

# Spectroscopic analysis of lead tin yellow pigment in medieval necklace beads from Kernavė-Kriveikiškės cemetery in Lithuania

J. Bagdzevičienė<sup>1\*</sup>,

G. Niaura<sup>2</sup>,

E. Garškaitė<sup>1</sup>,

J. Senvaitienė<sup>3</sup>,

J. Lukšėnienė<sup>3</sup>,

S. Tautkus<sup>1</sup>

<sup>1</sup>Department of Analytical  
and Environmental Chemistry,  
Vilnius University,  
Naugarduko 24, LT-01535 Vilnius,  
Lithuania

<sup>2</sup>Institute of Chemistry of  
Center for Physical Sciences  
and Technology, A. Goštauto 9,  
LT-01108 Vilnius, Lithuania

<sup>3</sup>Lithuanian Art Museum,  
Pranas Gudynas Restoration Center,  
Rūdninkų 8, LT-01135 Vilnius,  
Lithuania

A combination of X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM/EDX), infrared spectroscopy and Raman microspectroscopy was applied to identify the chemical composition and characterize pigments on glass beads from necklaces found in the Kernavė-Kriveikiškės cemetery in Lithuania, dated back to the 13–14th centuries. Raman measurements conclusively prove that lead tin yellow type II pigment is the main material of the yellow opaque beads. Based on XRD studies, the average crystallite size of the bead pigment ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) was found to be 159 nm. No evidence for the presence of other pigments was found. The analysis of the results has clearly demonstrated that the methodological approach applied for the investigation of such beads' composition is appropriate, effective and reliable. The spectroscopic analysis of the chemical composition and structure of necklace beads provided an important information on the technological features and potentiality of the ancient production of glass beads.

**Key words:** lead tin yellow, glass beads, FTIR, XRD, SEM / EDX, Raman spectroscopy

## INTRODUCTION

Lead tin yellow compounds were extensively applied for colouring the Roman (or immediate post-Roman) period glasses and have been used as a pigment in pictorial art since somewhere about 1300 A. D. [1, 2], and they continue to attract scientists today [3–5]. The pigment is complex because of a

possible interference of two chemically different forms called lead tin yellow type I ( $\text{Pb}_2\text{SnO}_4$ ) and type II ( $\text{PbSnO}_3$ ,  $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ). It should be noted that the lead tin yellow type II responsible for the opaque yellow of glass is of cubic ( $\text{PbSnO}_3$ ,  $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$  cubic pyrochlore type) but not of orthorhombic form ( $\text{Pb}_2\text{SnO}_4$ , lead tin yellow type I). As pointed out by Rooksby [6], when mixtures of lead oxide and tin oxide are heated to temperatures in the range of 700–900 °C, it is the orthorhombic form ( $\text{Pb}_2\text{SnO}_4$ ) that is formed. However, if

\* Corresponding author. E-mail: jbagdzeviciene@gmail.com

silica was added to  $\text{Pb}_2\text{SnO}_4$  and the resulting mixture was heated to 850 °C,  $\text{Pb}_2\text{SnO}_4$  was converted to the cubic  $\text{PbSnO}_3$  ( $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ), and a complete conversion was found to take place for the  $\text{Pb}_2\text{SnO}_4$  to  $\text{SiO}_2$  molar ratio of 3 to 2 (i. e. equivalent to 69.9%  $\text{PbO}$ , 23.8%  $\text{SnO}_2$  and 6.3%  $\text{SiO}_2$ ). The lead tin yellow type II pigment according to chemical composition can be considered as glass, but unlike glass (amorphous), the pigment has a crystalline structure. Thus, identification of the chemical structure of the yellow pigment is important in understanding the history of a particular artwork or an artefact of archeological importance.

The paper presents the results of composition analysis of beads from a necklace found in a female grave of the Kernavė-Kriveikiškės cemetery (Fig. 1). Excavations carried out during the last 23 years led to the conclusion that the Kernavė town existed here already in the second half of the 13th century and was an important and epoch-making medieval East Lithuanian town and political centre. The aforementioned necklace looked very decayed; it was difficult to tell from visual examination that this it was a glass bead necklace; it looked rather like a ceramic artifact because the beads were opaque and of light brownish colour. The initial examination with a microscope caused even more curiosity because it showed that inside the split beads were opaque and of a bright yellow colour.

The aim of this research was to identify the chemical composition of necklace beads and to describe their structure. Moreover, we focused on investigating the colouring components to produce yellow beads and the morphology of the pigment. For this purpose, we applied several spectroscopic techniques sensitive to the morphology, composition, structure, and chemical identity of the pigments. Infrared spectroscopy (IR) and scanning electron microscopy (SEM)

coupled with an energy-dispersive X-ray spectrometer (EDX), X-ray diffraction (XRD) [8, 9], and Raman spectroscopy were used for the analysis of the artifact. The employed techniques complemented each other. Infrared spectroscopy has a molecular specificity and is more suitable for the analysis of molecules containing highly polar groups (ester bonds, carboxyl and amide groups) which include a binding material, resins, and varnishes [10, 11]. However, this technique is less suitable for the analysis of inorganic pigments because the low-frequency region ( $10\text{--}300\text{ cm}^{-1}$ ) in which the main vibrations of molecular groups containing heavy metal atoms (Pb, Sb, Hg, Au) take place is difficult to access with conventional instruments [12]. Raman spectroscopy emerged as one of the most powerful non-destructive analytical tools for the characterization of micro-quantities of pigments with a molecular specificity [13–15]. It covers a wide spectral range (usually from 50 to  $3500\text{ cm}^{-1}$ ), might be used in-situ, and has a high spatial ( $\sim 1\text{ }\mu\text{m}$ ) and spectral ( $\leq 1\text{ cm}^{-1}$ ) resolution. Comprehensive Raman spectral databases of pigments and minerals have been developed [16, 17], providing a possibility to assign Raman peaks and subsequently to identify the compounds.

Accordingly, yellow glass compositions that are encountered in Kernavė were compared with data of published works devoted to studies of yellow opaque glass bead composition.

The present study may be considered as a pioneering work designed to enhance our knowledge of the chemical composition, technological features and production potentiality of glass beads found in Lithuanian burial grounds. Also, it is one of the rare and interesting archeological sites in East Europe, which contains a significant amount of information on the daily life of a small but affluent medieval community.



**Fig. 1.** Necklace from grave No. 232 of Kernavė–Kriveikiškės Cemetery consists of a cross, three diamond-shaped tin pendants, and about 230 bisser beads as well as of beads 1.5–3 mm in diameter, shaped as slightly flattened spheres. The necklace is shown after its cleaning procedure

## EXPERIMENTAL

Firstly, in order to characterize in broad outlines the composition of archaeological necklace beads, a microchemical qualitative analysis and IR spectroscopic studies were performed. Secondly, the necklace beads were morphologically and structurally characterized by the SEM/EDX and XRD analyses. Finally, micro-Raman spectroscopy was applied for the characterization of yellow pigments. The lead tin yellow type I (lead tin oxide) ( $\text{Pb}_2\text{SnO}_4$ ), lead tin yellow type II (lead tin silicon oxide) ( $\text{PbSnO}_3$  or  $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ) pigments from Kremer Pigmente GmbH & Co. KG (Germany) were used for comparison.

The pigment of the beads was analysed on the objective glass by observing its solubility in acids and alkalis, as well as applying specific microcrystaloscopic reactions for the identification of metal ions. The analysis was concluded by observing a sample and the reactions carried out in reflected light using the Nikon SMZ-1/SMZ-1ESD microscope (magnification 7 to 30).

The infrared spectra of the samples of beads and lead tin yellow pigments (Kremer Pigmente GmbH & Co. KG, Germany) were recorded at room temperature using a FT-IR-8400S spectrophotometer (Shimadzu). The spectrometer was connected to the IR AIM-8800 microscope equipped with a nitrogen-cooled MCT detector. The IR spectra in transmittance mode were registered under the following conditions: a small part of a sample was mixed with KBr and pressed into a pellet using the manual MHP-1 mini-press; the spectrum interval ranges from 4000 to 400  $\text{cm}^{-1}$  and 100 scans were applied at a 4  $\text{cm}^{-1}$  resolution. The presented spectra are baseline-corrected and converted to the absorbance mode.

The morphology of the samples was established using the Hitachi S-3500N (Ibaraki, Japan) scanning electron microscope (SEM) equipped with the energy-dispersive X-ray (EDX) detector. Quantitative analysis was carried out from the surface of a small sample of a yellow bead and from powders of a comparative lead tin yellow (types I and II, Kremer Pigmente GmbH & Co. KG, Germany) pigments. The element concentration was measured in the points at spots  $5 \times 10 \mu\text{m}$  in size. The chemical composition of the samples was calculated as an average of six measurements.

The X-ray diffraction (XRD) analysis was performed on the Bruker AXS D8 Focus diffractometer with the LynxEye detector,  $\text{CuK}\alpha$  radiation. The average crystallite size of the yellow bead sample was estimated by the Scherrer equation,  $d_{\text{XRD}} = K\lambda/\beta \cos \theta$ , as an average using the full-width at half maximum (FWHM) of the 222, 400, 440 and 622 reflections at theta values 29, 33.5, 48 and 57.

Raman spectra were recorded with the Horiba Jobin Yvon LabRam HR800 spectrometer equipped with 600 groove/mm grating. The 632.8 nm emission of a He-Ne laser was used to excite the spectra. The laser power at a sample was adjusted to 1 mW to avoid any sample degradation. Raman spectra were taken by using a long working distance 50 $\times$  / 0.50 NA

objective lens. The spectra were calibrated using the Si band at 520.6  $\text{cm}^{-1}$ . The integration time was 50 s. Specimens were not subject to prior chemical or mechanical treatment.

## RESULTS AND DISCUSSION

The initial examination under the microscope showed that the beads that looked light brownish on the surface were bright yellow inside. Lead and tin detected by microchemical tests indicated that the yellow colour of beads had been obtained by using the lead tin yellow pigment [17].

### FT-IR spectroscopy

From the IR spectra of the artifacts it was expected to obtain a preliminary information on the bead matrix. FT-IR spectroscopy is an effective way to obtain the basic chemical information on a sample, and with a typical mid-IR FT-IR instrument most inorganic compounds containing complex anions (carbonates, sulfates, silicates, etc.) could be identified in artworks and archaeological materials [18].

Figure 2 compares the IR spectra from the bead and comparative samples (lead tin yellow types I and II). The spec-

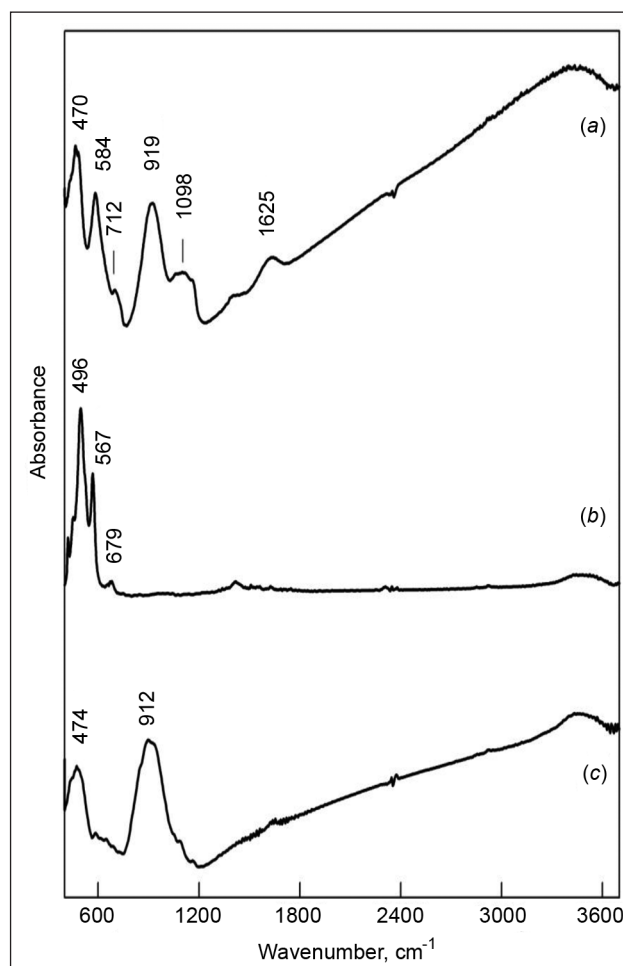


Fig. 2. FT-IR spectra of a yellow bead from grave No. 232 (a) and comparative samples of lead tin yellow type I (b) and II (c) pigments

trum of the studied artifacts clearly shows peaks at 919 and 470  $\text{cm}^{-1}$  (Fig. 2a), which well coincide with the comparative lead tin yellow type II pigment absorption bands (Fig. 2c) characteristic of metal–oxygen (Pb–O) vibrations [10] comparing the peak positions and relative intensities. However, the spectrum of the original sample contained additional bands located at 584, 712, and 1098  $\text{cm}^{-1}$ , which might be assigned to vibrations of the silica matrix [19]. It should be noted that infrared spectroscopy cannot show whether lead-tin yellow type I pigments are present in a sample. Two intensive bands observed in the comparative spectrum at 567 and 496  $\text{cm}^{-1}$  (Fig. 2b) might contribute to the rather broad features in the sample spectrum at 584 and 470  $\text{cm}^{-1}$  (Fig. 2a). Importantly, the infrared spectrum of original samples shows no presence of any organic material containing methylene and methyl (no bands in the 2800–3000  $\text{cm}^{-1}$  region) or ester ( $\sim 1730 \text{ cm}^{-1}$ ) groups [9, 19].

### SEM / EDX analysis

The results of EDX analyses of a bead and comparative samples (lead tin yellow types I and II pigments) are presented in Table. This analysis shows that the contents of a bead is high in lead (45.33 wt%) with a silica content in the range 2.86 wt%, also in tin (18.67 wt%). The elements (Pb, Sn, Si) identified in the necklace bead correspond to the composition of the comparative lead tin yellow type II, but differ in their contents ranging from 2 to 15 percent. In our opinion, these differences could indicate different initial recipes used for the production of lead tin yellow type II pigments, or they could be related to the removal of elements during the corrosion of

a bead glass. Based on the results of EDX analysis of a yellow bead, the calculated atomic lead-to-tin ratio was found to be about 1 : 0.7. This atomic ratio and the quantity of silica in the yellow bead lead us to the conclusion that the lead tin yellow type II pigment [3, 18] prevails in the composition of a bead. The SEM image of bead structure supports this opinion, but shows the presence of only 2–3  $\mu\text{m}$  spherical evenly distributed grains (Fig. 3).

### XRD analysis

The XRD patterns of the yellow bead sample and comparative lead tin yellow (types I and II) pigments are presented in Fig. 4. All significant reflections of the yellow bead sample were assigned to the polycrystalline lead tin silicon oxide ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) phase having a cubic crystal. It is a conventional structure, which is consistent with literature (JCPDS No. 49-1886). The XRD pattern of the comparative lead tin yellow pigment (type I) shows the presence of two phases – lead tin oxide, ( $\text{Pb}_2\text{SnO}_4$ ) (JCPDS No. 24-0589) having a tetragonal crystal structure, and tin oxide ( $\text{SnO}_2$ ) cassiterite (JCPDS No. 41-1445) of tetragonal structure. The main phases obtained from the comparative lead tin yellow pigment (type II) powders were assigned to the polycrystalline lead tin silicon oxide ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) phase,  $\text{SnO}_2$  cassiterite, and silicon oxide ( $\text{SiO}_2$ ) having a triclinic crystal structure (JCPDS No. 01-082-1573). The average crystallite size of the yellow bead sample was estimated to be 159 nm. The particle size determined from SEM measurements, however, was 2–3  $\mu\text{m}$ . This is not surprising, since SEM measurements provided information about the size of crystallite aggregates.

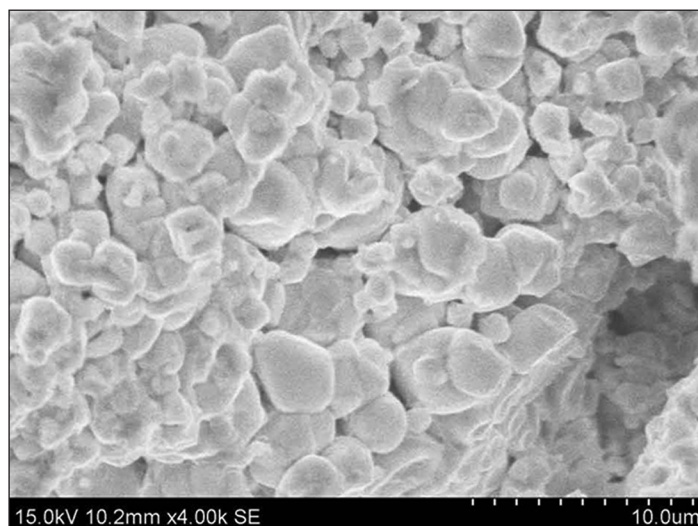


Fig. 3. SEM image of a yellow bead

Table. The SEM / EDX elemental composition of an archaeological necklace bead and comparative lead tin yellow (types I, II) pigments, samples (wt%)

	Samples	O	C	Si	Sn	Pb
1.	Necklace yellow bead	8.97	24.17	2.86	18.67	45.33
2.	Lead tin yellow type I	19.7	18.6	–	16.6	45.13
3.	Lead tin yellow type II	11.4	18.6	4.8	4.51	60.7

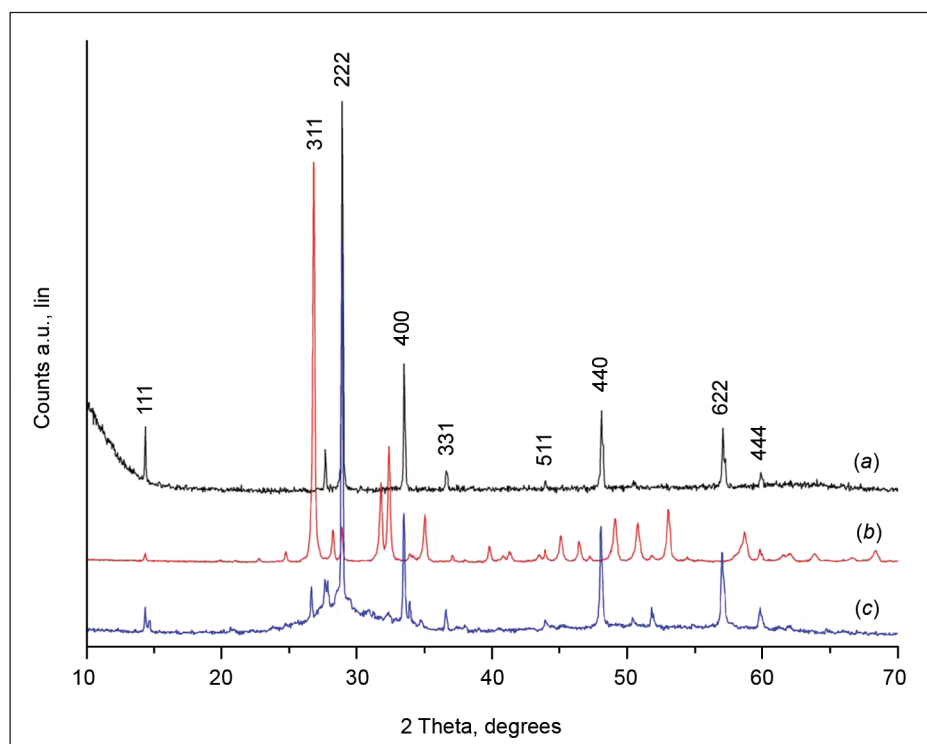


Fig. 4. X-ray diffraction patterns of an archaeological yellow bead (a) and powder of comparative lead tin yellow type I (b) and II (c) pigments

XRD analysis has shown that the lead tin yellow type II ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) pigment is the single crystalline phase in the studied yellow opaque beads. Interestingly, the comparative lead tin yellow type II pigment is not a homogeneous crystal substance but consists of three phases, which suggest a complicated production of the pigment. No further study of comparative lead tin yellow type I and II pigment production process was undertaken, as this would not have contributed directly to this study.

#### The Raman spectroscopy

The Raman micro-spectroscopy is extremely suitable for the analysis of pigments because of its high sensitivity and molecular specificity and provides the possibility to discriminate among various yellow pigments [3, 15, 16]. Figure 5 compares the Raman spectra from yellow bead and comparative samples (lead tin yellow types I and II pigments) taken with a 632.8 nm excitation. The spectrum of the beads clearly shows an intensive peak at  $138\text{ cm}^{-1}$  along with several low-intensity features at 67, 92, 261, and  $332\text{ cm}^{-1}$  (Fig. 5a). A comparison with the comparative sample spectrum (Fig. 5(c)) undoubtedly shows the presence of the lead tin yellow type II pigment. Similar spectra of this compound have been reported by Clark et al. [3] and Prinsloo and Colombari [20]. The dominant  $138\text{ cm}^{-1}$  peak was assigned to the lattice Pb stretching mode [3]; its position may slightly depend on the firing temperature [21, 22] used in the preparation of the artifact. No evidence of lead tin yellow type I pigment was found in the spectroscopic

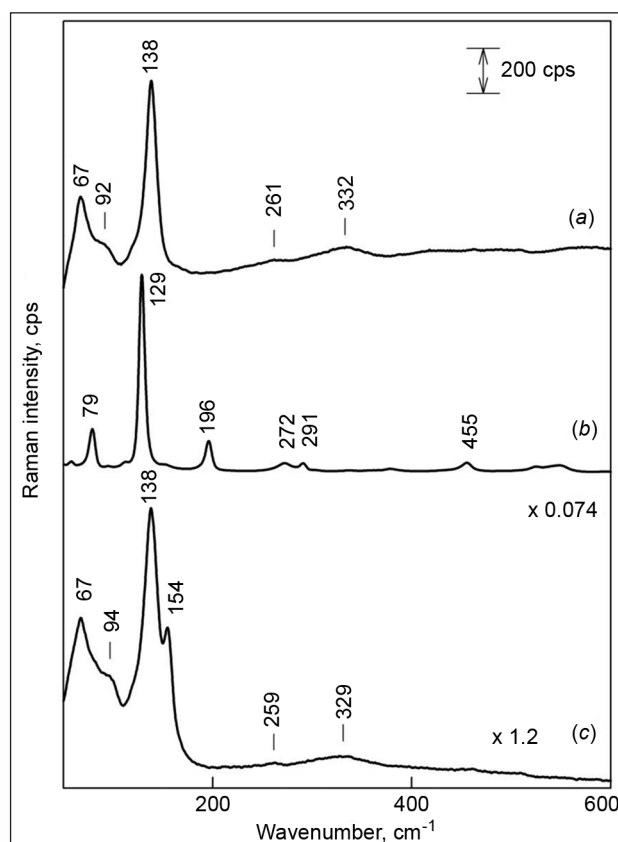


Fig. 5. Raman spectra of a yellow bead from grave No. 232 (a) and comparative samples of lead tin yellow type I (b), and II (c). Excitation wavelength 632.8 nm (1 mW)

analysis (Fig. 5b). It should be noted that the intensity of the dominant Pb–O band of the comparative lead tin yellow type I pigment was higher by a factor of 16 as compared with the band at  $138\text{ cm}^{-1}$  of the type II comparative sample. All the bands visible in the yellow bead spectrum coincide well with the comparative data of lead tin yellow type II pigment. In our comparative spectrum, a low-intensity extra band is visible near  $154\text{ cm}^{-1}$  (Fig. 5c), which was not reproduced in previous works [3, 20]. This feature might be associated with impurities or different pigment preparation procedures. Thus, Raman measurements in this study prove conclusively that lead tin yellow type II pigment is the main material of the yellow opaque beads.

## DISCUSSION

The analytical data indicate that the yellow opaque beads from the Kernavė-Kriveikiškės cemetery were made on the basis of the lead tin yellow type II pigment ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ). The obtained results could be compared only with a few published works on yellow opaque glass beads of different age. Thus, researches described yellow glass bead matrix composition of the Maastricht (6th–7th cc. AD) and Merovingian (5th–7th c. AD) period [23–26]. These samples resembled soda-lime glass coloured with lead tin oxide. Prinsloo and Colomban [20] presented the Raman spectra and XRF analysis of the Mapungubwe oblate beads and classified the glass as a typical soda-lime-potash glass similar to Islamic glass from the 8th century; its bright yellow colour was obtained by using a combination of cassiterite ( $\text{SnO}_2$ ) and lead tin yellow type II ( $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ) pigment. Henderson [23] noted that a lead stannate opacifier had been used for the yellow opaque glasses from Germany, so the yellow glass used for bead-making at Ribe may represent a technological continuity of this 6th–7th century glass. We were not able to find literature sources demonstrating that the opaque yellow glass beads were made of the lead tin yellow type II pigment. However, Tite et al. [5] in analysing the composition of yellow and green Islamic and Venetian enamels have stated that for their production the lead tin yellow type II pigment was used directly without being mixed with any colourless soda-lime glass. Analysis of the lead tin yellow type II pigment production process has indicated that there exist an optimal ratio of the components (lead oxide, tin oxide, and silica) and an optimal annealing temperature leading to a homogeneous polycrystalline lead–tin–silicon oxide ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) phase [5]. The question whether the yellow glass beads were made on the basis of the lead tin yellow type II pigment, which resembled the lead glass, remains open. The spectroscopic analysis of the chemical composition and structure of the necklace yellow beads provided an important information on the technological features and potentiality of the ancient production of glass beads found in the Kernavė-Kriveikiškės cemetery.

## CONCLUSIONS

By combining the analytical methods of microchemical qualitative tests, spectroscopy and scanning electron microscopy, materials of the yellow beads from a necklace found in the Kernavė-Kriveikiškės cemetery in Lithuania, dated back to the 13th–14th century, have been identified and characterized. The obtained data suggest that the yellow opaque beads are composed of a crystalline-glassy substance, and lead tin yellow type II ( $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ ) pigment is the main material of the yellow glass beads. No evidence of the presence of other pigments was found. The chemical composition and structure of the yellow necklace beads provided an important information on the technological potentiality of the production of glass beads.

## ACKNOWLEDGEMENT

We are grateful to the Department of Bioelectrochemistry and Biospectroscopy of the Institute of Biochemistry (Vilnius) for the possibility to use the Raman spectrometer. We thank Prof. Tor Grande (Norwegian University of Science and Technology (NTNU) for help in XRD and SEM measurements.

Received 19 September 2011

Accepted 12 October 2011

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J. Bagdzevičienė, G. Niaura, E. Garškaitė, J. Senvaitienė,  
J. Lukšėnienė, S. Tautkus

## VIDURAMŽIŲ VĒRINIO GELTONŲ KAROLIUKŲ IŠ KERNAVĖS-KRIVEIKIŠKIŲ KAPINYNŲ TYRIMAS

### S a n t r a u k a

Atliktas kaklo vėrinio (kapas Nr. 232) biserinių geltonų karoliukų iš Kernavės-Kriveikiškių kapinyno, kuris datuojamas XIII–XIV a., tyrimas. Derinant kelis analizinius metodus nustatyta karoliukų sudėtis bei geltoną spalvą suteikiantis pigmentas. Tiriamų karoliukų SEM nuotraukoje matyti sferinės formos 2–3 μm aglomeruoti grūdėliai, pasiskirstę gana tolygiai ir linkę sudaryti vientisą struktūrą. EDS rezultatai parodė, kad tiriamų karoliukų sudėtyje yra gana daug švino – 45,33 wt%, silicio – 2,86 wt%, taip pat alavo – 18,67 wt%. XRD difraktogramoje matyti viena kristalinė fazė, priskirtina junginiui  $PbSn_{0,76}Si_{0,24}O_3$ . Apibendrinę SEM / EDS ir RSD rezultatus padarėme išvadą, kad geltonus karoliukus sudaro kristalinė-stikliška medžiaga ir jie pagaminti II tipo Pn–Sn geltonojo pigmento ( $PbSn_{0,76}Si_{0,24}O_3$ ) pagrindu. Jokių kitų pigmentų nebuvo nustatyta. Nustatyta geltonų karoliukų cheminė sudėtis ir struktūra suteikė svarbios informacijos apie technologinį stiklo karoliukų gamybos potencialą, tačiau neatskleidė karoliukų kilmės; vis dėlto tai puiki pradžia tyrinėjant unikalius Kernavės kapinyno radinius.