Śląskie Sprawozdania Archeologiczne
Tom 58, s. 133–150 Wrocław 2016
DOI: 10.17427/SSA16010

FRANCISZEK CZECHOWSKI, KRZYSZTOF JAWORSKI, MAREK HOJNIAK

ORGANIC MATTER ON THE SO-CALLED SILESIAN TYPE EARLY MEDIEVAL IRON BOWLS

Abstract In 2014 and 2015 in Lower Silesia (Witostowice, Ząbkowice Śląskie district, Obiszów, Polkowice district) were discovered two hoards of early medieval iron bowls, known in the archaeological literature as the so-called Silesian type bowls. Both hoards were discovered during private amateur exploration work by metal detector. Information about the finds, along with the exact location of the discovery site, reached the archaeological circle. The collection of the Institute of Archaeology, University of Wrocław entered also the artefacts. The transferred bowls are two the most numerous, to date known to archaeologists, assemblages of the Silesian type bowls – the hoard from Witostowice contained at least 40 specimens, the one from Obiszów – 18 bowls. Bowls from both hoards were not conserved by the finders. Geochemical analyses were performed on concave and convex surfaces of a five representative single bowls and separately on the surfaces of one corrosively cemented specimen from both hoards. They included an analysis of the molecular composition of organic matter deposited on surfaces of iron bowls. The main group of the compounds of this matter consists of the n-alkanes and isoprenes (pristane and phytane), while occurring free n-alkanoic acids as well as wax esters are present in an accessory amount. Large proportions of n-alkanes are a structure derived from the currently growing vegetation, both trees and grass. They are represented by high molecular homologues of n-C25 – n-C33 with a large prevalence of representatives of the odd-carbon-numbered over the closest even-carbon-numbered ones. Biogenic origin is also attributed to free n-alkanoic acids (lauric, myristic and palmitic acids) as well as the wax components which are metabolites of plant root system. Low molecular homologues of n-alkanes (n-C14 – n-C21) present Gaussian course with a maximum concentration for the homologue n-C17, suggesting a connection with the petroleum hydrocarbon fraction. The determination of their non-controversial source, from which they penetrated surfaces of iron bowls requires further research on bowls from new discoveries in order to exclude their current anthropogenic source.

F. Czechowski, franciszek.czechowski@ing.uni.wroc.pl ,Instytut Nauk Geologicznych, Uniwersytet Wrocławski, pl. Maksa Borna 9, 50-204 Wrocław

K. Jaworski, krzysztof.jaworski@uwr.edu.pl, Instytut Archeologii, Uniwersytet Wrocławski, ul. Szewska 48, 50-139 Wrocław

M. Hojniak, marek.hojniak@chem.uni.wroc.pl, Wydział Chemii, Uniwersytet Wrocławski, ul. F. Joliot-Curie 14, 50-383 Wrocław

INTRODUCTION

The original function of early medieval iron bowls, described in the Central European archaeological literature as the so-called 'iron bowls of the Silesian type' is the subject of discussion for nearly a century. Despite its name (bowls of the Silesian type) these artefacts are an important component of the early medieval material culture of the Slavs, especially in the 9th and the 10th centuries. They were found both in today's Poland (mostly in Lower Silesia, but also in Upper Silesia, Lesser Poland, Greater Poland, Kuyavia and occasionally in other parts of Poland) as well as in eastern part of Germany, the Czech Republic (in Bohemia, Moravia and Czech Silesia) and Slovakia. Single specimens have also been found in other parts of the Slavs territory (Lower Austria, Romania, Hungary, Bulgaria). Descriptions of research on early medieval iron bowls of the Silesian type were published both in Polish-language scientific literature, as well as foreign, where research on these products undertook German, Czech and Slovak scholars.

In the study by Dr Paweł Rzeźnik from the Institute of Archaeology of the University of Wrocław were summarized the key findings and views of several dozens of scholars, both archaeologists and historians (including numismatists), who in their works undertook research on this category of archaeological artefacts (Rzeźnik 2006, 175–179). In his paper the author discussed in detail all published in the scientific literature suggestions indicating the function of the iron bowls, from the earliest theses expressed by Wrocław German archaeologist Hans Seger (1928, 142), through assumptions of other researchers – amongst them H. Kurtz (1936, 33–34), J. Herrmann (1966, 111–112) and J. Bubeník (1972) – ending with the most recent opinions of researchers published at the turn of the 20th century. To summarize exhaustively the aforementioned discussion, it should be noted that amongst many suggestions concerning the original function of the early medieval iron bowls, such as cult and sacrificial functions (Turek 1942, 167), attention deserve two more probable concepts. The first of them assumes that iron bowls are typically utilitarian objects which were used only for culinary purposes, as kitchen equipment or element of tableware by tribal and early state elites; Rzeźnik inclines to this concept (2006, 198-199). According to the second view, created in the last century by Kurtz (1936, 33–34) and developed by Herrmann (1966, 111–112), and recognized by many other researchers, the iron bowls were for Western Slavs a determinant of value, i.e. commodity money.

In his study on the original function of the iron bowls P. Rzeźnik points out – recalling also the opinion expressed by the historian P. Boroń (1998, 10) – that the amount of homogeneous hoards, i.e. ones containing exclusively iron bowls, is limited only to four enigmatic finds, which is, in his opinion, very weak basis for creating theoretical concepts referring to the occurrence of 'hoards' of iron bowls (in P. Rzeźnik's study the word 'hoard' appears always between quotation marks; Rzeźnik 2006, 178). The concept of H. Kurtz from 1936, developed by J. Herrmann thirty years later, in fact was based on only four iron bowls assemblages, discovered accidentally

in the second half of the 19th and early 20th century; the context of occurrence of these artefacts is unknown, and – what is particularly important – a large portion of these hoards was dispersed and lost. Hoards which allowed H. Kurtz to express his thesis were found in Lower Silesia: the Kaczawskie Foothills (Nowy Kościół, Złotoryja district - 14 specimens, Myślibórz, Jawor district – 7 specimens) and in the Barycz River valley (Żmigród, Trzebnica district – 3 specimens, Kaszyce Milickie, Trzebnica district – 4 specimens). His concept was transferred from analogous thesis related to the so-called axe-like iron bars, which is associated with a significantly larger number of assemblages included in the homogeneous hoards of such artefacts from Moravia, Slovakia and Lesser Poland. In an extreme case, the number reached 4212 specimens (the hoard from Kanonicza street No. 13 in Kraków), and this allowed researchers to determine the so-called axe-like iron bars as iron commodity money. The weakness of a similar argument to the original function of iron bowls of the Silesian type postulated by Kurtz (1936, 33–34) is too small number of specimens included in the various hoards, as well as a small number of found hoards.

NEW FINDS OF IRON BOWLS OF THE SILESIAN TYPE IN HOARDS IN LOWER SILESIA

The original function of the iron bowls may confirm or indicate their other destination, an in-depth interdisciplinary research on artefacts acquired during the new archaeological excavations. In the course of complex excavations on already known archaeological sites, using standard methods of the cultural layers exploration, a discovery of hoard of iron artefacts is rather unlikely though. Excavations are limited to a relatively small part of an archaeological site. Usually a broader detailed surface prospection (not to mention excavations) of the immediate vicinity of given site is not undertaken. In the last three decades on the Lower Silesia early medieval archaeological sites in the course of open-area excavations only four hoards of iron objects were discovered. In three cases they were found during excavating fortifications – two on stronghold from the end of 9th – the beginning of the 10th century in Gilów near Niemcza and one hoard (probably part of a larger assemblage) on stronghold Stary Książ near Wałbrzych (more on the circumstances of discoveries of these assemblages and description of the artefacts: Jaworski 2005a, 288 and following, Figs. 150–152). Only one of these hoards contained iron bowl, strongly deformed, bent as an 'envelope' (Fig. 1) and therefore completely devoid of its original utility function. It was found next to iron share and massive chisel (hoard No. 2 from Gilów; Jaworski, 2005a, Fig. 151 a-c). Two other assemblages contained the so-called spearhead-like bars (fines - grzywnas) and lump iron raw material (Gilów – hoard No. 1; Jaworski 2005a, Fig. 150 a–g), fragment of axe and semi scythe (Stary Książ; Jaworski 2005a Fig. 152 a–b). The fourth hoard was perfectly elaborated in the methodological terms assemblage of three iron bowls from settlement adjacent to stronghold in Obiszów, discovered in the immediate vicinity of remains of one of the building recorded in this settlement (Rzeźnik 2006, 179 and following, Table 5, Figs. 2–3).

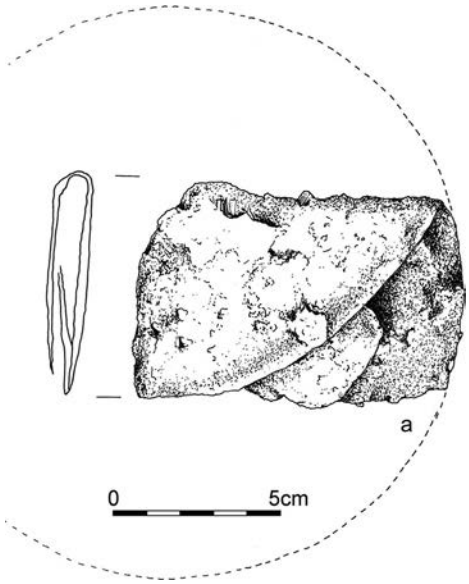

Fig. 1. Intentionally deformed iron bowl from stronghold from the end of the 9th – the beginning of the 10th century in Gilów near Niemcza (Dzierżoniów district). After Jaworski 2005, Fig. 151a

Fig. 2. Early medieval iron bowls from the Gromnik Mount. Photo by anonymous finder (Spring 2005). After Rzeźnik 2008, Fig. 1

Next discoveries of hoards of early medieval iron artefacts in Lower Silesia have been made in the last decade not by professional archaeologists, but by amateurs, the so-called treasure hunters, penetrating the area with metal detectors. During the last decade the archaeologists achieved materials from three hoards found in this way consisting of iron bowls of the Silesian type along with information about the places and circumstances of discoveries (it is not sure if all these finds are complete). These hoards were discovered in the vicinity of stronghold from the second half of the 9th – first half of the 10th century on the Gromnik Mount (Strzelin district; discovery from 2005), on stronghold in Witostowice (site 1, Ząbkowice Śląskie district; discovery from April 2014) and approximately 300 m from stronghold from the 10th century in Obiszów (Polkowice district; discovery from September 2015). In the first two cases, the materials were transferred to archaeologists, not by direct finders, but some time after the discovery, by people 'cooperating' both with treasure hunters and archaeologists. In the case of the find of iron bowls from Obiszów, the whole assemblage was transferred two days after the discovery to the Institute of Archaeology of the University of Wrocław by the finder.

The hoard of iron bowls from the Gromnik Mount (Figs. 2, 3) after the discovery was dispersed and went to different people. Thanks to help of cooperating with ar-

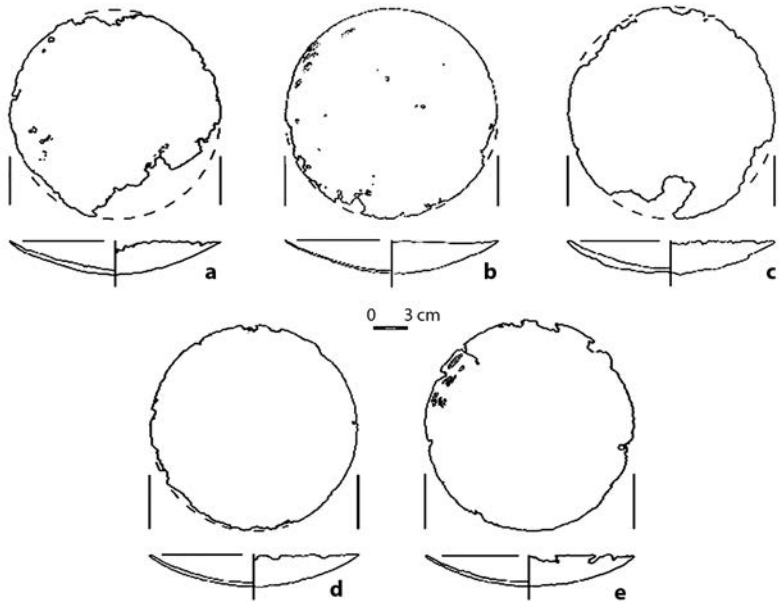

Fig. 3. Iron bowls from the Gromnik Mount in the Strzelińskie Hills. After Rzeźnik 2008, Fig. 4

chaeologists Mr Artur Troncik[1], a larger part of the hoard was recovered (the original assemblage consisted of 10 bowls) and transferred to the Institute of Archaeology at the University of Wrocław. The first five recovered specimens (later there were acquired two other specimens) were analysed and published by Dr Paweł Rzeźnik (Rzeźnik 2008). This researcher emphasized several times that the hoard of iron bowls from the Gromnik Mount constituted the most numerous assemblage of such artefacts known to archaeologists and available for research (Rzeźnik 2008, 161; from the originally slightly more numerous hoard from Nowy Kościół near Złotoryja to our times survived only three bowls).

Previous view presented by archaeologists that number of iron bowls in hoards rarely exceeds ten specimens, has changed dramatically in April 2014, when was found

[1] The best evidence of Mr A. Troncik's involvement in the case of iron bowls from Gromnik recovery are words of the author of the scientific study of these artefacts: 'The author of this study, anticipating somewhat the research results, wishes to acknowledge the contribution made by Artur Troncik to the recovery for science of the iron bowls hoard find from Gromnik, the largest such set associated with the environment of Early Piast culture recorded so far. To his kindness and involvement we owe much of the information on the subject of the context of discovery as well as the tracing, collecting and submitting for examination all the 5 bowls which we have at our disposal at present.' (Rzeźnik 2008, 161–162).

Fig. 4. The second part of the hoard from Witostowice, left on the archaeological site by the finder. Photo K. Jaworski

a hoard of iron bowls on stronghold in Witostowice (site 2 on the Piwniczna Hill), only 3.5 km south-west of Gromnik. On gentle south-facing slope descending towards the unnamed stream crossing the stronghold, about 40 specimens of iron bowls of the Silesian type were found. In find place the hoard was split into two comparable parts, one of which was taken by the finder, while the other one was left next to the place on the ground in the forest covering the stronghold. Information about the discovery made in Witostowice was given on 10 July 2014 by Andrzej Szeliga (for a dozen years participating in numerous archaeological excavations, carried out by various state scientific institutions) to the team conducting excavations on the Gromnik Mount by one of authors of this paper. It resulted in transferring to archaeologists 18 specimens of bowls, which after the discovery were taken by the finder from the stronghold in Witostowice. In addition, the exact location of the find of bowls was pointed. Near the loot trench, which was not completely backfilled, another 20 bowls, abandoned after the discovery, were found, three of them survived in small fragments (Fig. 4). A week later, after another conversation with an anonymous finder of the hoard, Mr Szeliga gave details on the arrangement of bowls in the pit. They were stacked tightly with each other (one inserted into the other) and were arranged vertically, or edgewise, in a pit about 60 cm deep and oval in plan view. The pit, in which the bowls were deposited, was covered with stones.

On 13 July 2014 started rescue excavations, which included pit and its immediate surroundings (carried out by Paweł Samborski, PhD student at Doctoral Study of

Fig. 5. Iron bowls from Witostowice secondarily arranged in the pit in which they were discovered. Visible portion of the metalling originally covering the pit. The photo was taken prior to knowing that the bowls were arranged in a different manner, each of them perpendicular to the ground surface. Photo K. Jaworski

Culture Studies at the Faculty of Historical and Pedagogical Sciences of the University of Wrocław, in collaboration with Dr Aleksandra Pankiewicz, Dr Ewa Lisowska and Dr hab. Krzysztof Jaworski). The results of these excavations confirmed previously obtained information – it was found out that the bowls were indeed arranged vertically (at the pit's bottom was stuck vertically driven a piece of broken edge of one of bowls) and that above the hoard was situated a metalling, which central part located directly above the bowls, was dismantled by the finder, and to the time of the rescue excavations survived only the outer, peripheral parts of the metalling (Fig. 5). In a relatively large trench no evidence indicating that the hoard was hidden inside of some building (e.g. a dwelling structure) was found. Preliminary analysis of the pottery material discovered during the excavations indicates that fragments of vessels found at the level of the metalling and next to it come from the period from the second half of the 9th to the beginnings of the 10th century (the analysis of pottery was carried out by Dr Aleksandra Pankiewicz). This allows to assume that the moment of hiding the hoard on stronghold in Witostowice also took place at this time.

In September 2015 on the edge of the forest adjacent to the stronghold and open settlement in Obiszów, approximately 300 m south-west of the site, Mr Patrycjusz Sewilski found another assemblage of early medieval iron bowls, consisting of 18 specimens. Bowls were deposited in a pit 55 cm deep in relation to the present level of the ground surface. Bowls were stacked one upon the other, and the upper bowl lay at the depth of 25 cm. According to the finder all bowls were arranged bottoms down, only

the upper bowl, covering the others had the bottom facing upward. The finder gave the archaeologists a map showing the hoard's location and a drawing presenting the find's context (Figs. 6–8). Such an arrangement of bowls in the pit differs from previous observations and findings. According to P. Rzeźnik in the case of hoards the rule was to deposit bowls in pits horizontally with bottoms facing upward (such a situation took place in the nearby settlement in Obiszów, in Nowy Kościół near Złotoryja and on Gromnik). The opposite situation was observed in Witostowice, where the bowls were arranged vertically, and next to the stronghold complex in Obiszów, where the bowls were stacked horizontally bottoms down, apart from the upper bowl.

In 1998 Dr Paweł Rzeźnik found three iron bowls during open-area excavations on nearby settlement from the 10th century in Obiszów. They occurred near relics of buildings No. 19 and 21 (Baron, Rzeźnik 1999, 269; Rzeźnik 2006, 179, Figs. 1–3). These bowls, inserted one into the other, were arranged bottoms up. These artefacts P. Rzeźnik considers utility items – vessels. However, the diameters of bowls discovered in settlement in Obiszów in 1998 differ significantly from size of bowls found in September 2015. The first ones are smaller, with a diameter of 15.8 to 16.4 cm, while diameter of bowls discovered in 2015 reaches 18–19 cm. It is possible that these two assemblages of iron bowls come from two chronologically different phases of operation of the Obiszów settlement complex; the use of bowls discovered during excavations on open settlement in Obiszów P. Rzeźnik determines at about 970 (Rzeźnik 2006, 190–191). Due to unknown archaeological context of iron bowls hoard discovered in September 2015 it is impossible – currently – to define more clearly the time of hiding this assemblage in the ground. Relevant archaeological excavations are planned to be carried out in autumn 2016.

Fig. 6. Find location of the iron bowls hoard from Obiszów

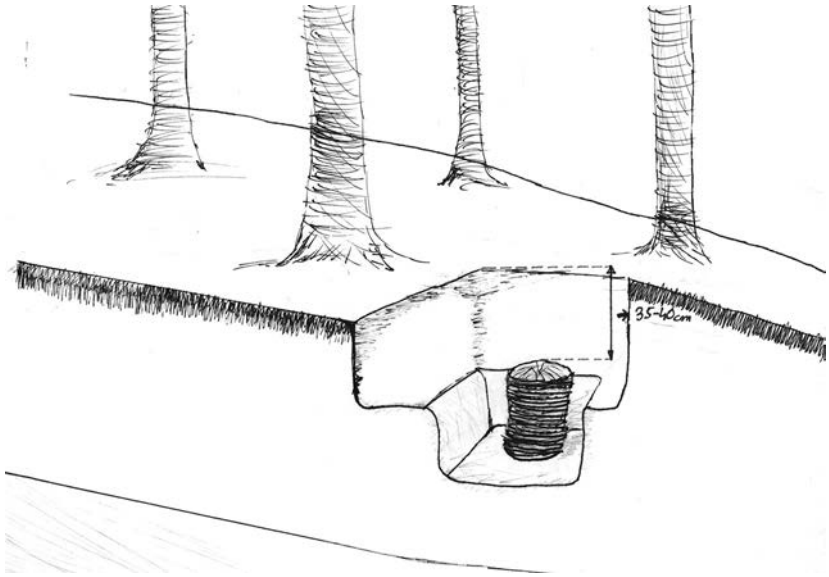

Fig. 7. Schematic drawing showing the context of discovery of iron bowls from Obiszów made by the finder

Fig. 8. Obiszów – the place of discovery of iron bowls. In the foreground there is visible the pit where the hoard was deposited. Amateur photography of the finder given to archaeologists

THE RESEARCH MATERIAL

The finds of as many as three hoards of iron bowls within the compact territory of Lower Silesia in a relatively short period of time (the hoard found on the Gromnik Mount - 2005, on stronghold in Witostowice – 2014 and in Obiszów – 2015) prompt a search for new evidence to confirm or verify of the hypotheses about the original function of these artefacts. Apart from strictly archaeological research on these assemblages (typological-formal and metric analysis, study on finds context), there were also undertaken geochemical studies to determine the chemical nature of the residual organic matter preserved on surface of these bowls, which may provide new knowledge about the bowls use. From these studies were excluded bowls from the earliest discovered, in 2005, hoard from Gromnik. All bowls from this assemblage have already undergone conservation work (by various factors, including the ones used by individual collectors). Moreover, before they were obtained by the Institute of Archaeology of the University of Wrocław, they were in collectors circulation without protection against the introduction on their surface of secondary anthropogenic organic matter.

Iron bowls from the Witostowice hoard were also not fully protected against secondary organic matter. Although none of them underwent conservation, but one part of them for three months was left on the forest grass exposed to atmospheric agents, while the second part was kept by the finder under undocumented conditions, were kept in used plastic bag, and finally in a cardboard box.

Bowls from Obiszów were preserved in the best condition for geochemical analyses. After they were excavated from the pit they were put into a cardboard box and in two days transferred to the Institute of Archaeology of the University of Wrocław. After the preliminary recording the bowls underwent first geochemical examination, while basic measurements of their metric features as well as drawing and photographic documentation were carried out later.

Amongst the iron bowls from hoards from Witostowice and Obiszów four specimens were selected for examination of the chemical nature of traces of organic matter present on surface of the bowls.

SOLVENT ELUTION OF ORGANIC MATTER DEPOSITED ON SURFACE OF BOWLS

The surface of iron bowls selected for chemical examination was initially carefully cleaned to remove adhering dust and grains of sand as well as clusters of strong corrosion by paintbrush and spatula. The organic components from mechanically cleaned surface of bowls were transferred to the solvent by washing bowls surface with dichloromethane. For elution of organic matter from the surface of a bowl was used approximately 50 mL of solvent by applying it with pipette in 2 mL portions. In the case of bowls from Obiszów, the organic matter was eluted separately from the inner

(concave) and outer (convex) surfaces of bowls. In addition, cemented by corrosion bowls from both locations, for which there is certainty about the lack of contamination of their surface after the discoveries, were freshly separated and organic matter from their surfaces was also eluted for geochemical investigation. The collected dichloromethane solutions before being subjected to analysis by gas chromatography coupled with mass spectrometry (GC-MS), were concentrated to the volume of 0.5 mL by solvent evaporation at room temperature.

GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY (GC-MS)

To the GC-MS were subjected concentrated dichloromethane solutions containing the components of organic matter eluted separately from inner and outer surfaces of the bowls from Obiszów and eluted from both surfaces of the bowls from Witostowice as well as from heavily corroded surfaces after separation of cemented by corrosion bowls.

Separation of organic components in the eluted solutions were performed using gas chromatograph HP 5890 II equipped with capillary column HP-5. 25 m long and with the internal diameter of 0.20 mm, coated with active phase film (5% of diphenyl polisiloxane and 95% of dimethylsiloxane) 0.33 μm thick. For analysis 1 μL of solution was injected (split 20). Helium was used as the carrier gas with flow rate of 1 mL/min. The GC oven was programmed from 50 °C to 320 °C at rate of 3 °C/min. Detection of the separated components was performed using HP5971A quadrupole mass detector operating at ionization energy of 70 eV and temperature of the ion source chamber of 180 °C. Scanning was performed in a full scan mode (from 50 to 600 atomic mass units with a cycle time of 1 s). Mass chromatograms showing the molecular composition of groups of compounds were obtained by extraction of selective fragment ions m/z from the total mass chromatogram TIC. There were analysed following groups of compounds: n-alkanes and chained isoprenes (m/z 85), free n-alkanoic acids (m/z 60), esters of palmitoleic acid (16:1) with fatty alcohols (m/z 236), and esters of palmitic acid with fatty alcohols (m/z 258). Concentration of other compounds in the analysed samples was below the detection limit. Identification of the compounds was based on the fragmentation of mass spectra and comparison of chromatographic retention times with the synthetic standards and literature data.

DESCRIPTION OF RESULTS OF THE ORGANIC MATTER EXAMINATION

In the organic matter eluted from surfaces of iron bowls by dichloromethane the main components are n-alkanes and isoprenes. Accessory group of compounds are low molecular free fatty acids as well as esters of palmitoleic acid and palmitic acid with higher fatty alcohols. No other groups of compounds were recorded.

Iron bowls from Obiszów

Bowls from Obiszów underwent examination of organic matter deposited on their surface two days after they were found. In interpretation of the results, it is important to point out the horizontal orientation of bowls arranged bottom down in relation to the ground surface. Homologous composition of the n-alkanes in organic matter eluted from the concave and convex surfaces as well as from both surfaces cemented by corrosion is shown in Fig. 9 – successive profiles (A), (B) and (C). Course of (A) and (B) profiles is similar, in which are distinguished three ranges of n-alkane homologues. Gaussian profile of the relative concentration of homologues within the low molecular weight range homologues between n-C14 – n-C20 with maximum at n-C17 and middle molecular weight between n-C21 – n-C25 with maximum at n-C22 is observed. Such a course of homologous composition of the n-alkanes in the above ranges strongly suggests their origin from petroleum. These hydrocarbons may have been used to protect the bowls against corrosion. In high molecular weight range the relative concentrations of odd-carbon-numbered homologues n-C25, n-C27, n-C29, n-C31 and n-C33 largely outweigh their closest even-carbon-numbered counterparts. This molecular composition is typical of biogenic origins of high molecular weight n-alkanes from currently growing vegetation (Peters *et al.* 2005). Domination of the homologue n-C27 is an evidence of the origins from woody plants (Schwark *et al.* 2002; Wiesenberg *et al.* 2004; Zhang *et al.* 2006), while the increased concentration of n-C31 over concentration of odd-carbon-numbered neighbours indicates a high proportion of grass in the plant material (Schwark *et al.,* 2002), which fully reflects the nature of vegetation at the site where the bowls were found. In the profile (C) regarding to concave and convex surfaces of bowls cemented by corrosion occur trace amounts of n-alkanes in the low molecular weight and biogenic ranges (with the specificity of composition like in profiles (A) and (B)), and there are no middle molecular weight homologues. Probably some bowls were less protected against corrosion by hydrocarbon preservative medium which in contact with moisture and atmospheric oxygen in the hiding place allowed increased corrosion combined with the biodegradation of hydrocarbons. As present stage on highly corroded bowls surface survived only a residual amount of low molecular weight n-alkanes and the high molecular ones derived from biogenic sources.

The second group of compounds determined on surfaces of all examined bowls are free n-alkanoic acids represented by lauric, myristic and palmitic acids. A typical mass chromatogram illustrating relative concentrations of these acids is shown in Fig. 10. Their presence on bowls' surfaces should be attributed to current vegetation, from which they adhered the bowls surface during deposition in the hiding place.

Next compounds of the biogenic origins detected on iron bowls surfaces are waxes composed of monounsaturated and saturated fatty acids esterified with higher fatty alcohols of the general formula RCOOR', where R represents a hydrocarbon chain of monounsaturated or saturated n-alkanoic acid, while R' represents a n-alkanoic alcohol. Series of esters with the highest concentration in the wax mixture represent

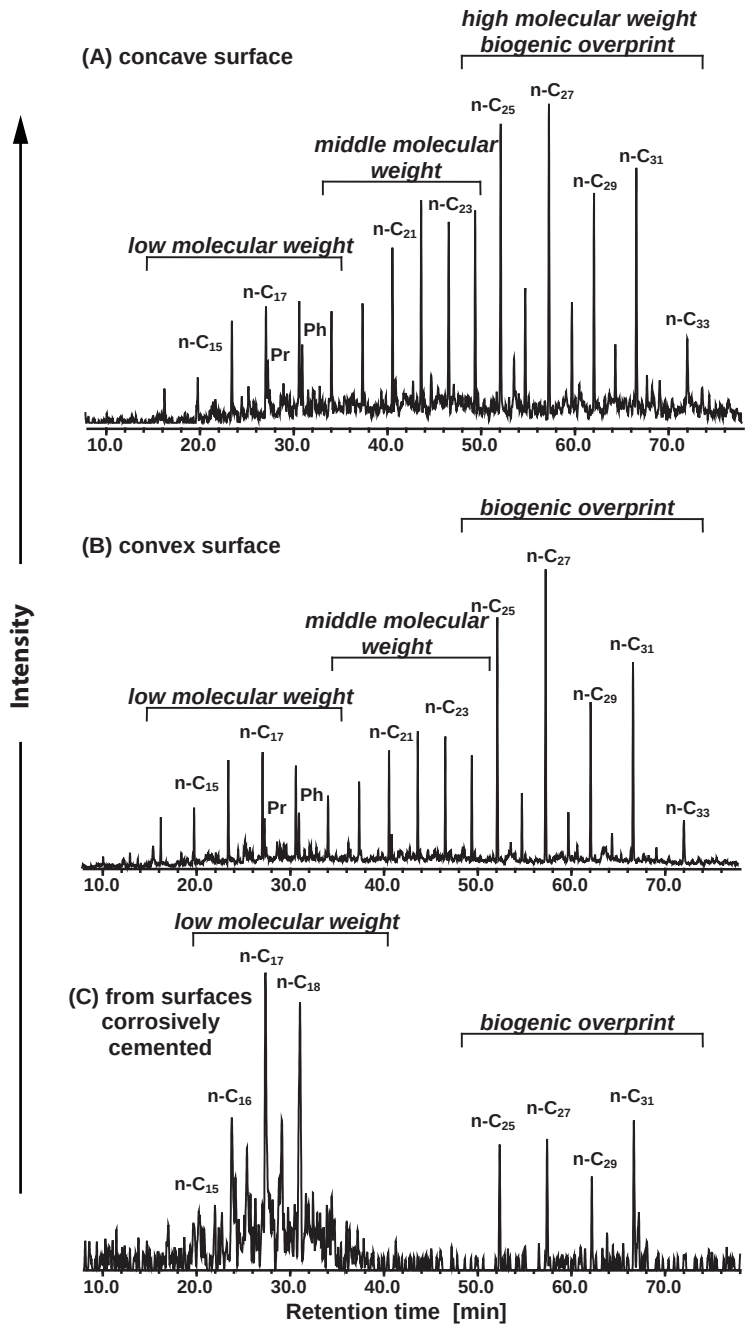

Fig. 9. The molecular composition of n-alkanes and isoprenes recovered from the surfaces of bowls from Obiszów. Pristane (Pr), phytane (Ph)

esters of the palmitoleic acid (16:1) and the palmitic acid (16:0) with higher fatty alcohols (12:0–25:0) – respective profiles (A) and (B) in Fig. 11. For the monounsaturated acids, they were characterized based on fragment ions [M - R'OH]+ (M-molar mass of acid), which for series of the palmitoleic acid is 236 – Fig. 11, profile (A). Instead series of esters of the palmitic acid with fatty alcohols based on fragment ion of the general formula [RCO2H2]+, which for the palmitic acid is 256 – Fig. 11, profile (B). Analysed wax represents a mixture of esters of monounsaturated and saturated n-alcanoic fatty acids with number of carbon atoms in a molecule from C12 to C18 as well as n-alcanoic fatty alcohols with number of carbon atoms in a molecule from C12 to C24. A similar molecular composition of wax is present in contemporary soil (Bai *et al.* 2006). It is a biosynthetic product found in plant root systems. As a result of contact of plant roots with analysed iron bowls during their deposition in the soil, these compounds were transferred to the surfaces of the bowls.

Iron bowls from Witostowice

The iron bowls from Witostowice hidden in the ground were arranged bottoms vertically in relation to the ground surface covered with metalling. The bowls delivered for examination were wrapped in newspaper. Visually, the majority of bowls from this find seemed better preserved with the exception of two bowls cemented by corrosion. On the iron bowls from Witostowice the occurrence of the n-alkanes and isoprenes was determined. In addition, there was found only trace amount of free n-alkanoic acids having the same molecular composition as the one determined on iron bowls from Obiszów. No presence of waxes was recorded.

In the profile of n-alkanes from the concave and convex surfaces of better preserved bowls (profile (A) in Fig. 12) dominate low molecular weight homologues which distribution is very similar to n-alkanes of this range as on bowls from Obiszów (Fig. 9, profiles (A) and (B)). However, its middle molecular weight and high molecular weight n-alkane profiles are different, where there is n-alkanes overprint by components deriving from the residual solvent used in printing ink, that were transferred from the newspaper print used for wrapping the bowls (profile (B) in Fig. 12). The lack on the surfaces of bowls from Witostowice of high molecular weight n-alkanes with biogenic fingerprint is associated with their location in the soil under the surface covered with metalling limiting plant growth. The exception are surfaces if the bowls cemented by corrosion, which had no contact with the newspaper. Here, apart from a small amount of n-alkanes of low molecular weight range, occur high molecular weight homologues (Fig. 12, profile (C)) having characteristics of composition of biogenic origins from vegetation with a larger contribution of grass (higher relative concentration of n-C_{31}) than in the case of bowls from Obiszów. Probably the bowls cemented by corrosion were deposited in a place not entirely covered by metalling on the ground surface, which facilitated penetration of biogenic material to the bowls surfaces as well as favoured corrosion and biodegradation of hydrocarbons. n-Alkanes are more readily biodegradable than isoprenes: pristane (Pr) and phytane (Ph) (Peters *et al.* 2005).

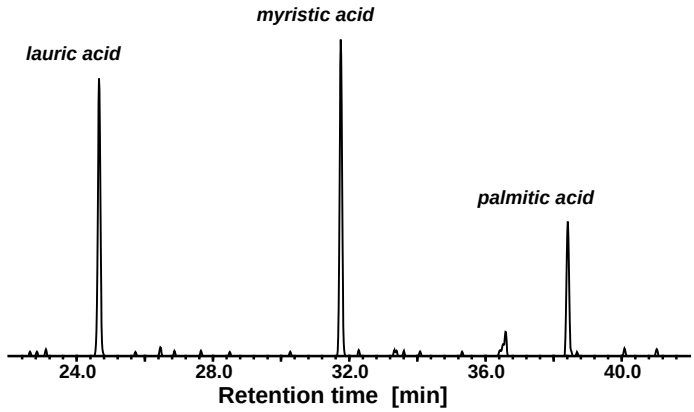

Fig. 10. The molecular composition of n-alkanoic acids on the convex surface of the bowl from Obiszów

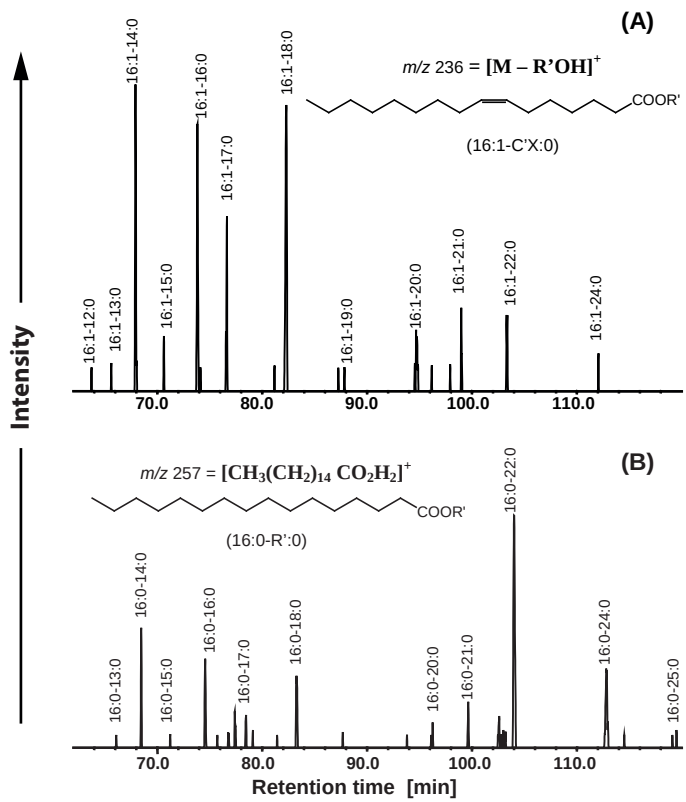

Fig. 11. The molecular composition of wax on the convex surface of the bowl from Obiszów. (A) esters of the palmitoleic acid with fatty alcohols; (B) esters of the palmitic acid with fatty alcohols

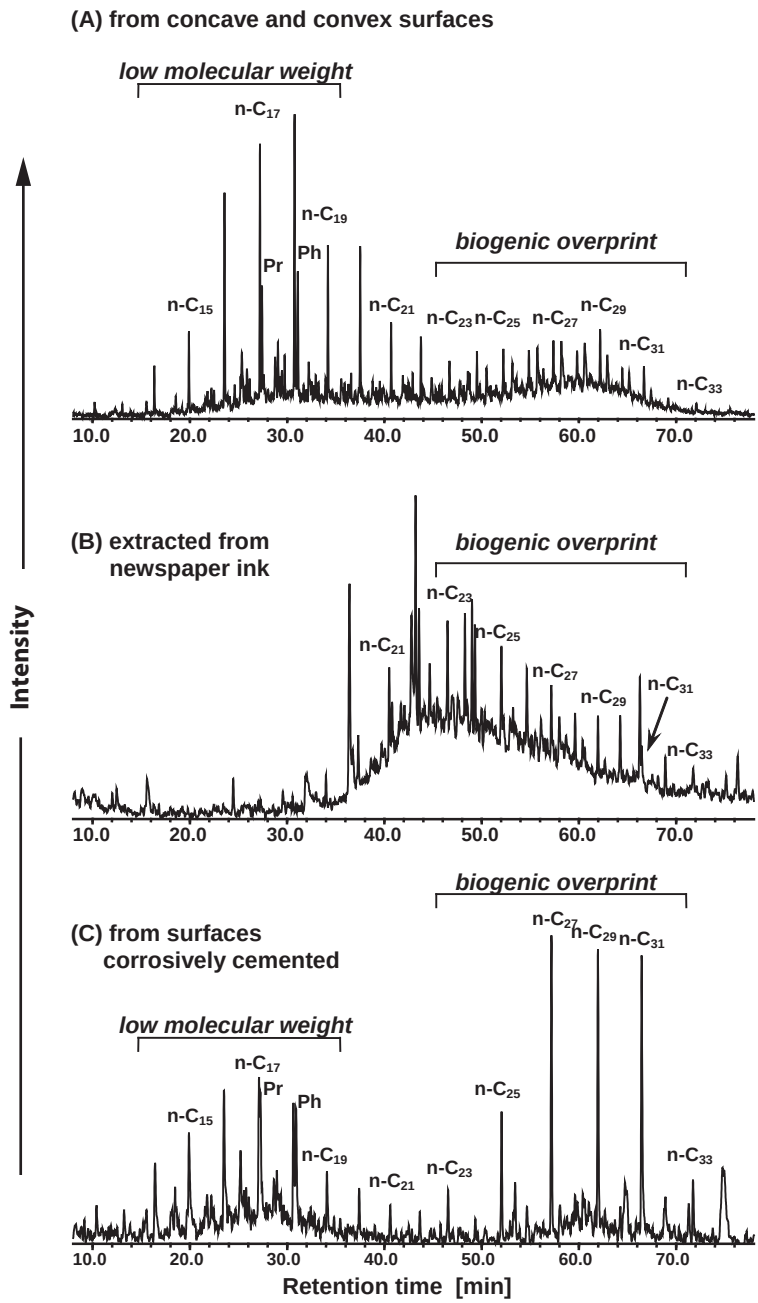

Fig. 12. The molecular composition of n-alkanes and isoprenes on the surfaces of bowls from Witostowice and separated from printing ink of the newspaper with which the bowl were wrapped. Pristane (Pr), phytane (Ph)

The higher advancement of n-alkanes biodegradation on the bowl's surfaces cemented by corrosion as compared to the better preserved bowls is clearly reflected by strong decrease in the relative concentrations of n-C_{17} to Pr and n-C_{18} to Ph – compare profiles (A) and (C) of low molecular n-alkanes range in Fig. 12.

SUMMARY AND EVALUATIVE REMARKS

The organic matter occurring on surfaces of early medieval iron bowls underwent examination of the molecular composition for the first time. Identified components of biogenic origins (high molecular n-alkanes with characteristic domination of odd-carbon-numbered homologues, free n-alkanoic acids, esters of straight-chained monounsaturated and saturated fatty acids esterified with fatty alcohols) raise no doubt in the context of the natural environment of places where the bowls were hidden. Apart from the biogenic compounds, the organic matter contains only low molecular weight and middle molecular weight n-alkanes (bowls from Obiszów) or only low molecular weight ones (bowls from Witostowice) with Gaussian homologous distribution, which strongly suggest hydrocarbons derived from petroleum. To date there are not known any indications that in Central Europe in the early Middle Ages, petroleum was used (petroleum was used in ancient times, amongst other for wood impregnation in the Middle East, including Babylonian and Assyrian civilizations; in the Book of Genesis of the Old Testament, God commanded Noah to cover the ark 'with pitch inside and outside').

The presented results should be considered as indicative. They require critical evaluation since there is no absolute certainty concerning used appropriate procedure providing prevention of the bowls at the finding place from contact with materials such as plastic bags, which may be a contamination source of the identified compounds. Hence, there are legitimate doubts about the precise and the source of found hydrocarbons, as well as period and circumstances of their introduction to surface of iron bowls. The additional reason for caution in the interpretation of petroleum derived hydrocarbons introduction on the bowls surface is often reported anthropogenic soil contamination by petroleum hydrocarbons, i.e. petrol or diesel. This could be resolved by analysis of the soil rim around the hidden bowls, but such material was not collected and studied in present work. In conclusion, the results should be regarded as preliminary. In future verification studies, should be applied the procedure of handling newly found bowls avoiding contact with external sources containing organic components.

BIBLIOGRAPHY

Adamczyk J. 2004. Płacidła w Europie Środkowej i Wschodniej w średniowieczu. Formy, funkcjonowanie, ewolucja, Warszawa.

Baron J., Rzeźnik P. 1999. Wczesnośredniowieczny budynek z tzw. korytarzykiem wejściowym z osady w Obiszowie na Wzgórzach Dalkowskich, Śląskie Sprawozdania Archeologiczne 41, 269–280.

Bartošková A. 1986. Slovanské depoty železných předmětů v Československu, Praha.

Bai Y., Fang X., Wang Y., Kenig F., Chen,X., Wang Y. 2006. Distribution of aliphatic ketones in Chinese soils: potential environmental implications, Organic Geochemistry 37, 860–869.

Boroń P. 1998. O rzekomych pieniężnych funkcjach niektórych przedmiotów żelaznych z wczesnośredniowiecznego Śląska, Studia i materiały z dziejów Śląska 23, 7–15.

Bubeník J. 1972. K problematyce železné misky tzv. slezského typu, Archeologické rozhledy 24, 542–567.

Jaworski K. 2005a. Grody w Sudetach (VIII-X w.), Wrocław.

Jaworski K. 2005b. Einige Bemerkungen über die frühmittelalterlichen Burgwälle in den polnischhen Karpaten – aus der Perspektive eines mit der Erforschung der Burgwälle in den Sudeten befassten Forschers (Erwägungen über die Arbeit von Jacek Poleski "Die frühmittelalterlichen Burgwälle im Dunajec-Gebiet"), Acta Archaeologica Carpathica 40, 163–194.

Jaworski K. 2005c. Die Eisenschatzfunde des 9. Jh. von den Burgwällen im Süden Niederschlesiens, [in:] P. Kouřil (ed.), Die frühmittelalterliche Elite bei den Völkern des östlichen Mitteleuropas. Materialien der internationalen Fachkonferenz, Mikulčice, 25.–26.5.2004, Spisy Archeologického ústavu AV ČR Brno, Bd. 25, Brno 2005, 359–374.

Herrmann J. 1966. Tornow und Verberg. Ein Beitrag zur Frühgeschichte der Lausitz, Berlin.

Kaletynowie M. i T., Lodowski J. 1968. Grody wczesnośredniowieczne województwa wrocławskiego, Wrocław-Warszawa-Kraków.

Kurtz H., 1936. Slawische Bodenfunde in Schlesien, Breslau.

Paternoga M., Rzeźnik P. 2005. Budownictwo obronne plemienia Dziadoszan w świetle badań grodziska w Obiszowie, [in:] K. Wachowski (ed.) XIV Śląskie Spotkania Archeologiczne. Streszczenia komunikatów i referatów. Polanica-Zdrój 19–21.05.2005, Wrocław, 52–54.

Peters K.E., Walters C.C. Moldowan J.M. 2005. The Biomarker Guide. Biomarkers and Isotopes in Petroleum Exploration and Earth History, Cambridge: Cambridge University Press.

Rzeźnik P. 2006. Problem tezauryzacji mis żelaznych typu śląskiego w świetle studiów źródłoznawczych tzw. skarbów jednorodnych, Fontes Archaeologici Posnanienses 42, 175–225.

Rzeźnik P. 2008. A set of early medieval sheet iron bowls from Gromnik. A study of a deposit partly reclaimed for archaeology, [in:] K. Jaworski, A. Pankiewicz (eds.), Mount Gromnik (Rummelsberg). From the History of Settlement and Management, Wrocław, 161–178.

Schwark L., Zink K., Lechterbeck J. 2002. Reconstruction of postglacial to early Holocene vegetation history in terrestrial Central Europe via cuticular lipid biomarkers and pollen records from lake sediments, Geology 30, 463–466.

Seger H. 1928. Die schlesischen Silberfunde der spät-slawischen Zeit, Altschlesien, Bd. 2, H. 2, 129–161.

Turek R. 1942. Ein Hortfund der älteren Burgwallzeit aus Böhmen, Nachrittenblatt für deutsche Vorzeit 18 (11-12), 263–268.

Wiesenberg G.L.B., Schwarzbauer J., Schmidt M.W.I., Schwark L. 2004. Sources and turnover of organic matter in agricultural soils derived from n-alkane/n-carboxylic acid compositions and C-isotope signature, Organic Geochemistry 35, 1371–1393.

Zhang Z., Zhao M., Eglinton G., Lu H., Huang C.-Y. 2006. Leaf wax lipids as paleovegetational and paleoenvironmental proxies for the Chinese Loess Plateau over the last 170 kyr, Quat. Sci. Rev., 25, 575–594.