Analytical characterization of Baltic amber and pottery

Aivaras Kareiva, Jonas Kiuberis, Algimantas Merkevičius

INTRODUCTION

Amber is the most numerous group of archaeological finds and its analysis reveals important information about the daily life and the ethnical and cultural aspects of the society of the period (Kaiserling, 2001, p. 285; Zompro, 2005, p. 251). The National Museums located all over the world contain thousands pieces of amber in its collections. These important amber objects in museums and archives sometimes suffer very serious damage (Waddington, 1988, p. 25; Williams, 1990, p. 65; Thickett, 1995, p. 217).

It is well known that the famous Baltic amber is a largest group of fossil resins from Europe (Starega, 2002, p. 601; Angelini, 2005, p. 441; Dlussky, 2006, p. 561). Therefore, in the present study attention has been focused on the characterization of amber samples found in Lithuania using FTIR spectroscopy and X-ray diffraction analysis (XRD). The amber samples of the present investigation were collected at the Baltic Coast in Nida district, in two archaeological complexes (Turlojiškės and Benaičiai) located in different regions of Lithuania.

Pottery analysis reveals important information about the daily life and the ethnical and cultural aspects of the society of the period. Therefore pottery studies are crucial for the reconstruction of the lifestyle of the society during the period under consideration. It is well known, that physical-chemical characterization of pottery used in prehistoric period provides cultural and technological information as regards their manufacture (Biscontin, 2002, p. 31; Benedetto, 2002, p. 177; Eramo, 2004, p. 157). Moreover, the knowledge of chemical and mineralogical compositions is mandatory in characterization studies of pottery: the former mainly depends on the raw materials used to produce the wares but also on processing and depositional changes, the latter on both the initial composition and the processing, as minerals are the “fingerprints” of the stable and also the metastable solid phases formed during firing (Bescher, 2000, p. 215; Caruso, 2001, p. 3272; Tickett, 1995, p. 217).

Accordingly, the production processes of prehistoric ceramics can be derived jointly with the changes in the manufacturing techniques; in this respect, maximum heating temperature, duration of firing and kiln redox atmosphere are important factors that help in understanding the transformations (Bakolas, 1995, p. 817; Wagner, 2004, p. 35). Therefore, careful characterization of prehistoric pottery is very important task not only for archaeologists but for people working in the field of conservation chemistry as well (Rice, 1987; Kiuberis, 2004, p. 334; Klein, 2004, p. 339).

In the present study, attention has been focused on the characterization of pottery samples obtained from these two regions of Lithuania.

EXPERIMENTAL

Amber and pottery samples found in Lithuanian village Benaičiai (West Lithuania) and Turlojiškės (South Lithuania) were chosen for the characterization. The exact locations of the above mentioned archaeological complexes are presented in Figure 1.

Seven different amber samples collected in Lithuania were chosen for the characterization: (a) four amber samples having different physical appearance (milky (sample I), dark (sample II), opaque (sample III) and transparent (sample IV)) found in 2005 at the Baltic Coast in Nida, (b) two archaeological amber samples excavated in different archaeological complexes (villages Benaičiai (sample V) and Turlojiškės (sample VI)) and (c) amber sample found in old town of Vilnius.

One more amber sample whose origin is not clear was provided by Lithuanian P. Gudynas Restoration Centre (see Fig. 2).
The pottery and amber samples were characterized by powder X-ray diffraction analysis (XRD) performed with a D8 Bruker AXS powder diffractometer using CuKα₁ radiation. The infrared (IR) spectra were recorded as KBr pellets on a Perkin Elmer Spectrum BX FTIR spectrometer.

RESULTS AND DISCUSSION

Archaeological Research

The Benaičiai archaeological complex (Fig. 3) was found accidentally, when local residents started excavating gravel. The archaeological complex comprises burial sites and settlements dated to different periods and situated on a few terraces of the Šventoji river. In 2000, the Department of Archaeology of Vilnius University launched investigations of the Benaičiai archaeological complex which were continued in 2002–2004. During four excavation seasons 25 trenches were excavated in the archaeological complex.

In the course of archaeological investigations two inhumation graves were recovered, one of which displayed a disturbed grave of a crouched female. The grave goods of the burial include a bone awl and three or four amber pendants. Also a grave of a child with grave goods which include a small flint knife and a bone pin was found. The graves were dated to the Early Bronze Age. Several cremation graves from the
Late Bronze Age were recovered as well. One of these was revealed in a simple pit, while burnt bones of two further individuals were split in the territory of the settlement. Besides burials, cultural layers of several settlements were found. The site was inhabited during different periods. The excavations revealed cultural layers of a Bronze Age settlement and a Late Iron Age settlement as well as remains of a medieval village site. Excavations of settlements revealed remains of buildings with preserved wooden postholes. The settlements yielded bronze, iron, flint, bone and amber artefacts. A large amount of pottery was found as well. The central and northern part of the complex yielded quite a lot of iron slag which points to processing of iron in the settlements (Merkevičius, 2002, p. 14–16; Merkevičius, Nemickienė, 2005, p. 16–18; Merkevičius, 2005, p. 10–12; Merkevičius, Nemickienė, Kanarskas, 2006, p. 17–19).

Approximately 0.5 km southwards of the Benaičiai archaeological complex, the barrows of Südėnai, dated to the Early Iron Age, have been excavated. The cultural layer of a settlement dated to the Bronze Age was found under the burials in these barrows. The data of investigations lead to the supposition that the Benaičiai community came from the present Südėnai area at the end of the Early Bronze Age while in the Early Iron Age it moved further to the south, to the spot where the above mentioned barrows were excavated.

The Turlojiškės archaeological complex (Fig. 4) includes settlements, cemeteries, sacrificial sites, roads and other archaeological objects. The first archaeological finds from the site were recovered in 1930, during works related to amelioration and straightening of the river bed (Žilinskas, 1931). Archaeological finds were also revealed later on, before and after the war, in the course of different land digging works. Regrettably, the spots which had yielded archaeological finds were forgotten, confused and wrongly indicated after the war.

In 1995, an archaeological fieldwalking expedition from the Department of Archaeology of Vilnius University and Marijampolė Museum established the approximate find spots of the archaeological finds recovered before and after the war. Unfortunately, nobody was able to indicate the precise find spots. For seven excavation seasons, i.e. from 1996 to 2003, except the year 2000, an expedition from the Department of Archaeology of Vilnius University investigated various sites of the Turlojiškės archaeological complex. Fieldwalking surveys and excavations revealed five sites of settlements, 3 graves, 2 sacrificed individuals, 3 human skulls in settlements (apparently also belonging to sacrificed individuals) and contours of a road. Some finds were delivered by local residents. During excavations of the settlements, well preserved remains of wooden buildings were found. Inside and beside the buildings, bark floorings, sticks interwoven with
twigs, planks, timber and other construction remains were found. There were also finds of wooden articles, including a wooden bow and a spear haft. Finds of stone articles include clubheads, axes and a quern stone. There were quite a lot of flint articles, including arrowheads. Trenches yielded a large amount of animal, bird and fish bones as well as nutshells. During excavations, three burials without grave goods were found and dated to the Early Bronze Age. Furthermore, two sacrificed individuals were found in a once shallow lake close to a bygone settlement. Beside one of them there was a copper pendant, 2 wooden sticks with traces of processing and a milling stone. Next to the other sacrificed individual, a triangle-shaped arrowhead of flint was found. The skull of this individual exposes three lesions resulting from a blow on the skull with a blunt object. On the basis of the available evidence, Turlojiškės archaeological complex is dated to the Bronze Age (Merkevičius, 1998, p. 26–29; Merkevičius, 2000, p. 44–46; Merkevičius, 2002, p. 22–23; Merkevičius, 2005, p. 12–13; Merkevičius, 2005, p. 19–20).

Analytical Characterization of Amber

The FTIR spectra of four amber samples collected in 2005 at the coast of Baltic Sea in Nida are presented in Fig. 1 (see after references). It is interesting to note that the spectra of all milky, dark, opaque and transparent amber samples were nearly the same, irrespective of the physical appearance of the sample. The spectra shows the characteristic absorption bands of vibrations in a number of functional groups, such as OH, CH₂, CH₃, C=C, and –CO–O. These absorption bands are summarized in Table 1 (see after references). A broad absorption in the spectra at around 3450 cm⁻¹ indicates the presence of adsorbed water vapour during formation of amber. In the 1245–1175 cm⁻¹ region the FTIR spectra of the ambers from Baltic Coast contain broad and almost horizontal shoulder which is highly characteristic feature of the Baltic amber. Moreover, this shoulder is followed by a sharp absorption peak which reaches maximum intensity around 1160 cm⁻¹, attributed to the C-O stretch vibrations. The similarity of distinctive features observed in these FTIR spectra let us to conclude that the chemical composition of milky, dark, opaque and transparent amber samples is very similar despite their physical appearance is different.

The FTIR spectra of two archaeological amber samples are presented in Fig. 2 (see after references). The FTIR spectra of archaeological amber samples are very similar to previous ones, showing the definitive Baltic shoulder area. This fact let us to predict that these amber samples also belongs to the group of the Baltic amber. Especially well resolved horizontal shoulder could be detected in the FTIR spectrum of the amber from the
archaeological complex of Benaičiai (see Fig. 2, a). A negligible change in the slope of the shoulder between 1245 and 1175 cm\(^{-1}\) can be seen in the FTIR spectrum of the amber from the archaeological complex of Turlojiškės (see Fig. 2, b, see after references).

The main characteristic Baltic amber features are also evident in the FTIR spectrum of amber sample found in old town of Vilnius (Fig. 3, see after references). The positions of all peaks observed in this FTIR spectrum exactly fit with the results presented in Table 1. Therefore, once again we can draw a similar conclusion that the amber sample found in old town of Vilnius also belongs to the same Baltic ambers group.

Accordingly, the crystallization of inorganic salts during formation of amber could also occur. Therefore, all seven amber samples were examined by powder XRD analysis. The XRD patterns of amber samples collected at the Baltic Coast are presented in Fig. 4. As was expected, the X-ray diffraction patterns of amber specimens exhibited amorphous character. All four XRD patterns indicates an unidentified amorphous humps between 2θ = 10–25°, reaching maximum height at around 18°. No peak what would have been characteristic of metal salts crystallization could be detected in any of the XRD patterns. On the other hand, the XRD pattern of milky amber (see Fig. 4, a) contains rather sharp and intensive peak at around 2θ ≈ 32.0°. Surprisingly, this diffraction peak is the most intensive diffraction line for the quartz (SiO\(_2\)) phase [PDF 46-1045]. These results suggest that during formation of amber the small amount of silica is trapped inside amber.

The XRD patterns of two archaeological amber samples are shown in Fig. 5 (see after references). As seen, these samples are essentially amorphous as well. Again, no peaks attributable to the metal salts or unknown contaminating phase in the XRD patterns of the archaeological amber samples could be identified. Both XRD patterns contain the same diffraction line at 2θ ≈ 32.0°. Apparently, the sample excavated in Turlojiškės archaeological complex contains higher amount of SiO\(_2\) phase.

The presence of large amount of quartz phase in the historical amber sample was determined as well. The X-ray diffraction pattern for the amber sample found in old town of Vilnius is shown in Fig. 6 (see after references). The three most intensive peaks of quartz phase at 2θ values of 32.0°, 24.3° and 49.9° are present in the XRD pattern of analyzed amber sample. From XRD analysis, we concluded for the first time that during formation process the Baltic amber in some cases can accumulate SiO\(_2\) phase.

Analytical Characterization of Pottery

Two types of pottery chosen for study: the ceramic pot chips from Western (Fig. 5) and Southern (Fig. 6) parts of Lithuania.

The pottery from Benaičiai has a smooth surface, a dark brown colour as well as crushed stone temper in the clay body. The pottery bears a decoration of short oblique dash impressions.

The pottery from Turlojiškės has a smooth surface, a dark grey colour as well as crushed snail shell and small amount of crushed stone temper in the clay body. The pottery bears a decoration of impressed stamps.

The chemical composition and phase purity of the ceramic samples were investigated by powder XRD analysis and IR spectroscopy. As was expected, the X-ray diffraction patterns of prehistoric pottery specimens exhibited multiphasic character of the investigated polycrystalline samples. The results obtained from the XRD analysis data are summarized in Table 1. As seen, quite different phase composition was determined for two prehistoric pottery samples obtained from different archaeological complexes. The Benaičiai pottery is characterized by the presence of quartz as a main phase, ant muscovite, titanite and sodium anorthite as secondary phases. The presence of large amount of quartz phase in the Turlojiškės pottery was determined as well. However, the main crystalline component of this ceramic sample evidently is calcite. The secondary phases, such as muscovite, calcium hydrogen sulphate and nontronite were also identified. Therefore, only two common phases, quartz and muscovite, were found to be in both prehistoric pottery samples obtained from different places of Lithuania. These results suggest different manufacture of two prehistoric pottery samples. The presence of calcium carbonate in the Turlojiškės pottery clearly confirms this assumption – apparently, the firing temperature of pottery from Turlojiškės is lower to compare with calcinations temperature of ceramic sample from Benaičiai.
Fig. 5. Pottery sample from Benaičiai archaeological complex.
5 pav. Keramika iš Benaičių archeologinio komplekso

Fig. 6. Pottery sample from Turlojiškės archaeological complex.
6 pav. Keramika iš Turlojiškės archeologinio komplekso
Analytical characterization of Baltic amber and pottery

**Table 1. Phase analysis data for the Benaičiai and Turlojiškės pottery samples.**

<table>
<thead>
<tr>
<th>Pottery sample</th>
<th>Phases obtained from XRD analysis</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benaičiai</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO₂ (quartz)</td>
<td>Main</td>
</tr>
<tr>
<td></td>
<td>(K, Na)(Al, Mg, Fe)₂(Si₃.1Al₀.9)O₁₀(OH)₂ (muscovite)</td>
<td>Secondary</td>
</tr>
<tr>
<td></td>
<td>CaTiO₃(SiO₄)₃ (titanite)</td>
<td>Secondary</td>
</tr>
<tr>
<td></td>
<td>(Ca, Na)(Si, Al)₄O₈ (sodium anorthite)</td>
<td>Secondary</td>
</tr>
<tr>
<td><strong>Turlojiškės</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaCO₃ (calcite)</td>
<td>Main</td>
</tr>
<tr>
<td></td>
<td>SiO₂ (quartz)</td>
<td>Secondary</td>
</tr>
<tr>
<td></td>
<td>(K, Na)(Al, Mg, Fe)₂(Si₃.1Al₀.9)O₁₀(OH)₂ (muscovite)</td>
<td>Secondary</td>
</tr>
<tr>
<td></td>
<td>CaH₂(SO₄)₂ (calcium hydrogen sulphate)</td>
<td>Secondary</td>
</tr>
<tr>
<td></td>
<td>Ca₀.₁Fe₂(Si,Al)₄O₁₀(OH)₄·4H₂O (nontronite)</td>
<td>Secondary</td>
</tr>
</tbody>
</table>

To facilitate the interpretation of the XRD results, the pottery samples were analyzed by IR spectroscopy. Fig. 7 shows IR spectra for the ceramics obtained from Benaičiai and Turlojiškės archaeological complexes. A broad band between 3700–3000 cm⁻¹ and less intensive absorptions at 1635 cm⁻¹ observed in both IR spectra can be assigned to the adsorbed water (or water of crystallization) and O-H vibrations. The absorptions from the quartz phase (Si-O) could be also easily identified (1160, 1082, 797, 778, 695, 512 cm⁻¹) for both samples. Very well resolved several intense bands in the range 800–550 cm⁻¹ (725, 648, 595 cm⁻¹) are characteristic of the metal-oxygen vibrations in the ceramic samples. However, in the IR spectrum of pottery from Turlojiškės additionally the characteristic carbonate (calcite phase) vibrations at 1797, 1420, 877, 714 cm⁻¹ and typical sulphate (calcium hydrogen sulphate phase) vibrations at 1105 ir 611 cm⁻¹ could be also determined.

Thus, the IR spectroscopy could be effectively employed for a qualitative characterization of pottery.

**Fig. 7. IR spectra of the prehistoric pottery from Benaičiai (top) and Turlojiškės (bottom) archaeological complexes.**

7 pav. Priešistorinės keramikos iš Benaičių (viršuje) ir Turlojiškės (apačioje) archeologinių kompleksų infraraudonieji spektrai

**CONCLUSIONS**

For the first time the amber samples from different localities of Lithuania were investigated and characterized by FTIR and XRD techniques. The amber samples of the present investigation were collected at the Baltic Coast in Nida district, in two archaeological complexes located in different regions of Lithuania, and obtained at the Lithuanian P. Gudynas Restoration...
village, eastwards of the Šventoji river. The Turlojiškės archaeological complex is situated in a large peaty area of over a hundred hectares in Kalvarijos district, in Turlojiškės village as well as in the neighbouring villages along the right bank of the Kirsna river. Prehistoric pottery and amber from two places in Lithuania was characterized by different analytical methods. XRD analyses clearly showed that all investigated ceramic samples are polycrystalline materials and composed by different phases. Moreover, we have demonstrated that IR spectroscopy is an indispensable tool for the characterization of amber and pottery.

REFERENCES


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Table 1. The main absorption frequencies of the milky, dark, opaque and transparent amber samples from Baltic Coast (Lithuania) in the 3700–500 cm\(^{-1}\) range.

<table>
<thead>
<tr>
<th>Group</th>
<th>Band, cm(^{-1})</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>–O–H</td>
<td>3500–3400</td>
<td>O–H stretching, broad</td>
</tr>
<tr>
<td>&gt;CH(_2), (-CH_3) and (-CH_2)–</td>
<td>2940–2840</td>
<td>C–H stretching, strong</td>
</tr>
<tr>
<td></td>
<td>1460–1445</td>
<td>C–H deformations, medium</td>
</tr>
<tr>
<td></td>
<td>1380–1370</td>
<td>C–H bending, medium</td>
</tr>
<tr>
<td></td>
<td>889–887</td>
<td>C–H out of plane bending of H atoms, medium</td>
</tr>
<tr>
<td>–CO–O–</td>
<td>1740–1700</td>
<td>C=O, strong</td>
</tr>
<tr>
<td></td>
<td>1245–1010</td>
<td>C–O bonds, characteristic for succinate, medium</td>
</tr>
<tr>
<td>C=C</td>
<td>1650–1640</td>
<td>C=C stretch, weak</td>
</tr>
</tbody>
</table>

Apéndice

Fig. 1. FTIR spectra of milky (a), dark (b), opaque (c) and transparent (d) amber samples from Baltic Coast in Nida.

1 pav. Baltojo (a), tamsiojo (b), matinio (c) ir skaidraus (d) gintaro mėginių, rastų Baltijos pajūryje, Nidoje, Furje transformacijos infraraudonieji spektrai
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2 pav. Archeologinio gintaro iš Benaičių (a) ir Turlojiškių (b) radaviečių mėginių Furje transformacijos infraraudonieji spektrai

Fig. 3. FTIR spectrum of amber sample found in old town of Vilnius.

3 pav. Gintaro mėginio, rasto Vilniaus senamiestyje, Furje transformacijos infraraudonasis spektros

Fig. 4. XRD patterns of milky (a), dark (b), opaque (c) and transparent (d) amber samples from Baltic Coast in Nida.

4 pav. Baltojo (a), tamsiojo (b), matinio (c) ir skaidraus (d) gintaro mėginių, rastų Baltijos pajūryje, Nidoje, rentgeno spindulių difrakcinės analizės spektrai
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Fig. 6. XRD pattern of amber sample found in old town of Vilnius.
6 pav: Gintaro mėginio, rasto Vilniaus senamiestyje, rentgeno spindulių difrakcinės analizės spektras

Fig. 5. XRD patterns of archaeological amber samples from villages Benaičiai (a) and Turlojiškės (b).
5 pav: Archeologinio gintaro iš Benaičių (a) ir Turlojiškių (b) radaviečių mėginiių rentgeno spindulių difrakcinės analizės spektrai

BALTIJOS GINTARO IR ARCHEOLOGINĖS KERAMIKOS APIBŪDINIMAS

Aivaras Kareiva, Jonas Kiuberis, Algimantas Merkevičius

Santrauka

Šiame straipsnyje rentgeno difrakcinės analizės (XRD) ir Furje transformacijos infrarudonosios spektroskopijos (FTIR) metodais buvo apibūdinė Balticos gintaro ir archeologinės keramikos mėginiai iš dviejų Lietuvos archeologinių radaviečių: Benaičių (Vakarų Lietuva) ir Turlojiškių (Pietų Lietuva). Palyginimui buvo tirti Balticos pajūrio (ties Nida) ir nežinomos kilmės gintaro, rasto Vilniaus senamiesčio archeologinių kasinėjimų metu, mėginiai.

Tyrimo metu nustatyta, kad keturi gintaro mėginiai iš Balticos pajūrio, du mėginiai iš archeologinių radaviečių ir nežinomos kilmės gintaro mėginys iš Vilniaus senamiesčio savo chemine sudėtimi niekuo nesiskiria. Todėl daroma išvada, kad visi tirti gintaro mėginiai priskirtini Balticos jūros regiono gintarams.

Archeologinių keramikos mėginiių tyrimo pirmiaus metais metodais metu iš dviejų Lietuvos archeologinių kompleksų buvo nustatyta, kad pagal fazinę sudėtį šie mėginiai skiriasi, t. y., be vyraujančios abiejųose mėginiuose kvarco fazės, Turlojiškių mėginiai, kitaip nei Benaičių archeologiniame kompleksame aptiktam ir tirtam mėginiui, būdinga kalciato kristalinė fazė. Tikėtina, kad keramikos gamyba Turlojiškėse vyko žemesnėje temperatūroje, negu Benaičiūose.

Daroma išvada, kad tiek XRD, tiek FTIR yra ypač vertingi gintaro ir archeologinės keramikos mėginiių apibūdinimo metodai.

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