spectroscopy. The FTIR results of the ground are presented in Fig. 1.
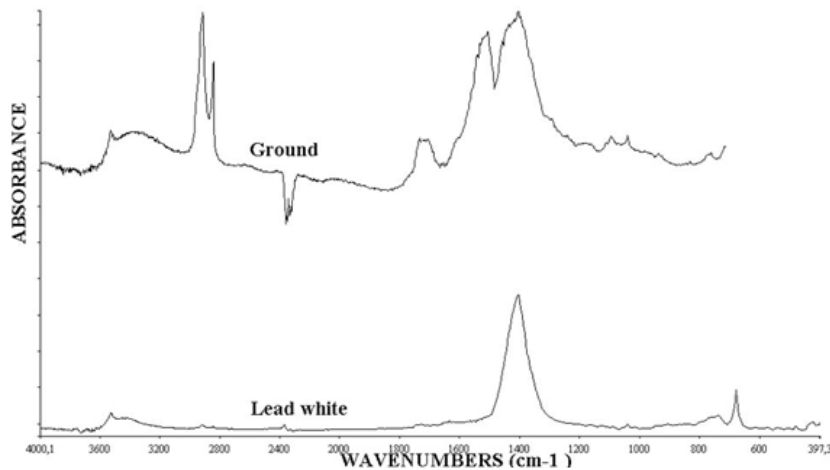

Fig. 1. IR spectra of the painting ground sample and the lead white pigment

Sharp absorption bands in painting ground and of the lead white $(2PbCO_3 \cdot Pb(OH)_2)$ pigment spectra at 3538 cm^{-1} (O–H), at 1431 cm^{-1} (C–O), at 839 cm^{-1} (C–O) are clearly present and coincide well enough. The IR spectrum of the painting ground shows rather intensive absorption bands at 2923 cm^{-1} and at 2850 cm^{-1} (C–H), as well as absorption bands at 1722 cm^{-1} (C=O). These absorption bands are attributable to

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

The greenish brown paint contains a azurite, the lead white and smalt pigments, in which the blue color has faded. The FTIR results of the greenish brown paint are presented in Fig.2.
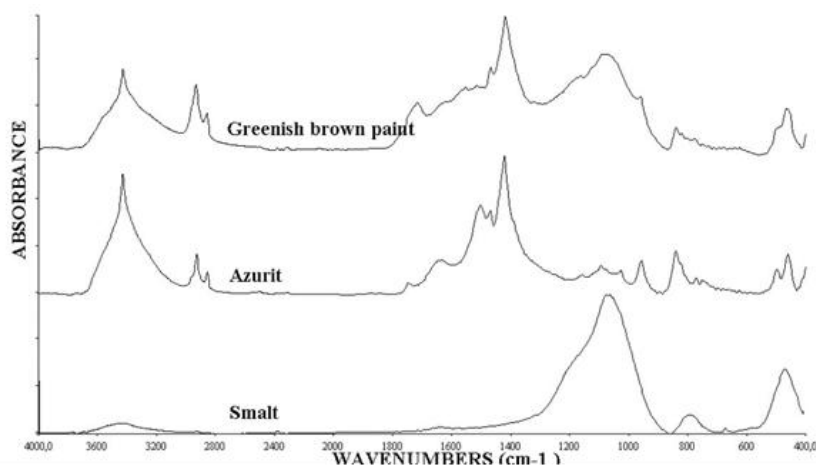

Fig. 2. FTIR spectra of the greenish brown paint, azurite and smalt pigments

The IR spectrum of the greenish brown paint clearly demonstrates the main sharp absorption bands and peaks that coincide with the absorption bands of azurite 3425 cm^{-1} (O–H), 1415 cm^{-1}, 835 cm^{-1} (C–O)) and smalt 1077 cm^{-1} (Si–O) pigments provided for comparison. Based on the FTIR analysis results, the presence of the lead white pigment is not reflected, which was identified by the microchemical analysis.

The pigments of the red paint are mainly a mixture of cinnabar and lead white; this layer of paint is covered with a red translucent layer, which contains a red organic pigment. The red paint sample was prepared in order to obtain the IR spectrum of the red organic pigment, which is 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. The FTIR results of the red paint are presented in Fig.3.
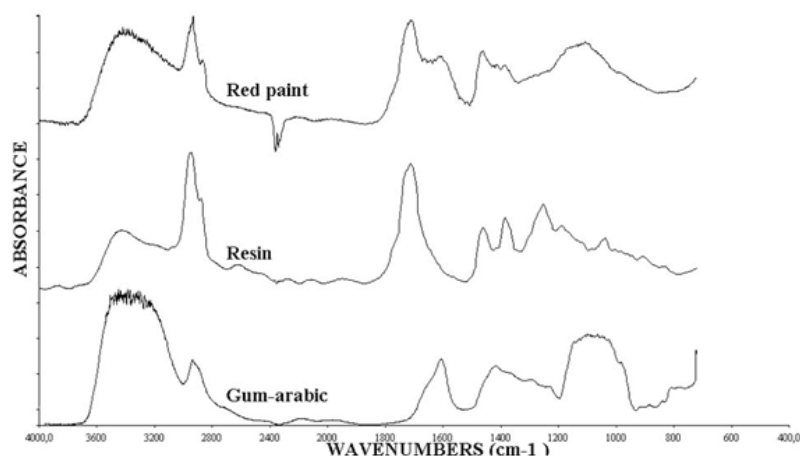
Fig. 3. IR spectra of the red paint, rosin and gum arabic standards

The absorption bands and peaks found in the IR spectrum of the red paint are attributable to natural rosin (1710 cm^{-1} C=O) and natural gum arabic (2965–2880 cm^{-1} and 1415–1380 cm^{-1}, –CH$_3$ and –CH$_2$–), which in its chemical composition is similar to other natural hydrocarbons, such as plums, cherries and other gums.

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. In the IR spectrum of the red paint the red pigment cinnabar HgS is not reflected at all, which was initially identified by the microchemical method.

Optical microscopy and SEM/EDX analysis

In this part description of the greenish brown and red paint samples cross-section in the visible and UV light and identification elemental composition of the paints was performed using of optical microscopy and SEM/EDX analysis.
The results of SEM/EDX analysis of the greenish brown and red paint samples at different cross-section points are given in Table 2 and 3.

Table 2. SEM/EDX elemental composition of greenish brown paint sample (wt%)

	Si	S	Ca	Cu	Pb	Al	Cl	K	Fe	Co	As
Ground 1	2.7	0.4	1.8	2.7	92.4	–	–	–	–	–	–
Paint layer 2a	35.2	0.6	2.7	4.0	41.2	1.4	1.1	8.6	2.7	2.6	0
Paint layer 2b	67.5	0.4	3.3	2.3	10.5	2.0	0.5	6.8	3.3	3.2	0.3
Paint layer 2c	41.2	0	3.3	2.2	37.3	1.9	0.8	7.2	2.6	2.5	0.9
Paint layer 3a	4.7	–	0.5	89.3	2.9	1.5	–	0.6	0.5	–	–
Paint layer 3b	5.6	–	2.9	81.3	4.7	3.0	–	1.0	0.7	–	0.6
Paint layer 3c	7.4	–	2.5	49.2	34.0	0.9	1.5	2.8	1.1	0.7	–

Table 3. SEM/EDX elemental composition of red paint sample (wt%)

	Si	K	S	Ca	Pb	Al	Hg
Ground 1a	–	–	–	–	100	–	–
Ground 1b	–	–	–	–	100	–	–
Paint layer 2a	0.6	–	–	–	–	–	99.5
Paint layer 2b	–	–	7.6	4.1	25.9	3.5	48.9
Paint layer 2c	0.6	–	–	2.9	65.0	1.3	30.3
Paint layer 3a	0.5	–	–	4.2	–	8.3	87.0
Paint layer 3b	–	39.7	–	0.5	–	58.1	–

By applying the SEM/EDX methods it has been determined that the layer of ground contains lead white pigment. By applying the optical microscopy, SEM/EDX methods it has been determined that the layer of paint, which was visually estimated as greenish brown, actually includes two layers of blue paint characterized by different chemical compositions. The greenish brown paint leave no doubts that the paint contains azurite and smalt pigments. In the painting, 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 SEM/EDX analysis results allow determining the specific technological characteristics of a fragment of the red paint. In order to make the red color 'deeper' and darker, the areas painted with carmine-red paint made of the compound of cinnabar and lead white pigments were covered with a glazing of transparent paint with a red organic pigment.

3.1.2. Painting *St. Bruno. A Miracle in the Church:* Investigation of the technique of painting and characterization of pigments

A detailed investigation of the painting *St. Bruno. A Miracle in the Church* (1674) from the St. Francis of Assisi and Bernardine Church in Vilnius was carried out. The ground, the pigments and restoration materials were identified using combined analytical methods (microchemical, optical microscopy, FTIR, SEM/EDX, µXRD). Also the structure of painted layers was described. Information obtained is crucial in answering questions concerning the technological particularities of this work of art, its identity and authorship, the time of its creation and authenticity.

Having performed fiber morphological analysis, it was determined that the painting support is made of a linen. The painting support is covered with relatively thick, brown-red one-layer ground, which consists of chalk, ochre, lead white pigment, minium and black carbon pigments. The smalt, azurite, lead tin yellow type I pigment, cinnabar, black carbon pigment as well as lead white pigment, which is a mixture of hydrocerussite and cerussite, have been identified. The binding material of paint layer is oil. The surface of the painting is covered with a layer of medium thickness of a yellowish varnish.

FTIR spectroscopy

This part presents the results of identification of pigments in painting ground, blue paint samples and restoration materials using FTIR spectroscopy. On the basis of these FTIR analysis results, we conclude that the pigment of the painting ground is chalck and ochre, as well as blue paints contains of azurite.

Ten samples of the restoration materials from different areas of the back side of the painting were taken for FTIR analysis. It was found that during previous restorations adhesives of several kinds were used for gluing the lining, its folds and patches: a) a paste made of flour glue, natural resin and chalk. The IR spectrum of the lining paste is given in Fig. 4; b) a red ground whose composition includes chalk, red ochre and oil as a binding material; c) synthetic glue based on vinyl acetate copolymer was used to glue a patch.
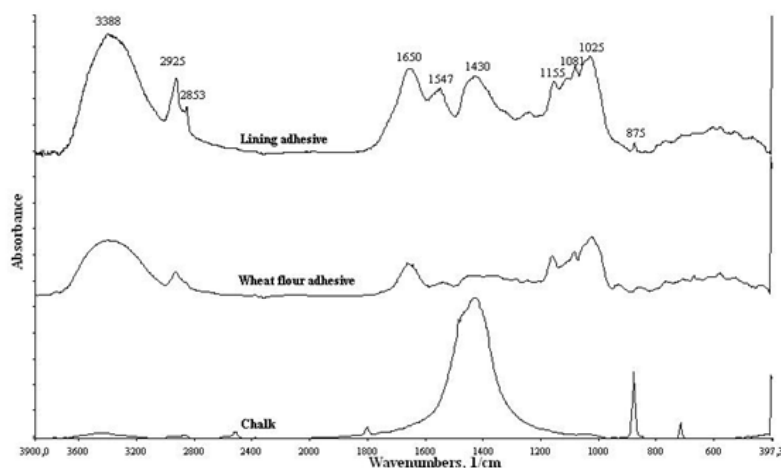
Fig. 4. IR spectra of the lining adhesive, wheat flour adhesive and the chalk

Optical microscopy and SEM/EDX analysis

In this part description of the nine various colours paint samples cross-section in the visible and UV light and identification of the paints elemental composition was performed using optical microscopy and SEM/EDX analysis. The stratigraphic image of the paints provided information on the order of the main layers of painting, the size of pigment particles, their distribution within the paint as well as colour, also information on the layer(s) of varnish. We presented description of three paint samples: light grey, blue-brownish, yellowish.

The stratigraphic image of the light grey paint sample consists of three layers of painting: a layer of a brown-red ground of uneven thickness; a layer of a light grey paint that consists of two layers of different blue colours: light greyish and dark blue vitreous smalt particles mixed with a white pigment. The results of SEM/EDX analysis of the light grey paint sample at different cross-section points are given in Table 4. The stratigraphic description of the light grey paint sample after the results of microchemical and SEM/EDX analysis have been summarized:

1) The first layer is a brown-red ground that contains natural chalk, ochre, lead white, minium and black carbon pigments;

2) The second layer is the original layer of dark blue paint that consists of smalt and lead white pigments as well as chalk as small impurities;

3) The third layer is the original layer of light greyish paint that contains smalt and lead white pigments. It also contains small amount of chalk impurities.

The identified smalts of different colours (the 2nd and 3rd layers) have a different amount of potassium that let as to predict that the processes of smalt production were different.

Table 4. SEM/EDX elemental composition of the light grey paint sample in different cross-section points (wt%)

	Mg	Al	Na	Si	Cl	K	Ca	Fe	Pb	Co	Ni	As
Ground1a	1.38	1.8	–	4.1	0.0	0.9	79.6	4.2	7.9	–	–	–
Ground1b	–	1.5	–	13.5	0.4	0.9	72.8	4.2	6.7	–	–	–
Ground1c	–	–	–	0.8	–	–	4.3	0.8	94.1	–	–	–
Paint.2a	–	1.2	–	24.7	–	5.1	4.9	1.8	59.1	1.8	1.1	0.4
Paint.2b	–	1.7	–	65.0	–	14.5	2.8	2.1	10.2	3.3	–	0.5
Paint3a	–	1.5	–	59.4	–	25.0	2.1	1.6	7.3	2.3	–	0.9
Paint3b	–	1.2	–	20.6	–	1.8	9.2	0.8	65.9	0.6	–	0.0
Paint.3c	–	1,6	–	54.5	–	25.4	2.5	2.1	9.9	3.3	–	0.9

The stratigraphic image of the blue-brownish paint sample consists of four layers of painting: the layer of brown-red ground of uneven thickness, two layers of different blue-brownish colours of uneven thickness and the layer of varnish. The results of SEM/EDX analysis of the blue-brownish paint sample at different cross-section points are given in Table 5. The stratigraphic description of the blue-brownish paint sample after summarizing the results of microchemical qualitative and SEM/EDX analysis are following:

1) The first layer is a brown-red ground that includes natural chalk, ochre, lead white, minium and black carbon pigments;

2) The second layer is an original layer of a brown-blue paint which includes smalt in lead white pigment with azurite and chalk as small impurities;

3) The third layer is the original layer of a bluish-brownish paint, which contains azurite in lead white pigment and chalk as small impurities;

4) The fourth layer is varnish.

Table 5. SEM/EDX elemental composition of the blue-brownish paint sample in different cross-section points (wt%)

	Mg	Al	Si	K	Ca	Fe	Cu	Pb	P	Cl
Ground1a	–	1.4	5.1	1.3	74.9	6.2	1.2	10.0	–	–
Ground1b	–	–	–	–	3.8	0.7	0.8	94.7	–	–
Ground1c	2.5	1.5	2.6	–	32.3	6.5	2.7	52.0	–	–
Ground1d	1.2	2.5	4.8	0.7	76.9	3.9	1.5	7.2	1.3	6.4
Paint.2a	1.6	2.1	8.9	2.7	4.8	1.2	32.3	39.9	–	–
Paint .2b	–	1.2	2.6	0.7	5.3	0.6	73.7	12.7	–	3.2
Paint .2c	1.0	1.5	17.7	2.5	8.5	1.8	31.1	31.1	–	4.6
Paint .3a	–	–	1.7	0.2	1.6	0.7	80.7	7.5	–	7.5
Paint .3b	–	0.5	1.5	–	2.1	0.7	65.9	20.1	–	9.2

The layer of the blue-brownish paint consists of two layers of paint of a different chemical composition. The bottom layer contains cleared greyish smalt mixed with the pigment of bright blue azurite and lead white pigment, and the top layer is dominated by bright blue, roughly ground particles of the azurite pigment mixed with lead white pigment. IR spectroscopic analysis has confirmed the presence of azurite pigment in the blue paint. The visible browning of the layer of blue paint was caused by the binding materials of the paint and the fact that the layer of varnish covering the paint has yellowed.

The stratigraphic image of the yellowish paint sample consists of four layers of painting. The SEM/EDX results of the yellowish paint at different cross-section points are given in Table 6. The stratigraphic description of the yellowish paint sample after summarizing the results of microchemical, SEM/EDX and μXRD analysis are following:

1) The first layer is a layer of brown-red ground which contains natural chalk, ochre, lead white, minium and carbon pigments;

2) The second layer is a brown layer that contains natural chalk, ochre (including Mn), lead white, minium and auripigment as impurities;

3) The third layer is an original brown layer of paint, which contains natural chalk, ochre (including Mn) and lead white pigments;

4) The fourth layer is a yellowish layer of paint that contains lead tin yellow type I and lead white pigments.

Table 6. SEM/EDX elemental composition of yellowish paint sample in different cross-section points (wt%)

	Mg	Al	Si	K	Ca	Fe	As	Pb	P	Ti	S	Mn	Sn
Ground1a	2.1	2.5	8.1	1.0	69.1	6.3	–	10.9	–	–	–	–	–
Ground2a	0.8	6.4	11.6	0.9	50.5	9.2	–	18.9	1.3	0.6	–	–	–
Ground2b	–	–	–	–	4.7	0.4	–	93.9	–	–	–	–	–
Ground2c	–	–	1.1	–	2.8	0.9	45.6	–	–	–	49.6	–	–
Ground2d	–	5.3	6.7	1.5	17.6	5.5	–	63.4	–	–	–	–	–
Ground2e	1.7	4.3	13.5	1.1	35.5	16.7	–	20.4	4.2	0.7	–	1.9	–
Ground2f	–	2.3	4.4	–	11.5	4.2	–	77.7	–	–	–	–	–
Paint 3a	–	–	92.0	–	2.1	0.9	–	5.0	–	–	–	–	–
Paint 3b	1.4	3.7	8.9	0.9	40.3	16.1	–	24.1	2.3	0.9	–	1.4	–
Paint 4a	–	5.2	8.6	–	3.3	3.9	–	72.4	–	–	–	–	6.7
Paint 4b	–	2.0	4.6	–	2.5	1.6	–	69.2	–	–	–	–	20.2
Paint 4c	–	–	0.9	–	2.5	0.9	–	54.3	–	–	–	–	41.5
Paint 4d	–	–	0.9	–	1.8	1.1	–	96.23	–	–	–	–	–
Paint 4e	–	–	2.6	–	5.9	2.7	–	88.74	–	–	–	–	–

μXRD analysis

The μXRD analysis of yellowish paint the fourth layer has allowed us to establish that the yellow pigment is lead tin yellow type I Pb_2SnO_4. The X-ray diffraction pattern is given in Fig. 5. Three phases have been identified in the X-ray diffraction pattern of the yellowish paint and attributed to lead tin oxide Pb_2SnO_4 (JCPDS No. 24-0589), lead white pigment, which consists of hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$ (JCPDS No.13-0131) and cerussite $PbCO_3$ (JCPDS No. 47-1734).
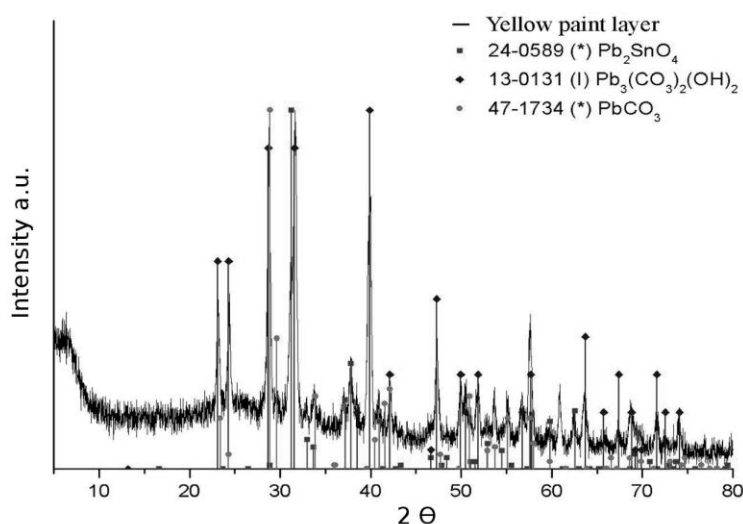

Fig. 5. The X-ray diffraction pattern of yellow layer (4th layer) of yellowish paint sample

3.1.3. Painting *St. Mary and St. Anthony with Child:* Investigation of the technique of painting and characterization of pigments

A detailed investigation of the painting *St. Mary and St. Anthony with Child* stored in Lithuanian Folk Museum was carried out. The ground and the pigments were identified using combined analytical methods (microchemical, optical microscopy, FTIR, SEM/EDX, µXRD). Also the structure of painted layers was described.

Having performed fiber morphological analysis, it was determined that the painting's support is made of a linen, which treated with protein glue. The painting support is covered with brownisch one-layer ground, which consists of chalk, ochre, minium and black carbon pigments. The painting's ground binding media are a mixture of protein glue and oil. In all studied paint samples, betwen ground and paint layer is a white layer (imprimatur) of lead white pigment. The Prussian blue, cinnabar, verdigris, gilding, black carbon pigment as well as lead white pigment, which is a mixture of hydrocerussite and cerussite, have been identified. The binding material of paint layer is oil. The surface of the painting is covered with a layer of medium thickness of a yellowish varnish.

FTIR spectroscopy

This part presents the results of identification of pigments in painting ground, blue, white, green paint samples using FTIR spectroscopy.The FTIR results of the ground are presented in Fig. 6.
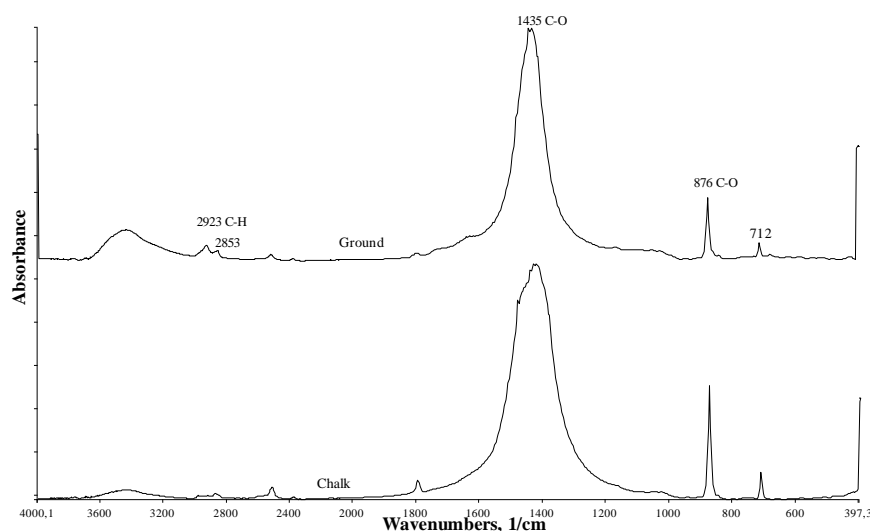

Fig. 6. IR spectra of the painting ground sample and chalk

19

The spectrum of the painting ground clearly demonstrates the main absorption bands and peaks that coincide with the absorption bands of chalk 1435 cm^{-1}, 876 cm^{-1}, 712 cm^{-1} (C–O) provided for comparison.
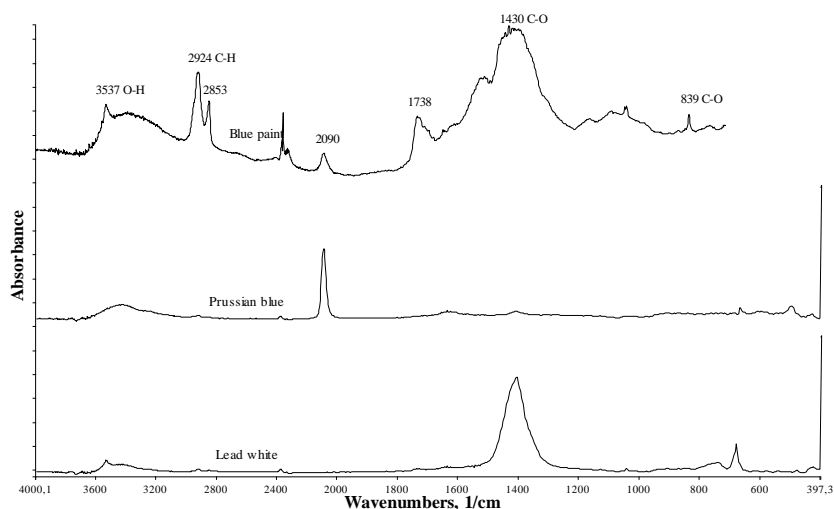

Fig. 7. IR spectra of the blue paint sample, Prussian blue, lead white pigment

Based FTIR and microchemical test results, it was determined that blue paint is a mixture of Prussian blue and lead white pigment. The IR specra of the blue paint are presented in Fig. 7. Absorption bands in white paint IR pectrum at 3538 cm^{-1} (O–H), at 1431 cm^{-1} (C–O), at 839 cm^{-1} (C–O) are attributable to the lead white pigment. The IR spectra of the all paint samples (white, blue, green) shows rather intensive absorption bands at 2923 cm^{-1} and at 2850 cm^{-1} (C–H), as well as absorption bands at 1722 cm^{-1} (C=O). These absorption bands are attributable to the vibrations of the oil functional group of the paints binding media.

On the basis of these FTIR analysis results, we conclude that the layer of the green paint consists of two layers of paint of a different chemical composition. The bottom green layer contains copper resinate mixed with lead white pigment, and the top light green layer is mixture of copper acetate (verdigris) and lead white pigments.

Optical microscopy and SEM/EDX analysis

In this part description of the four various colours paint samples cross-section in the visible and UV light and identification of the paints elemental composition was performed using optical microscopy and SEM/EDX analysis.

The SEM/EDX results of the green paint at different cross-section points are given in Table 7. The stratigraphic description of the green paint sample after the results of microchemical, FTIR and SEM/EDX analysis have been summarized:

1) The first layer is a brownisch ground that contains natural chalk, ochre, minium and black carbon pigments;

2) The second layer is the original layer of green paint that consists of copper resinate and lead white pigments;

3) The third layer is the original layer of light green paint that contains verdigris (copper acetate) and lead white pigments.

Table 7. SEM/EDX elemental composition of green paint sample in different cross-section points (wt%)

	Si	Al	Ca	Pb	Fe	Cu	Cl	K
Groumd 1	1.7	–	89.3	9.0	–	–	–	–
Ground 1a	0.4	0.6	3.5	95.4	–	–	–	–
Ground 1 b	8.9	–	82.6	8.5	–	–	–	–
Paint 2	0.5	0.6	6.3	91.3	0.7	0.5	–	–
Paint 2a	0.9	–	3.1	90.6	1.0	4.4	–	–
Paint 2b	0.9	–	4.4	90.9	–	3.8	–	–
Paint 3	1.2	–	28.8	29.2	–	38.7	1.2	0.8
Paint 3a	–	–	1.3	9.4	–	86.3	2.7	0.4
Paint 3b	–	–	2.3	56.6	–	41.1	–	–

The SEM/EDX results of the blue paint at different cross-section points are given in Table 8. The stratigraphic description of the blue paint sample after the results of microchemical, FTIR and SEM/EDX analysis have been summarized:

1) The first layer is a brownisch ground that contains natural chalk, ochre, minium and black carbon pigments as well as cinabar as small impurities;

2) The second layer is white ground (imprimatur) that consists of chalk and lead white pigments;

3) The third layer is the original layer of blue paint that contains Prussian blue and lead white pigments as well as chalk and ochre as small impurities;

4) The fourth layer is varnish.

Table 8. SEM/EDX elemental composition of blue paint sample in different cross-section points (wt%)

	Si	Mg	K	Na	Al	Ca	Pb	S	P	Fe	Hg
Ground 1	0.1	–	–	–	–	5.8	2.5	19.3	–	–	72.4
Ground1a	13.7	0.8	–	–	0.8	74.6	9.4	–	–	0.7	–
Paint 3	0.9	–	–	–	–	43.7	48.1	–	–	7.3	–
Paint 3a	1.5	–	–	–	–	85.8	7.6	–	–	5.0	–
Paint 3b	1.2	–	–	–	–	2.9	85.5	–	–	10.5	–
Paint 3c	0.9	–	–	–	–	56.4	36.2	–	–	6.5	–
Paint 3d	22.1	3.0	2.8	1.1	12.6	15.0	36.3	–	3.0	4.1	–
Paint 3e	2.3	–	0.0	–	2.8	5.9	87.9	–	–	1.0	–
Paint 3f	1.5	–	–	–	1.5	6.7	88.5	–	–	1.8	–

The SEM/EDX results of the red paint at different cross-section points are given in Table 9. The stratigraphic description of the red paint sample after the results of microchemical and SEM/EDX analysis have been summarized:

1) The brownisch ground layer that contains natural chalk, ochre, minium and black carbon pigments as well as cinabar as small impurities;

2) The white ground (imprimatur)layer that consists of chalk and lead white pigments;

3) The red paint layer containing cinnabar and lead white pigments;

4) The red paint layer containing cinnabar and red organic pigments as well as chalk and ochre as small impurities;

5) Varnish layer.

Table 9. SEM/EDX elemental composition of red paint sample in different cross-section points (wt%)

	Si	Mg	K	Na	Al	Ca	Pb	S	P	Cl	Fe	Hg	Cu
Ground 1	–	–	–	–	–	7.6	92.4	–	–	–	–	–	–
Ground 1a	–	–	–	–	–	36.4	53.9	–	6.5	3.2	–	–	–
Ground 1b	1.3	–	–	–	–	92.0	6.7	–	–	–	–	–	–
Imprimatur 2	–	–	–	–	–	3.7	96.3	–	–	–	–	–	–
Imprimatur 2a	89.0	–	–	–	–	4.9	6.1	–	–	–	–	–	–
Imprimatur 2b	0.3	–	–	–	–	48.6	51.1	–	–	–	–	–	–
Paint 3	0.4	–	–	–	2.5	25.3	23.1	11.2	–	–	0.8	36.8	–
Paint 4	2.2	2.3	1.6	–	19.4	34.0	38.0	–	–	1.4	1.1	–	–
Paint 4a	5.0	1.2	2.0	1.1	12.2	19.6	52.5	–	2.2	1.9	1.1	–	1.2

μXRD analysis

In this part the μXRD results of the green paint at different cross-section points are described. The X-ray diffraction patterns of the green paint at different green layers are schown in Fig. 8 and Fig. 9. It is clear that the XRD patterns of both green layers are similar. Two phases have been identified in the X-ray diffraction patterns of the top light green layer and of the bottom green layer and attributed to lead white pigment, which consists of hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$ (JCPDS No.13-0131) and cerussite $PbCO_3$ (JCPDS No. 85-1088).
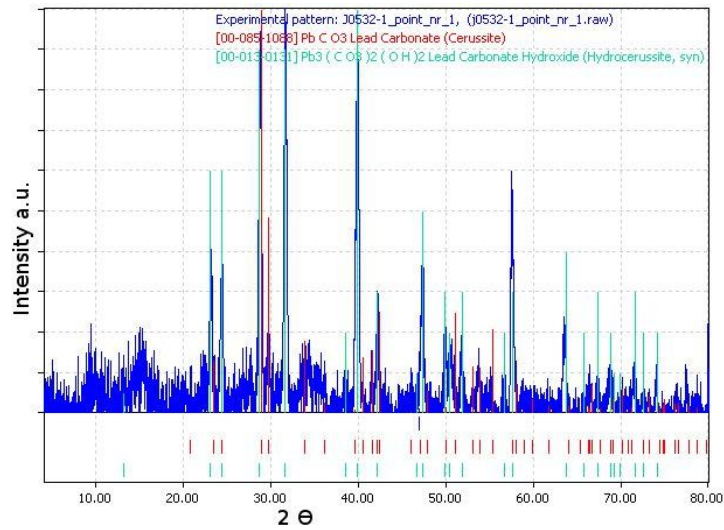
Fig. 8. The X-ray diffraction pattern of light green layer (3th layer) of green paint sample
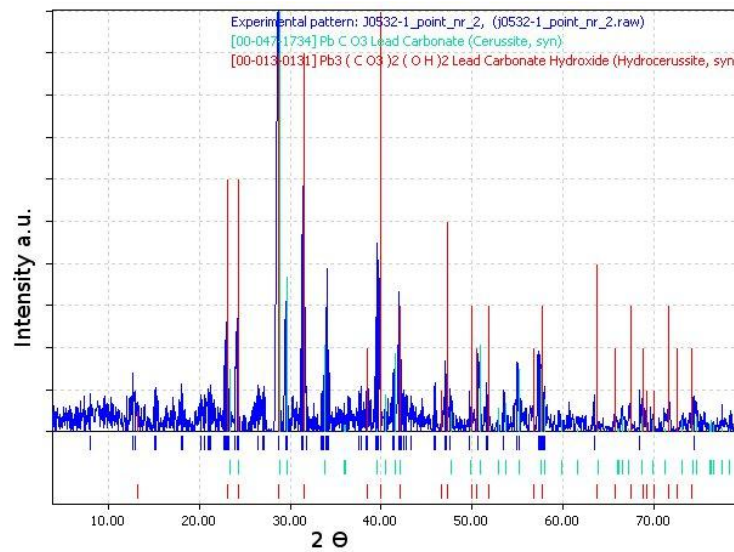
Fig. 9. The X-ray diffraction pattern of green layer (2th layer) of green paint sample

Unfortunately XRD analysis failured to identify the green pigment in the light green top layer, which by microchemical and FTIR analysis has been listed as copper acetate (verdigris). Comparison of X-ray diffraction patterns showed that part of the peaks coincide with peaks of copper acetate pigment, and the main peak at $2\theta \sim 12.2$ ° is the noise zone. Green pigment was not identified probably because the paint color is not very intense and it is likely that the green pigment concentration is low. XRD analysis did not identify the green pigment, the bottom green layer was performed by FTIR and mikrochemical analysis and it has been listed as copper resinate because it is an amorphous material.

3.1.4. Sarcophagus of a singer of God Amon: Investigation of the technique of polichromy and characterization of pigments

By combining the analytical methods (microchemical, optical microscopy, FTIR and XRD) polychromy materials were determined, the ground and pigments were identified and the structure of painted layers was described. The sarcophagus of a singer of God Amon is a wooden coffin of an anthropoid form made of Ficus sycomorus wood.

Ground layers

Boards of the sarcophagus are primed with two layers of light brown ground whose thickness fluctuates from 0,1 to 1,5 mm. This is illustrated by a picture of the cross-section of the white paint sample (Fig. 10). The bottom layer of the ground was determined filaments of vegetable fibre.
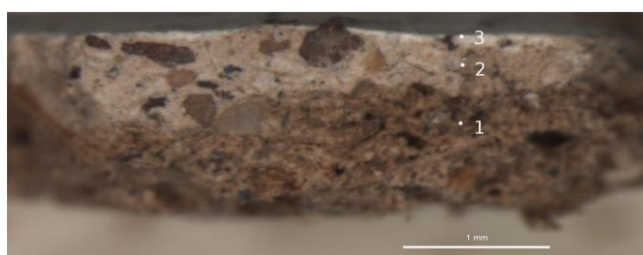

Fig. 10. An optical photograph of the cross-section of the sample of white paint of the sarcophagus: ground (1), the top layer of the ground (2) and the paint layer (3)

The FTIR and XRD results of the top layer of the ground are presented in Fig. 11 and Fig. 12. Absorption bands at 3549 and 3407 cm^{-1}, 1684 and 1621 cm^{-1} (O–H), 1144 and 1116 cm^{-1}, 670 and 595 cm^{-1} (S–O) characteristic of gypsum $CaSO_4 \cdot 2H_2O$ can be seen in the IR spectrum. Also, absorption bands are distinguished at 1434 cm^{-1} and 875 cm^{-1}, which correspond to C–O vibrations of chalk $CaCO_3$. A broad and intensive absorption band characteristic of quartz sand SiO_2 partly overlap the absorption band that is characteristic of gypsum, however, a non-intensive double absorption band is seen at 797 and 779 cm^{-1}, which is characteristic of quartz sand.
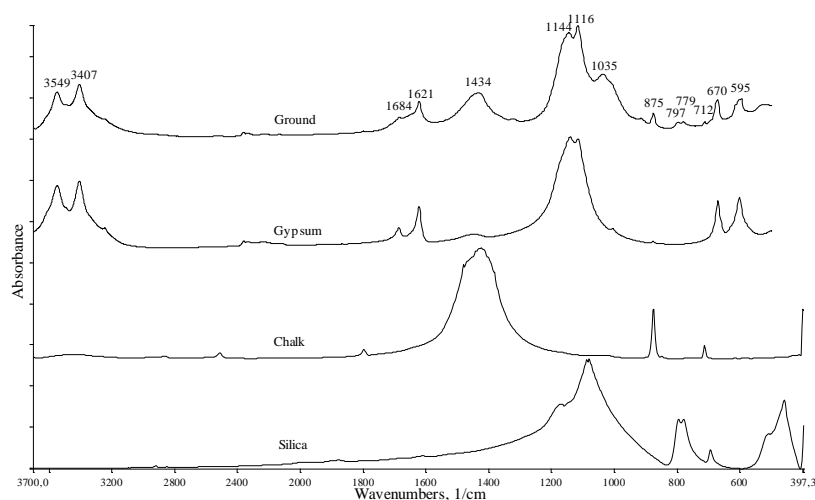
Fig. 11. The IR spectra of the ground sample and standard samples of gypsum, chalk and quartz sand

Four phases can be singled out in the presented ground X-ray diffraction pattern (Fig. 12): those of calcium sulfate dihydrate $CaSO_4 \cdot 2H_2O$ (gypsum), non-hydrated calcium sulfate $CaSO_4$ (anhydrite), calcite $CaCO_3$ (chalk), and silica dioxide SiO_2 (quartz). It is quite complicated to qualitatively establish whether gypsum $CaSO_4 \cdot 2H_2O$ or anhydrite $CaSO_4$, prevail in the composition of the ground because the anhydrite phase has not been identified in other X-ray diffraction patterns. These differences could be accounted for by an uneven distribution of materials in the ground mass.
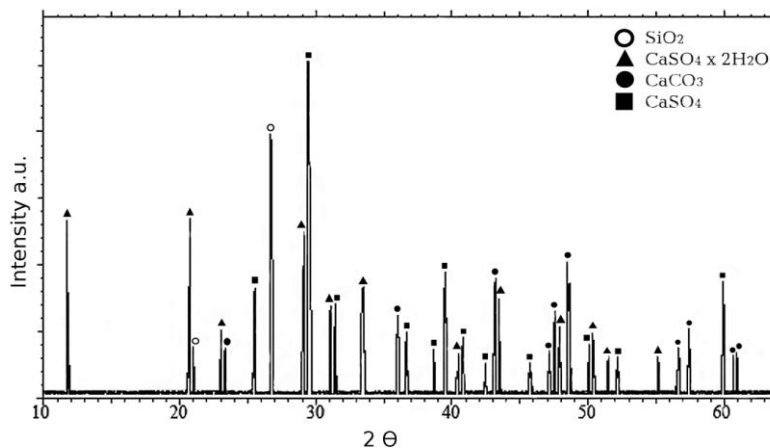
Fig. 12. The X-ray diffraction pattern of the ground

Having generalised the results of the microchemical, FTIR and XRD analyses of each ground it can be stated that: the bottom layer of the ground contains gypsum, chalk, sand, clay, charcoal and filament of vegetable fibre; the top layer of the ground contains gypsum, chalk, clay and sand.

Binding media

Binding media of two ground layers and the paint, as well as the IR spectra of standard gum arabic are presented in Fig. 13. The absorption bands of the IR spectra of the binding media of both ground layers and the paint are identical to the bands characteristic of polysacharides visible in the IR spectrum of standard gum arabic: 3300 cm^{-1}(O–H) and 1620 cm^{-1} (HOOC–), 1480–1300 cm^{-1} (C–H), 1080 cm^{-1} (C–O).
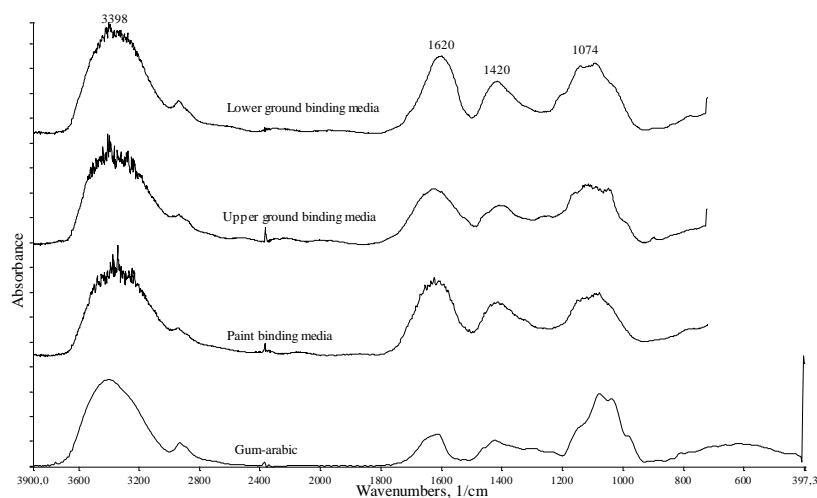
Fig. 13. The IR spectra of two ground layers and the binding media of blue paint, and a standard sample of gum arabic

Paint layers

The sarcophagus is polychromed with six colours: white, yellow, red, blue, green and black. Having summed up the results of the microchemical, FTIR and XRD analyses it has been established that huntite was used to obtain the white colour, yellow ochre was used to obtain the yellow colour, red ochre gave the red colour, Egyptian blue was used to obtain the blue colour, green earth or a mixture of green earth and Egyptian blue was used to obtain the green colour, and charcoal produced the black colour. Pure colours were used for painting; the principle of multi-layer painting was applied.

By means of the FTIR and XRD analysis methods it has been established that pigment huntite $CaMg_3(CO_3)_4$ was used to obtain the white colour. The absorption bands characteristic of huntite (1535, 1511, 1444 cm^{-1} C–O; the doublet absorption band at 891 and 869 cm^{-1}, according to *IRUG Spectral Database*) and gypsum (3545 and 3402 cm^{-1} (O–H), 1140, 1118 cm^{-1} (S–O)) are seen in the IR spectrum of the white paint (Fig. 14). It is probable that gypsum was left when separating the ground layers mechanically.
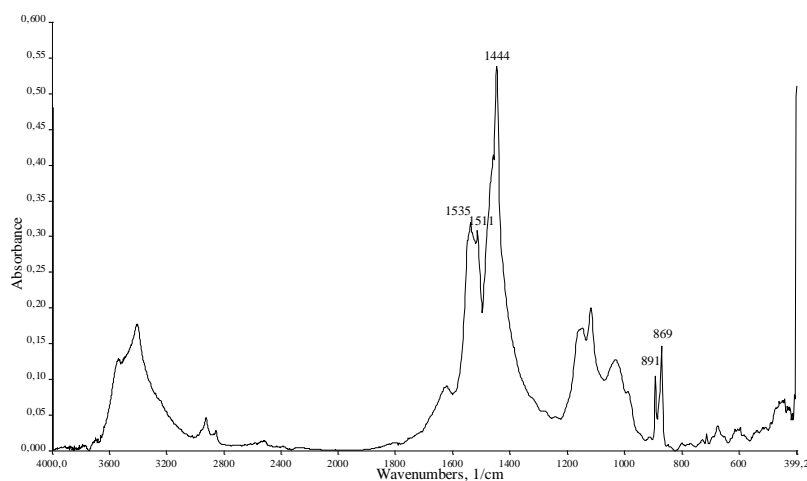

Fig.14. The IR spectrum of white paint

The huntite, dolomite and calcite phases identified in the X-ray diffraction pattern of the white paint sample point to the natural origin of huntite.

By means by the FTIR and XRD analysis methods it has been identified that Egyptian blue was used to obtain the blue colour. A broad and intense typical absorption band is visible in the IR spectrum of the blue paint sample at 1077 cm^{-1} (Si–O), which is

to be attributed to Egyptian blue pigment. Also, the doublet absorption band at 795 and 779 cm^{-1} (Fig. 15) highly characteristic of quartz SiO_2 manifests itself in the IR spectrum. Phases of Cuprorivaite $CaCuSi_4O_{10}$ (PDF No.12–512) and quartz SiO_2 prevail in the X-ray diffraction pattern of the blue paint (Fig. 16). Egyptian blue is, in fact, the first synthetic pigment to have been produced by firing copper oxide, calcium oxide and silica together.
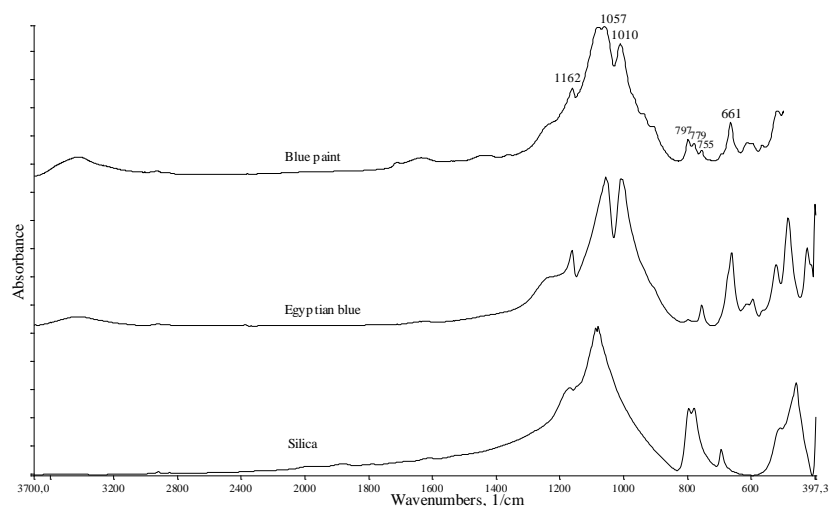

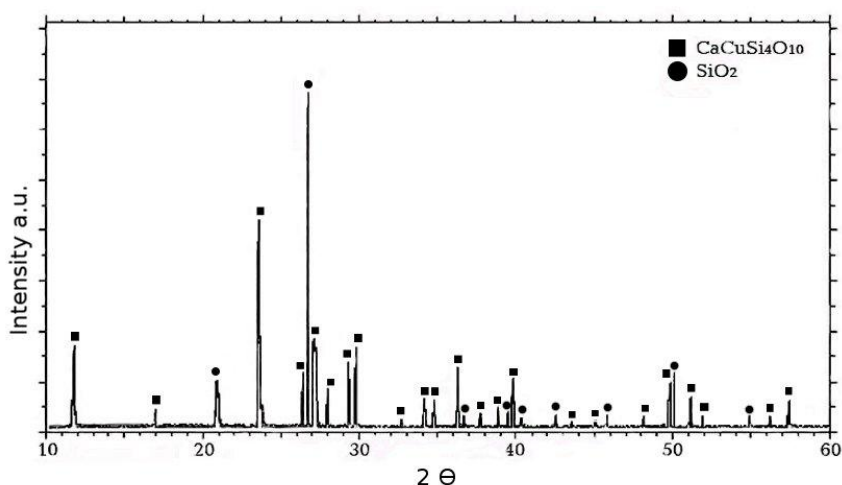**Fig. 15.** The IR spectra of the blue paint sample and standard Egyptian blue pigment

Fig. 16. The X-ray diffraction pattern of the blue paint sample of the sarcophagus' painting

3.2. **Investigation of chemical composition of archaeological glass beads**

A combination of optical microscopy, SEM/EDX, ATR-FTIR, XRD, and micro-Raman spectroscopy was applied to identify and compare the chemical composition, and characterize pigments on glass beads from three necklaces (grave No. 21, 191, 232) found in the Kernavė-Kriveikiškės cemetery in Lithuania dated back to the 13th – 14th century.

Optical microscopy and SEM/EDX analysis

Optical photographs of the cross-section of three yellow beads in the visible light provided information on the order of the real colour inside and corrosion degree of the beads. The futher SEM/EDX morphological and quantitative analysis was carried out compared composition of beads in different areas that is of surface of beads (area 1), opaque bright yellow corroded area (area 2) and glassy yellow beads core (area 3).

The results of EDX analyses of beads in different areas are presented in Table 10. This analysis shows that the contents of all yellow beads are high in lead (19–71 wt%), tin (0–19 wt%) and silicon (1–12 wt%) and the calcium, aluminium, phosphorus in the range of a few persent by weight.

Table 10. The SEM/EDX elemental composition of an archaeological necklaces yellow beads samples in diferrent areas (wt%)

	Bead from grave No. 21			Bead from grave No. 191			Bead from grave No. 232	
	Area 1	Area 2	Area 3	Area 1	Area 2	Area 3	Area 1	Area 2
Pb	60.8	43.1	67.9	18.9	57.8	71.0	38.2	47.6
Sn	–	11.0	8.8	1.5	9.3	7.8	14.1	18.5
Si	2.2	11,52	7.2	1.3	6.2	7.3	2.6	2.7
O	13.8	24.5	10.9	26.9	13.4	9.1	18.9	23.9
C	12.9	8.9	5.2	42.7	10.7	3.9	15.1	5.6
P	5.0	–	–	0.7	–	–	1.1	–
Ca	4.2	–	–	8.0	2.6	0.9	–	–
Al	0.8	1.0	–	–	–	–	–	–
Br	–	–	–	–	–	–	–	1.6

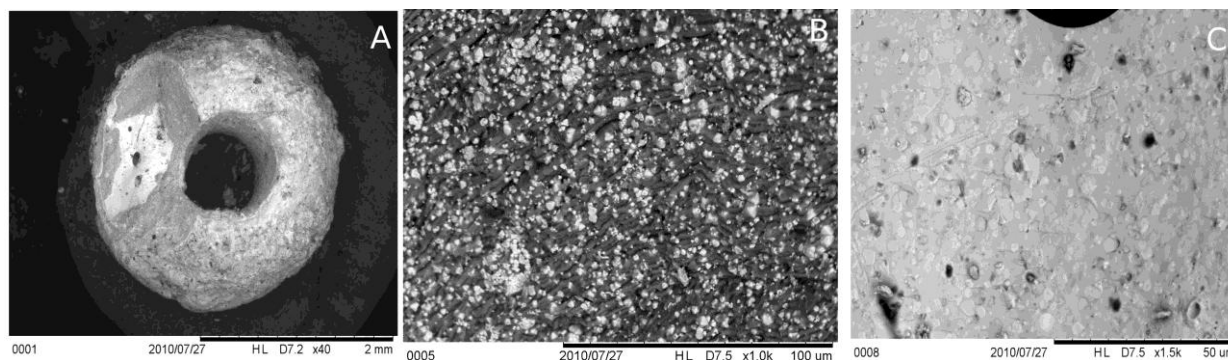SEM photographs of beads in different areas are presented in Fig. 17 and Fig. 18.

Fig. 17. SEM micrographs of the yellow bead from gave No. 21: A) general view; B) bead corroded area – lead-tin oxide (white) distributed in weathering lead rich glass; note the leaching of lead oxide from the glas due to weathering, witch results in a lower averange atomic number of the glass and hence a darker shade of grey in the image; C) yellow bead core (lead rich glass) – in lead rich glass (grey) located the lead-tin oxide 2–5 µm spherical form evenly distributed grains
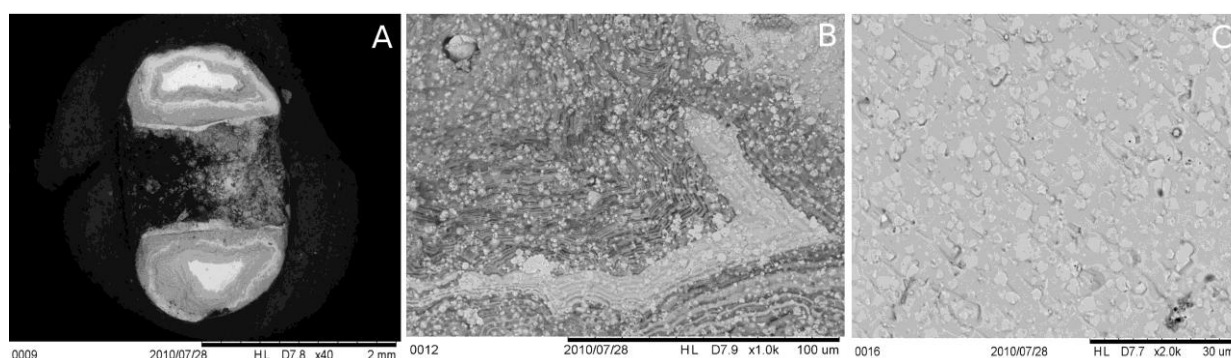
Fig. 18. SEM micrographs of the yellow bead from gave No. 191: A) general view; B) bead corroded; C) yellow bead core.

According to data obtained it can be presumed that yellow beads were made of rich lead-silica glass matrix, which as pigment used lead tin yellow pigment. The visual differences between the yellow beads are determined by unequale degree of glass destruction.

FTIR spectroscopy

This part presents the results of identification of composition of beads in different areas that is surface of beads, in opaque bright yellow corroded area and glassy yellow beads core using ATR-FTIR spectroscopy. IR spectra of all investigated beads are similar. The ATR-FTIR results of glass bead from grave No. 21 are presented in Fig. 19. The IR spectrum of the glassy yellow bead core clearly demonstrates the main

absorption bands that coincide with the absorption bands of lead tin yellow type II pigments 881 cm^{-1}, 586 cm^{-1} and 456 cm^{-1} provided for comparison. The literature source on the analysis and description of lead tin yellow type II pigments IR spectrum can not be found. The IR spectrum of the opaque bright yellow corroded area shows absorption bands of lead tin yellow type II pigments, as well as absorbtion bands of lead carbonate PbCO$_3$ at 1391 cm^{-1}, 840 cm^{-1} and 679 cm^{-1} (C–O). These results suggest that in the lead silicate glass corrosion process is formed PbCO$_3$.

The absorption bands and peaks at 1018 cm^{-1}, 597 cm^{-1}, 560 cm^{-1} (P–O) found in the IR spectrum of the whitish surface are attributable to calcium phosphate, which comprised due to a long interaction between glass materials and archaeological environment.
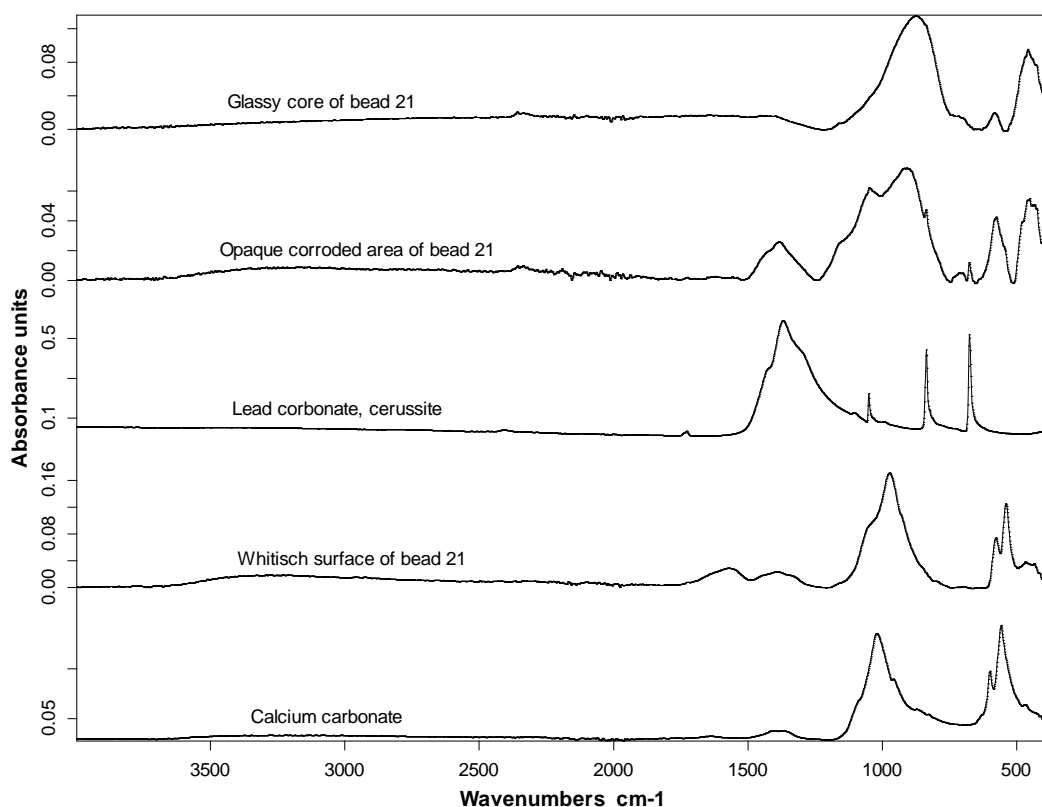

Fig. 19. The IR spectra of glassy yellow bead core, of opaque bright yellow corroded area and of whitish surface of bead, as well as lead carbonate and calcium phoshate

The results show that the ATR-FTIR method is considered to be effective in determining the destruction of lead silicate glass products.

XRD analysis

All significant reflections of the yellow beads samples (grave 21, 191, 232) were assigned to the polycrystalline lead tin silicon oxide $PbSnO_3$ phase (PDF [17-0607] having a cubic crystaline structure. XRD paterns of the yellow beads samples are presented in Fig. 20.
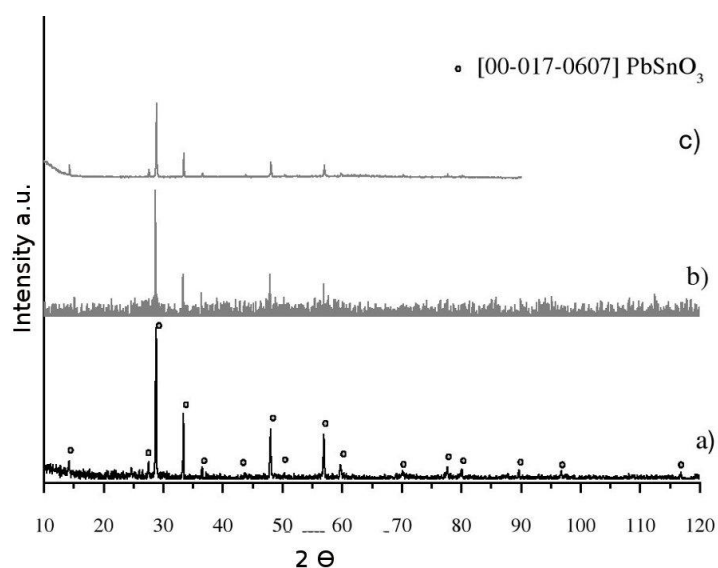

Fig. 20. X-ray diffraction patterns of the archaeological yellow beads: grave No. 21 (a), grave No. 191 (b), grave No. 232 (c)

micro-Raman spectroscopy

Raman spectroscopy was used to identify the pigments of the archaeological glass bead (grave No. 232) for the first time in Lithuania.

Figure 21 compares the Raman spectra from yellow bead and comparative samples (lead tin yellow types I and II pigments).
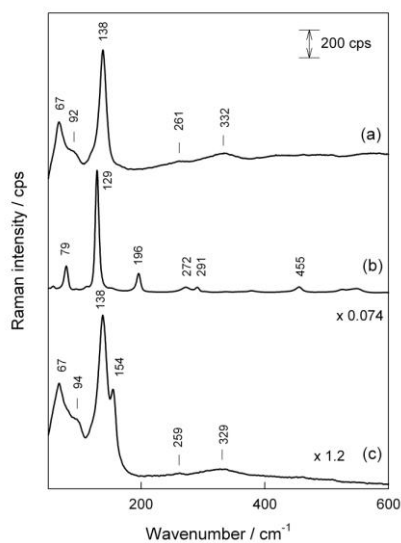
Fig. 21. The Raman spectra of the yellow bead from the grave No. 232 (a), and comparative samples of lead tin yellow type I (b), and II (c).

The spectrum of studied beads clearly shows an intense peak at 138 cm^{-1} along with the several low intensity features at 67, 92, 261, and 332 cm^{-1} (Fig. 21(a)). All the bands visible in the yellow bead spectrum coincide well with the comparative data of lead tin yellow type II pigment. Raman measurements conclusively prove that lead tin yellow type II pigment is the main pigment of the yellow opaque bead from grave No. 232. No evidence for presence of other pigments was found.

4.   CONCLUSIONS

1.   In this dissertation, the results of detailed investigation of the seven unique art objects are presented. The presented results show that complex apllying of the instrumental analytical methods of OM, FTIR, SEM/EDX, XRD, µXRD and µRS is accurate and efficient way to identify composition of works of art and archaeological finds of glass, pigments or describe their technology.

2.   IR spectroscopy has been successfully applied to determine pigments and some pigment mixtures in painting's ground, paint layers, and destruction products in archaeological glass: chalk, hydrocerussite, cerussite, azurite, calcium phosphate, gypsum, smalt, Egyptian blue, Prussian blue, ocher, verdigris. Identification of the dispersed in the paint binding media by IR spectroscopy method was not always

successfull without extraction because of its relatively low concentration (up to 5%) and parcel of pigments in the paints mixture.

3. The elemental composition of the samples of paintings and archaeological glass was determined using the SEM/EDX analysis. EDX analysis successfully can be used in determining the main elements of the paint samples at different cross-section points whose amounts exceed 0.5% of the overall elemental composition i.e., perform a qualitative analysis of the pigments (cinnabar, lead white, chalk, smalt et. al.), in some cases, to discuss the features of the production of pigments.

4. The SEM/EDX provided a possibility to examine three archaeological glass beads from Kernavė-Kriveikiškės cemetery. According to the elemental composition, microstructure, and the specific features in different areas of the glass was defined nature of the destruction of glass. The SEM images show the strong morphological differences between the glass beads. The SEM images of the beads from the graves No. 21 and 191 show the microstructure close to the glass. The SEM image of the bead from the grave No. 232 shows the presence of only evenly distributed spherical form grains of 2-3μm which tend to form solid structure.

5. XRD and μXRD analysis successfully can be used in determining the crystalline phases in the paint and archaeological glass samples. Analysis has been successful in identify following pigments and their mixtures: calcite $CaCO_3$, carbon, lead tin yellow type I Pb_2SnO_4, lead tin yellow type II $PbSn0_3$, hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$, cerussite $PbCO_3$, Egyptian blue $CaCuSi_4O_{10}$, gypsum $CaSO_4 \cdot 2H_2O$, anhydrite $CaSO_4$, huntite $Mg_3Ca(CO_3)_4$, dolomite $CaMg(CO_3)_2$. It was demostrated that XRD analysis is significant analytical tool for the characterization of ancient pigments.

6. For the first time μRS was applied to determine lead tin yellow type II pigment in archaeological glass. μRS analysis is significant analytical tool for characterization of archaeological coloured glass.

The List of Original Publications by the Author

Articles in journals

1. J. Bagdzevičienė, J. Senvaitienė, J. Lukšėnienė, S. Tautkus. Investigation of the Technique of painting on a tin alloy plate. *Chemija*, **20** (2009) 93–100.

2. J. Bagdzevičienė, S. Tautkus. St. Bruno. A Miracle in the Church: Investigation of the Painting Technique. *Chemija*, **22** (2011) 33–40.

3. J. Bagdzevičienė, G. Niaura, E. Garškaitė, J. Senvaitienė, J. Lukšėnienė, S. Tautkus, Spectroscopic analysis of lead tin yellow pigment in medieval necklace beads from Kernavė-Kriveikiškės cemetery in Lithuania. *Chemija*, **22**, (2011) 216–222.

Published contributions to academic conferences

1. J. Bagdzevičienė, S. Tautkus. Study of Painting „Madonna and Child, 8th National Lithuanian Conference. Vilnius (2007) 19.

2. J. Bagdzevičienė, S. Tautkus. Studies of painting gound composition by IR spectroscopy method. Conference" Chemistry and technology of Inorganic Compounds". Kaunas (2008) 88.

3. J. Bagdzevičienė, S. Tautkus. Analysis of a Medieval Yellow Beads Necklace from Kernavė-Kriveikiškės Cemetry. Conference „Chemistry and Technology of Inorganic Compounds". Kaunas (2009) 79.

4. J. Bagdzevičienė, S. Tautkus. St. Bruno. Miracle in the Church: Investigation of the Painting Technique. 9th National Lithuanian Conference „Chemistry 2009". Vilnius, Lithuanian, October 16 (2009) 16.

5. J. Bagdzevičienė, J. Kiuberis, R. Juškėnas, S. Tautkus. Sarcophagus of the Singer of God Amon: Investigation of the Technique of Polychromy. 10th National Lithuanian Conference Chemistry 2011 dedicated to the International Year. Vilnius (2011) 24.

CURRICULUM VITAE

Jurga Bagdzevičienė

1991–1995 the bachelor studies at the Vilnius University, Faculty of Chemistry.

2000–2001 specialized professional studies Conservation of Cultural Heritage, Vilnius University, Faculty of Chemistry. Qualification: scientist of conservation of Cultural Heritage.

2004–2006 the master studies at the Vilnius University, Faculty of Chemistry.

2006–2011 post-graduate studies at the Vilnius University, Faculty of Chemistry, Department of Analytical and Environmental Chemistry.

Since 1995 conservation scientist at the Pranas Gudynas Restoration Centre of Lithuanian Art Museum.

SENOVINIŲ PIGMENTŲ TAPYBOS KŪRINIUOSE IR ARCHEOLOGINIO STIKLO RADINIUOSE TYRIMAS IR APIBŪDINIMAS

SANTRAUKA

Septynių unikalių, didelę istorinę ir meninę vertę turinčių objektų – trijų XVII ir XVIII a. paveikslų, Senovės Egipto sarkofago bei trijų archeologinių stiklo karolių – tyrimams sėkmingai pritaikyti OM, FTIR, SEM/EDX, XRD, µXRD ir µRS analizės metodai. Konstatuota, kad taikant kompleksinius tyrimus ir juos derinant galima tiksliai ir efektyviai identifikuoti kūrinių medžiagas, charakterizuoti jų sandarą, apibūdinti technologijas.

IR spektroskopija sėkmingai panaudota identifikuojant tapybos grunto ir dažų sluoksnių neorganinius tapybos pigmentus ir jų mišinius bei stiklo korozijos produktus; apibūdinta kreida, hidrocerusitas, cerusitas, kalcio fosfatas, azuritas, gipsas, smalta, Egipto mėlynasis, Berlyno mėlynasis, ochra, vario acetatas (verdigris). Kai daugiakomponenčiuose grunto ir dažų mėginiuose yra iki 5 % rišamosios medžiagos, ją nustatyti be ekstrahavimo ne visada pavyksta. Parodyta, kad IR spektroskopija gali būti sėkmingai panaudota identifikuojant istorines restauravimo medžiagas.

SEM/EDX analizės metodu nustatyta tapybos elementinė sudėtis, tyrimus vykdant skirtinguose mėginių skerspjūvių taškuose. Pagal pagrindinius elementus, kurių kiekiai

viršija 0,5 %, identifikuoti cinoberio, švino baltojo, kreidos, smaltos, suriko ir kt. pigmentai. Parodyta, kad pagal smaltos specifinius elementinės sudėties bruožus galima charakterizuoti šio pigmento gamybos ypatumus. Artimos elementinės sudėties pigmentai, kaip I ir II tipo švino alavo geltonasis, cerusitas ar hidrocerusitas identifikuoti XRD ar µRS analizės metodais.

SEM/EDX analizės metodu ištirti trys archeologiniai stiklo karoliukai iš Kernavės-Kriveikiškių kapinyno. Pagal elementinės sudėties skirtumus ir specifinius mikrostruktūros bruožus skirtinguose stiklo lūžimo taškuose nustatytas stiklo destrukcijos pobūdis, nevienodas švino alavo oksido dalelių pasiskirstymas švino silikatinio stiklo matricoje. Įrodyta, kad dviejų karoliukų (kapai Nr. 21, Nr. 191) mikrostruktūra artimesnė stiklui nei trečiojo karoliuko (kapas Nr. 232).

XRD ir µXRD analizės metodais, kai rentgeno spindulių srautas fokusuojamas ir kiekvienas dažų sluoksnis analizuojamas atskirai, sėkmingai identifikuoti šie pigmentai ir/ar jų mišiniai: kalcitas $CaCO_3$, anglis, I tipo Pb–Sn geltonasis Pb_2SnO_4, II tipo Pb–Sn geltonasis $PbSn0_3$, hidrocerusitas $2PbCO_3 \cdot Pb(OH)_2$, cerusitas $PbCO_3$, Egipto mėlynasis $CaCuSi_4O_{10}$, gipsas $CaSO_4 \cdot 2H_2O$, anhidritas $CaSO_4$, huntitas $Mg_3Ca(CO_3)_4$, dolomitas $CaMg(CO_3)_2$.

Pirmą kartą µRS metodu identifikuotas II tipo švino alavo geltonasis pigmentas, suteikiantis geltoną spalvą archeologiniam stiklui. Disertaciniame darbe gauti rezultatai leidžia daryti išvadą, kad µRS metodas gali būti efektyviai panaudotas destruktavusiam spalvotam stiklui analizuoti.