WOOD TAR IN THE DNIEPER AND ELBE COMMUNITIES: VI – II MILLENIUM BC

Sławomir Pietrzak

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Editor's Foreword

The study '*Wood Tars in the Dnieper and Elbe Communities: 6th – 2nd Millenium BC*' is the first European monograph of its kind in the professional literature devoted to the general question of the craft technology and application of wood tars among proto-agrarian communities across the long line of the Neolithic, Eneolithic and beginning of the Bronze Age across the vast expanse of borderlands joining Eastern and Western Europe.

The research for the purpose of this monograph was undertaken at the University of Adam Mickiewicz in Poznań in partnership with the Institute of Prehistory and the Physico-Chemical Materials and Nanotechnology Section at the Faculty of Chemistry. The study was completed with the aid of chemical analyses of a comprehensive collection of wood tar samples documented in the course of excavations conducted in collaboration with a number of research-related institutions.

The original work in Polish, '*Zastosowanie i technologie wytwarzania dziegciu przez społeczeństwa międzyrzecza Dniepru i Łaby od VI do II tys BC*' [Wood Tar Crafts and Their Application Among Dnieper and Elbe Interfluvial Communities: 6th – 2nd millennium BC] was published in 2010 ['*Archaeologia Bimaris Monografie*', vol. 4] and received broad-ranging 'interdisciplinary recognition' from many scholarly circles in Central-Eastern Europe for the issues raised in respect to wood tars and their applications among prehistoric peoples. This consequently saw the decision to aim for a potentially broader readership through an abridged English version in the '*Baltic-Pontic Studies*' series.

The study was supervised in respect to on-going work and research methods by Professor Jerzy J. Langer at the University of Adam Mickiewicz, who also reviewed the monograph for publication.

Editorial comment

1. All dates in the B-PS are calibrated [BC; see: Radiocarbon vol. 28, 1986, and the next volumes]. Deviations from this rule will be point out in notes [bc].
2. The names of the archaelogical cultures and sites are standarized to the English literature on the subject (e.g. M. Gimbutas, J.P. Mallory). In the case of a new term, the author's original name has been retained.
3. The spelling of names of localities having the rank of administrative centres follows official, state, English language cartographic publications (e.g. *Ukraine, scale 1 : 2 000 000*, Kiev: Mapa LTD, edition of 1996; *Rèspublika BELARUS', REVIEW-TOPOGRAPHIC MAP*, scale 1:1 000 000, Minsk: *BYELORUSSIAN CARTOGRAPHIC AN GEODETIC ENTERPISE*, edition 1993).

FOREWORD FROM THE AUTHOR

This study is the fruit of the research programme of the Department of Prehistory, Polish Institute of Prehistory, AMU in Poznań in collaboration with the Physico-chemical Materials and Nanotechnology Section, Faculty of Chemistry, AMU based in Śrem. Its main task is to exam the manufacture and application of wood tars in the prehistoric past in the Central European Lowland and as such represents foremost an interdisciplinary 'perspective' on the Stone and Bronze Ages in regard to the use and manufacture of wood tar.

At the same time this work is a consequence of the research discourse conducted in the broader community of both archaeologists specialising in the Stone and Bronze Ages, as well as scholars conducting archaeometric research (physico-chemical); thus bringing together two perspectives; one of the humanities (archaeology) and that of the sciences (physics and chemistry). It is therefore my pleasure to sincerely thank all those concerned without whom this work would not be possible.

My sincere gratitude goes to Professor Aleksandra Cofta-Broniewska, founder and head of the Kujawy Research Group, formed later into the Department of Polish Prehistory, my supervisor, Professor Jerzy J. Langer, Head of the Organic Semi-Conductor Laboratory transformed later into the Physico-chemical Materials and Nanotechnology Section, for his patience, motivation and inspiration, as well help given during the course of laboratory research.

Equally, I would like to express my gratitude to Professor Aleksander Kośko, Head, Department of Polish Prehistory, for his generous help, as well as his kindness and engagement beyond the call of duty, which were a driving force for even greater intensification of work on my part. At the same time I would like to express my sincere debt to the respective Heads of the Institute of Prehistory, AMU – Professors Hanna Kóčka-Krenz and Dobrochna Jankowska, for their enduring kindness and opportunity to complete Dr.al studies, whose final fruit is this particular study.

In addition I would like to sincerely thank the following: Professor Lech Czerniak, Professor Janusz Kruk, Professor Włodzimierz Wojciechowski, Professor Michał Kobusiewicz, Professor Marzena Szmyt, Professor Lucyna Domańska, Professor Janusz Czebreszuk, Professor Stanisław Kukawka, Dr. Mark Chłod-

nicki, Dr. Bartosz Józwiak, Dr. Marcin Ignaczak, Dr. Przemysław Makarowicz, Dr. Barbara Baczyńska, Dr. Hanna Kowalewska-Marszałek, Dr. Halina Taras, Dr. Katarzyna Ślusarska-Michalik, Dr. Jacek Górski, Dr. Krzysztof Tunia, Dr. Jacek Kabaciński, Dr. Piotr Chachlikowski, Dr. Seweryn Rzepecki, Dr. Andrzej Wiśniewski, Dr. Małgorzata Rybicka, Dr. Jarosław Rola, Dr. Józef Bednarczyk, Jarosław Sobieraj, Dr. Agnieszka Przybył, Magister Danuta Prinke, Piotr Dmochowski, Magister Iwona Sobkowiak-Tabak, Paweł Jarosz, Magister Danuta Kozłowska, Ryszard Pietrzak and Ryszard Kirkowski for their invaluable assistance in making available all the relevant collections and documents in the respective archaeological institutions, as well as their assistance in the ensuing research of these materials.

In particular, I would like to record my gratitude towards Dr. Tomasz Gibiński and Dr. Sebastian Golczak for their comments, engagement, invaluable and constant help, encouragement and opportunity for numerous research consultations.

I would like to also thank all those I had the good fortune to meet thanks to archaeology and chemistry, as well as beyond: Bartłomiej Szmoniewski, Krzysztof Langer, Magdalena Rapp, Andrzej Gwoździk, Monika Gaździk, Grzegorz Framski, Piotr Włodarczak, Henryk Machajewski, Agnieszka Matuszewska, Marcinowi Szydłowski, Andrzej Michałowski, Michał Wieczork, Agnieszka Mączyńska, Piotr Decyk, Halina Thiel-Pawlicka, Monika Dolat, Małgorzata Brzezna, Anna Leciejewska, Ewa Brzozowska, Renata Groszewska, Hanna Grochowska, Hanna Cubal, Anna Tomaszewska, Monika Adamska, Piotr Hauser, Jarosław Libelt – and all who remain unamed in this place that I have not forgotten.

Special warm thanks to *Those Closest*, for their support not only in times of success, but most of all, in times of doubt. It is thanks to their help and patience, and in many cases outright sacrifice that made it possible to complete this work.

Last but not least, the research completed and preparation of the this Dr.al study was made possible by the financial support of the Scholarly Research Committee (grant nr 5 H01H 019 21).

INTRODUCTION

1. STUDY OBJECTIVES

Being one of the first-ever chemical manufacturing processes in the history of mankind, wood-tar production belongs to those emerging issues of prehistory that have not been comprehensively addressed so far. Evidence for wood tar is specific and, as such, often escapes notice or recording during surveys or fieldwork. Consequently, until recently, this very sphere of human activity remained perceived as having little research value and hence inadequately studied. Under these circumstances, all knowledge of wood-tar production and applications in prehistoric European societies was obtained solely from macrographic examination (humanistic approach) during field recording. However, given its wide chronological (Mesolithic period to Bronze Age, Roman Age, and Middle Ages inclusive) and geographical (relevant finds are ascertained in the area largely corresponding to modern Austria, Czech Republic, France, Germany, Poland, Slovenia, Sweden, Ukraine and the United Kingdom, etc.) span, dry distillation of wood and bark is essential for in-depth exploration of prehistoric Europe, including specifically the Polish Lowland.

This study aims to determine the research potential of wood tar that has been uncovered at archaeological excavations but one that has tended to be largely neglected in studies on source materials. This dissertation is also the first step towards interdisciplinary archaeometric investigations on wood tar. However, at this point, significant insufficiency of source material from geographies covered by our research coupled with relevant physico-chemical analyses remaining unpublished, effectively prevents a complete tracking of development tendencies in wood-tar production and application technologies across prehistoric European societies.

The primary objective of this study is to present issues pertaining to wood-tar production and use between the Dnieper and Elbe rivers during the 6th to 2nd millennia BC based on available source material. This dissertation aims at examining a set of putative wood-pitch samples collected during archaeological excavations at Neolithic and Bronze Age sites. Through comprehensive physico-chemical analysis, tests properly identify the sampled materials (including their distinctiveness from bituminous substances of geogenic origin, food remains, and mineral colorants that contain iron and/or manganese oxides), determine chemical affinity and evaluate for similarities in manufacturing methods. As our research progresses, primary raw materials for prehistoric wood-tar production (species of bark or wood) as well as wood tar applications are identified. Once this is done, clear and coherent classification criteria for particular technological and functional groups of wood tar are developed. Thereupon, conclusions are drawn about production technology and subsequent processing of wood tar.

This dissertation will also attempt an assessment of the usefulness of natural products in prehistory and the identification of original applications of artefacts that bear traces of organic products.

This multi-aspectual study of all available finds, which ascertain wood-tar production and application, is to provide the fullest possible description of wood-pitch economy. The results of this study are expected to add considerably to our understanding of both economic and non-economic spheres of cultural activity of prehistoric and early historic societies. So far, scholars of European prehistory have not specifically addressed the issues pertaining to wood-tar production and its applications. Thus, this is the first comprehensive study to extensively apply physico-chemical methods and draw on relevant research findings to date.

2. MATERIAL SCOPE

An important step in studies on formation and development of wood-tar manufacturing processes is to determine the extent to which it is feasible to reconstruct such processes based on ‘putative wood tar samples’.

The issues relevant to wood-tar production and applications are discussed based on both an extensive review of materials published in the literature, and, first and foremost, recent results of laboratory testing of archaeological samples. It seems practicable that the following four categories or types of source material should be considered, i.e. post-production residues, binders, vessel sealing, and colorants, which represent the most common applications of wood tar in prehistory.

A primary source for this study is a set of 218 samples of ‘putative wood tar’ collected at 80 archaeological sites belonging to various periods and cultures. These samples have been subjected to complex laboratory tests to determine: wood-tar manufacturing methods; wood or bark species used in wood tar manufacturing; wood tar applications; and production patterns in wood tar manufacturing and reprocessing by prehistoric European societies. Since wood tar remnants are primary determinants of both the general and local specificity of the process, they are our primary focus in drawing conclusions for the purpose of this study.

The majority of the samples are collected from sites investigated by the Institute of Prehistory, Adam Mickiewicz University, whereas other samples are obtained in cooperation with the Institute of Archaeology and Ethnology of the Polish Academy of Sciences in Warsaw, Institute of Archaeology and Ethnology of the Polish Academy of Sciences (Branch in Poznań), Institute of Archaeology and Ethnology of the Polish Academy of Sciences (Branch in Kraków), Institute of Archaeology of the University of Łódź in Łódź, Institute of Archaeology of the University of Wrocław in Wrocław, Institute of Archaeology of the Maria Curie-Skłodowska University in Lublin, Museum of Archaeology in Poznań, Museum of Archaeology and Ethnography in Łódź, Museum of Archaeology in Kraków, National Museum in Szczecin and the District Museum in Piła. Completing the source material are samples obtained by cooperation with the Institute of Archaeology of the National Academy of Sciences of Ukraine in Kiev, Institute of the National Academy of Sciences of Belarus in Minsk, and Institute of Archaeology of the Slovak Academy of Sciences in Nitra.

3. CHOROLOGICAL AND CHRONOLOGICAL SCOPE

The chronological span of this study between the early Neolithic period and the Bronze Age (6th to 2nd millennia BC) inclusive reflects the dating of the available source material. So delimited, the timespan to study cultural transformations associated with wood-tar production encompasses 4000 years from the emergence of the first Linear Pottery agrarian communities until the Bronze Age inclusive. It is also when wood tar started to play a considerable role not only in economy but also in other non-economic activities of prehistoric European societies. To properly address the genesis and development of prehistoric wood-tar production, reference works are consulted which discuss materials from the Mesolithic period as well as from Iron and Middle Ages. Such a wide chronological perspective is crucial to understand trends in wood-tar production and applications in Poland or, more broadly, between the Dnieper and Elbe rivers.

Europe, including specifically the region between the Dnieper and Elbe rivers or one of primary development zones of the time, is a territory fundamental for gaining knowledge of, or understanding the wood-tar production and application processes. With the territory so delimited for research purposes, a specific zone is assigned a diagnostic role. This diagnostic zone encompasses sub-territories occupied by cultures that emerged in the Baltic Sea catchment area, i.e. the Late Linear Pottery culture, Late Band Pottery culture, Funnel Beaker culture, Globular Amphora culture, Trzciniec culture circle, and Lusatian culture circle. Comparative material for these locations comes from territories where three wood-tar production centres or culture circles emerged (*Steppe and Forest Steppe culture circle*: Tripolye culture, Proto-Pit Grave culture, and Catacomb culture; *Eastern European forest zone culture circle*: Dnieper-Donets culture, Zedmar culture, Neman culture, Comb culture, eastern Trzciniec culture circle, and North Belarus culture; *Carpathian Basin culture circle*: Eastern Linear Pottery and Bükk cultures) that are clearly distinguishable in terms of intangible and tangible (including wood-pitch production and use) cultural heritage. Given these points, this study encompasses the region between the Dnieper and Elbe, and, for a broader approach, entire Europe. The reason for such geographical scope is our sources: the vast majority of „putative wood-tar" samples come from these territories.

4. HISTORY OF RESEARCH

This chapter addresses the present state of the art in studies on wood pitches, including specifically wood tar. Investigations of these specific organic substances began in the mid-19th century when papers on pitch finds were first published. Remnants of wood pitch and tar were always identified in pottery contexts datable to the Stone Age, Bronze Age, Iron Age, or Middle Ages. The remnants tended to be designated by various names, such as '*urn – pitch*', '*urn resins*', '*flumigating cakes*', '*resin cakes*', '*harze*', '*urnenharze*', '*harzkitt*', '*gräberharze*', carbon formations, etc., and were identified with the products of destructive distillation of wood or bark. A noteworthy fact is that the then valid archaeological identifications for this specific group of organic sources remain informatively valuable insofar as they provide descriptions. The earliest physico-chemical testing of archaeological samples of what had been tentatively designated as 'putative wood tar' upon initial macrographical examination (humanistic approach), were described in the 1920s [Eichhorn 1927] and 1940s [Vogt 1949]. However, the earliest attempt to determine the chemical composition of wood tar was not made until 1830–1833 by an Austrian scientist, Karl Freiherr von Reichenbach (1788–1869). The followers to continue Reichenbach's studies were Friedrich August von Kekulé (in 1865), Hans Heinrich Landolt (1831–1910), and Carl Heinzel (in 1880). They were mostly focused on the chemical composition analysis of various types of wood pitches, giving little or no consideration to possible functions of wood pitch in the prehistoric European economy. Consequently, their results failed to add any substantial technical value or methodical experience to support development of techno-archaeological studies on prehistoric and medieval wood-tar production.

The next step in wood pitch research was triggered by tar finds from medieval Poland [Szafrański 1949–1950; Szafrańscy 1961; Dymaczewski 1953; Leciejewicz 1953; Rajewski 1970]. A major breakthrough was evidence gathered for early Medieval wood-tar production, consisting of production facilities in Polish lands. The facilities were also the earliest traces of a deliberate manufacturing (wood-tar production) activity in Europe.

At that time, parallel scientific efforts were also made by German, Austrian, Czech, and Slovak scholars. Particularly noteworthy are publications from the 1950s to 1970s, discussing materials from the Iron and Middle Ages [Novotný 1952; Bialekowá 1962; Pleiner 1961; Šaurová 1968; Remiášowa, Ruttkay 1967; Rottländer 1974; Persy 1967; Barthel 1967; Schoknecht, Schwarze 1967]. However, the focus of these studies was on archaeological analysis rather than on physico-chemical tests for tar as a basis for interpretative conclusions. The only work that deviated from that general trend was that of an Austrian scientist, Sauter [1967], who performed laboratory tests for wood tar used to repair vessels of the Hallstatt period. His innovation was the use of infrared spectrophotometry to test materials of archaeological origin, which method allowed the materials to be identified as birch tar.

The significant modification of the approach to issues relevant to dry distillation of wood and bark was made in the 1980s-90s when several independent European laboratories (in Austria, Germany, Poland, and the United Kingdom) successfully performed first analyses of wood tar samples from various time points [Lange 1983; Evershed, Jerman, Eglinton 1982; Kośko, Langer 1986; Langer 1989; Langer, Kośko 1992; Hayek *et al.* 1990; Heron, Nemcek, Bonfield 1994]. At that time, no other Central European country published anything that would be comparable therewith in terms of scientific importance. Over time, scientists started to publish more on the material datable to the Iron and Middle Ages, including specifically evidence of the medieval and 14th- and 16th-century boatbuilding [Beck, Borromeo 1990: 51-58; Evershed, Jerman, Eglinton 1982: 528-530; Reunanen, Ekman, Heinonen 1989: 33--39; Robinson *et al.* 1987: 637-644; Mills and White 1989: 37-44].

The results of physico-chemical tests for „putative wood tar" of the late Neolithic and early Eneolithic periods were first explored by Kośko and Langer [1986: 587-600]. Their research primarily involved microscopic examination, physico-chemical measurements, and elemental analysis. Physico-chemical methods included thin layer chromatography with silica gel, measurement of melting points and light absorption across the full visible spectrum, mass spectrometry, and measurement of luminescence and optical activity. Kośko and Langer were probably the first to use such a broad range of physico-chemical methods to provide firm evidence confirming the presence of Neolithic wood tar. At that time, the increasing number of physico-chemical tests of archaeological organic preparations pointed to the need for extending the classification of wood-tar remnants beyond only the formal.

Progress in methods enabled intensification of research into the development of tar production in prehistoric Europe. Since then, scientists from all over the world started testing natural products in addition to archaeological samples. Among analytical procedures used in testing were chromatography and spectroscopy that allowed separation and identification of chemical compounds such as food remains or other organic archaeological preparations [Kośko, Langer 1986; Langer 1989; Mills, White 1987; Evershed, Heron, Goad 1990]. Relevant tests correlate archaeological materials with modern natural reference products with respect to characteristic components or component distribution [e.g. Charters *et al.* 1993]. The use of such '*molecular tracers*' is a complicated procedure given the degradation of organic substances in soil [Langer, Kośko 1999]. Despite these challenges, physico-chemical analytical tools offer a wide array of possibilities to draw relevant conclusions, as shown by the examples given below.

The relevant research efforts led to successive works having been published on the subject. For example, in 1990, laboratory results for samples from Mondsee (Upper Austria) and Ergolding Fischergasse (Germany) sites of Eneolithic Altheim and Mondsee cultures were published [Hayek *et al.* 1990; Heron *et al.* 1989; Heron, Nemcek, Bonfield 1994; Evans, Heron 1993]. The region of the Alpine borderlands between Austria and Italy (Ötzaler) also yielded a famous 'Iceman' datable to 3330 BC, whose equipment included tools and weapons with organic residues [Spindler 1993; Pollard, Heron 1996]. Research carried out by the British, Austrian, and German scientists was also contributing to increasing the knowledge of dry distillation of wood and bark in prehistoric times [Fox, Heron, Sutton 1995; Hayek, Krenmayr, Lohninger 1991].

In the early 1990s, wood tar was also identified among earlier materials, i.e. those datable to 3940 – 3700 BC (Łącko, Province of Bydgoszcz, site no. 6A: phase III A) or 3940 – 3700 BC (Łojewo, Province of Bydgoszcz, site no. 35: phase III A) [Szmyt 1992]. In light of the above-discussed application of physico-chemical testing for research into prehistoric wood-tar production, which testing is often occasional and performed by commercial providers of laboratory testing services, an interdisciplinary field of archaeometry needs to be highlighted. As far as archaeometry is concerned, particular attention should be given to techno-archaeological activities of the Department of Prehistory of Poland, Institute of Prehistory, Adam Mickiewicz University, carried out in collaboration with the archaeometric laboratory of the Faculty of Chemistry, Adam Mickiewicz University, at Śrem [Kośko, Langer 1997; Langer, Pietrzak 2000; Langer, Pietrzak 2004a; 2004b; 2004c]. Through physico-chemical examinations, these institutions established that, among others, late Neolithic cultures of Kujawy used wood tar as a pottery colorant (3650 – 2350 BC) [Langer, Kośko 1999], possibly enriching it intentionally with blood [Langer, Kośko 1992]. Also, noteworthy are the results of investigations that revealed the use of wood pitches among the Band Pottery culture communities of Kujawy in the mid-4th millennium BC [Pietrzak 1999].

These both findings shed new light on origins of the ‘wood-tar invention’ as well as on development of wood-tar manufacturing activity in Europe.

In response to great interest among scientists from all over the world in wood-tar production as a sphere of prehistoric processing industry, the First International Symposium on wood pitches was held in Biskupin in 1993, which largely contributed to enriching our knowledge of the subject [Brzeziński, Piotrowski 1997].

The above observations provide a basis for reinterpretation of finds recorded before the 1980s, and, as such, gain higher credibility [Vogt 1949; Wojciechowski 1972; Gumiński 1989]. In conclusion, it is noticeable that the supply of relevant information is still unsatisfactory despite the increasing number of specialist tests for prehistoric wood tar. Our present knowledge of tar-related sphere of prehistoric raw material economy proves particularly insufficient when compared with what we know about other manufacturing activities.

5. RESEARCH METHOD AND METHODOLOGY

For this part of the study, we relied directly on methodological experience of the archaeometric laboratory of the Faculty of Chemistry, Adam Mickiewicz University, at Śrem, directed by Prof. J.J. Langer [Kośko, Langer 1986; Langer 1989; 1993; 1997a; 2005; Langer, Pietrzak 2000: 411-414; 2004a: 100-117]. One of chief methods used for testing was infrared spectrophotometry. The IR spectra were measured in KBr pellets, using a Bruker IFS 113v infared spectrometer. The outcome was complemented by results of chromatographic tests (thin layer chronatography, SiO_2, Merck, hexane-carbon tetrachloride 5:1 and 3:1, cyclohexane-chloroform 10:1, chloroform-methanol 10:1, 5:1, and 3:1), measurements of melting points (Boetius PHMK 05 polarizing microscope equipped with a hot stage, temperature range: 0 °C to 300 °C), and microscopic examination under visible and ultraviolet light (polarizing optical microscope and Philips 515 scanning electron microscope) [Kośko, Langer 1986, Langer 1989, Pollard, Heron 1996; Langer, Kośko 1999]. In addition to these research techniques, electron paramagnetic resonance was applied using a PDP Radiopan SE/X 2547 spectrometer [Krzyminiewski, Langer, Kośko 1998].

The comparative tests were performed using modern wood-pitch standard samples obtained in the arachaeometric laboratory. To identify the substances submitted to testing, the chemical similarity between samples was established and tracers permitting correlation with currently available substances were detected. A wide array of methods applied during testing made it feasible to identify and correlate the substances. Also, they enabled both in-depth study of the technological arcana of how wood tar was obtained, and precise determination of wood tar composition, raw materials processing methods and original applications.

6. STRUCTURE

This study consists of five chapters. The first chapter discusses both the terminology used in literature, and technological procedures applied in producing and preparing wood tar, referencing written sources and ethnolinguistic data. In our reconstruction of the procedures, we are relying on what is known about prehistoric skills, as well as on relevant observations from ethnology and experimental archaeology. The second chapter addresses physico-chemical properties of raw materials, and methods applied to manufacture and prepare wood tar. The information from the second chapter is subsequently used to interpret results of physico-chemical analysis in the fourth chapter. Furthermore, the second chapter provides details of archaeological and fossil remains of wood tar. The third chapter examines objectives, methods, and methodology of archaeometric testing, with consideration given to its applicability in archaeological inference. The fourth chapter provides archaeological interpretation of physico-chemical test results and groups technologies into those for obtaining and those for modifying given products, and specifies their uses. The fifth chapter presents catalogued results of the analysis, with figures compiled into tables and illustrated by graphs and microscopic images. The concluding chapter sums up the research results and formulates future research avenues. The bibliography as well as the list of abbreviations, the latter included at the beginning of this study for convenience, are integral constituents in this context. A catalogue of sources, which briefly describes samples submitted to testing, either in tables is a separate part of this study.

Chronological terms used in this study deserve explanation. All dates are given in calibrated years expressed as ‘BC’. For unspecific time frames, which are not based on ^{14}C dates, average values are provided (e.g. 2900/2700 conv. BC) or Bronze Age phases are used as developed by Paul Reinecke or Oskar Montelius – Józef Kostrzewski in their chronological schemes.

EI – Electron impact ionization
EPR – Electron paramagnetic resonance
FTIR – Fourier transform infrared spectroscopy
g – Landé g factor
GC – Gas chromatography
GC-MS – Gas chromatography – mass spectrometry
HCl – Hydrochloric acid
HPLC-MS – High-performance liquid chromatography
KBr – Potassium bromide
MAS NMR – Magic angle spinning nuclear magnetic resonance spectroscopy
M/z – Molecular mass
MIR – Mid-infrared
MS – Mass spectrometry
MS-MS – Mass spectrometry – mass spectrometry
mT – Millitesla
NaCl – Sodium chloride
NaOH – Sodium hydroxide
NMR – Nuclear magnetic resonance spectroscopy
POM – Polarized optical microscopy
R_f – Retardation factor
RT – Retention time
SEM – Scanning electron microscopy
TLC – Thin-layer chromatography
TMS – Tetrametylosilan
ΔH – Inclination width (mT)

CULTURAL UNIT ABBREVIATION LIST

BB	Bell Beakers
BC	Baden culture
BDC	Boh-Dniester culture
BKG	Brześć-Kujawski group
BüC	Bükk culture
CaC	Catacomb culture
CC	Cortaillod culture
CoC	Comb culture
CVC	Chłopice-Veselé culture
CWC	Corded Ware culture
DDC	Dnieper-Donets culture
ELPC	Eastern Liner Pottery culture
FBC	Funnel Beaker culture
GAC	Globular Amphora culture
IC	Iwno culture
KC	Komarovo culture
LBPC	Late Band Pottery culture
LC	Lusatian culture
LG	Linin group
LH	Linin horizon
LIPC	Linear Pottery culture
LPC	Lengyel-Polgar culture
LT	Linin type
ŁH	Łódź horizon
ŁPh	Łódź phase
MC	Mierzanowice culture
MDC	Middle Dnieper culture
NaC	Narva culture
NBC	North Belarus culture
NiC	Neman culture
OC	Otomani culture
PCC	Pit-Comb culture
PLC	Pre-Lusatian culture
PNC	Pripet-Neman culture
PYC	Pre-Yamnaya culture
SGC	Single Grave culture
SoC	Sosnitsa culture
StC	Strzyżów culture
TC	Trzciniec culture
TCC	Trzciniec Cultural circle
TCC-EB	Trzciniec Cultural circle – eastern branch
TH	Trzciniec horizon
ToC	Tomaszów culture
TrC	Tripolye culture
TuC	Tumulus culture
TuCC	Tumulus culture circle
UrC	Urnfield culture
UnC	Unetice culture
UVC	Upper Volga culture
VC	Věteřov culture
WBKC	West-Baltic Kurgan culture
YC	Yamnya culture (Pit-Grave culture)
ZC	Zedmar culture

I. EVIDENCE FOR WOOD-TAR PRODUCTION IN HISTORIC TIMES

This chapter gives an overview of key terms used in this thesis for prehistoric wood-tar production and applications. Contained in the literature, these terms tend to be obscure and imprecise. Therefore, it is essential that they are properly defined so as to reduce ambiguity and facilitate better understanding and proper use. Further in this chapter, relevant evidence for wood-tar production and applications is presented from written and ethnographic sources. Although considerably postdating the period covered by this study, the evidence constitutes a riveting comparative material for research in prehistoric wood-tar production. Toward the end of this chapter, an attempt is made to investigate the origin of the Polish words *dziegieć* and *dziegciarstwo* meaning wood tar and wood-tar production, respectively. Moreover, the symbolic dimension of words describing prehistoric wood-tar uses is examined.

I.1. TERMINOLOGY: DEFINITIONS OF THE TERMS ‘WOOD TAR’ / ‘WOOD-TAR PRODUCTION’

The prevailing view among scholars is that wood tar is a product generated by dry distillation of birch bark through flameless combustion in the absence of air [Alexandrowicz 1855: 277; Kossakowski 1891: 798; Stieber 1922: 186; Szafrański 1961: 132; Moszyński 1967: 389; Surmiński 1996: 55]. Through such chemical processing, prehistoric wood tar producers sought to extract valuable chemical compounds from bark (Chapter II.2).

However, in addition to the most common raw material in wood-tar production, i.e. birch bark and birch wood, pinewood and pine bark were also used [Wężyk 1872: 183; Dominikiewicz 1927: 72-75; Szafrański 1949–1950: 463 et seq.; Kośko, Langer 1997: 25]. Both the archaeological record [Kośko, Langer 1986] and ethnographic data [Wrębiak 1971: 32; Brylak-Załuska 1983: 28] prove that, occasionally, birch wood or birch bark was mixed with resinous pinewood to give a mixed product also referred to as wood tar.

A description of yet another wood-tar production method is provided by Wrębiak who relies on the tradition of obtaining wood tar by repeated distillation of birch sap [1971: 30-31]. In the past, wood tar was also produced by thermolysis of softwood resins, including chiefly pine resins. [Kurzweil, Todtenhaupt 1991: 65].

The above observations indicate that the term ‘wood tar’ was also applied to a product generated by pyrolysis of wood or bark of various tree species. This is confirmed by Kossakowski distinguishing the following several kinds of wood tar [1891: 799]:

a) pure birch tar – used for tanning the best leather and recognized for its ability to remain liquid even in hard frost

b) birch tar with addition of small amounts of wood pitch – used for tanning lower quality leather

c) mixture of birch tar and softwood pitch – used chiefly as a lubricant for wheels

d) substance erroneously termed ‘wood tar’ for it is pure pine tar – used chiefly as axle grease;

e) wheel tar – pine tar somewhat thicker than the one described in the immediately preceding item, used as grease, including axle grease.

More recent studies on wood chemistry and technology present a different approach to the discussed issue. These apply the term ‘wood tar’ exclusively to a substance obtained from the thin outer bark layers of young white birch [Surmiński *et al.* 1995: 157-161; Surmiński 1996: 55]. By pyrolosis, the following three separate fractions are isolated:

I. at approx. 110 °C an aqueous layer is obtained, containing such compounds as acetic acid, acetaldehyde, methanol, etc.

II. at approx. 110 – 220 °C, wood tar is obtained, which is the lightest and smallest volume fraction that creates a thin opalescent layer on the surface;

III. at approx. 220 – 280 °C, heavy wood-tar pitch is obtained.

In the Neolithic period and Bronze Age, the wood-tar production activities between the Dnieper and Elbe rivers were closely connected with the abundance of birch trees either in pure stands or, more often, mixed with other species such as pine [Chotinski, Starkel 1982; Kośko, Langer 1986]. A noteworthy fact is that bark was among those organic materials that were easily available in prehistoric times. Prehistoric Europeans used bark for various purposes, including hut construction, house floor covering, or basic container or flaming torch production [Clark 1957: 246]. Bark processing was surely a Palaeolithic inheritance. As already noted, birch bark, or bark of the tree species dominant in the first forests of the post-glacial age, was most readily used [Chotinski, Starkel 1982; Fengel, Wegener 1989: 407-413].

Archaeological discoveries datable to the Palaeolithic or Mesolithic periods prove that destructive distillation of wood and bark was the first ever man-made technological and chemical process [Clark 1954; Mania, Toepfer 1973; Andersen 1982–1983; Larsson 1983; Aveling, Heron, Larsson 1996; Sulgostowska 1997;

Grünberg *et al.* 1999; Koller, Baumer, Mania 2001; Grünberg 2002]. Among occasional finds, there are also prehistoric poles and posts either covered or permeated with wood pitch [Ruthenberg, Weiner 1997: 29-34]. The relative abundance of wood-tar finds datable to Neolithic and Eneolithic periods might reflect an increase in the importance of wood tar in household activities, as well as in magic and healing practices [Gonzenbach 1949:tables 5, 10, 12-13; Klejn 1961: 105-109; Kośko, Langer 1986: 587-600; 1997: 25-28; Langer, Kośko 1992; 1999]. However, the archaeological records point to considerable intensification in the use of wood tar occurring not until the early 4th millennium BC when wood tar became known to culturally diversified societies populating the region bounded by the Rhine, Dnieper and Danube rivers. The region witnessed the production of two different types of wood tar: birch tar (i.e. tar obtained from birch bark – Upper Austria) [Vogt 1949: 50-52; Hayek *et al.* 1990: 2038-2043; Hayek, Krenmayr, Lohninger 1991: 153-156; Pollard, Heron 1996: 251-258] and mixed birch-pine tar (i.e. tar obtained from birch bark mixed with pine bark in a proportion two to one: Kujawy and Ukraine) [Kośko, Langer 1992: 61-68; 1997: 25-28].

It is no exaggeration to say that, due to its properties, wood tar is a very useful although today largely forgotten product. However, the term 'wood tar' is frequently used to denote totally different wood pitches. Scientists working on the subject usually arbitrarily and inaccurately assign this term to products of pyrolysis, formerly known as dry distillation, of wood and bark.

The product termed 'wood tar' is actually a multi-component substance. Frequently, throughout the entire production process, one and the same vessel was used to contain the product that we are going to call 'wood tar'. It is, therefore, clear, that a distillate deemed by many scholars to be wood tar is actually a hybrid substance composed of the lightest fraction, the aqueous layer, and wood-tar pitch or the thickest and heaviest part of the distillate [Langer 1989]. Also, not infrequently, the same reactor was used to produce various types of wood pitches [Langer, Pietrzak, Cichocka 2004]; in consequence, a mix was actually obtained, e.g. birch-pine tar. Therefore, despite the term being so strictly defined, for the purpose of this study, we are going to apply 'wood tar' both to denote proper tar, i.e. birch tar, as well as all other slowly volatile products of thermal decomposition of wood and bark, obtained from tree species other than birch.

For completeness, the following model description of properties typical of fossil wood tar is required here to allow archaeological excavators to reliably identify wood-tar remains:

> „petrified lumps or layers (e.g. on vessels) of wood tar are associated mostly with petrified pitch used for roofing or road construction. Indeed, there are colour (usually very dark grey…), glossiness, and texture (…) similarities. Differences between these two raw materials remain indiscernible until visual examination of a fracture: wood tar lumps are less glossy and have cracks that are sometimes filled with white (rarely), grey, or, most often, rust-coloured substance deemed to be remains of incompletely processed bark flakes" [Kośko, Langer 1986: 590].

I.2. WOOD TAR IN WRITTEN SOURCES

I.2.1. PRODUCTION PROCESS EVIDENCE

Wood tar belongs to the earliest man-made products. The history of wood tar spans at least several millennia during which the production process was evolving and the range of wood tar applications was widening. Wood tar is believed to have been produced in Persia and Mesopotamia as early as 7000 year ago; it then spread to Europe as reported by the Roman military doctor Dioskurides (1st century AD). A noteworthy fact is that the analysis of numerous manuscripts shows importance of technical and scientific information about production and uses of wood tar and plant-derived pitches.

Initially, wood and bark were subjected to thermal decomposition in plain pits dug into the ground; later on, a one-vessel method was favoured. The next step in the dry distillation development process was a two-vessel method or „*büt – bär – büt*" referred to by the Arabian physician Yahya ibn Masawaih al-Mardini. In his „De medicinis universalibus et particularibus", Masawaih al-Mardini describes extraction of pitch from bituminous materials [Kurzweil, Todtenhaupt 1989; Prouveur 1997: 231-234]. His production method uses „*destillatio per descensum*" or descending distillation referred to by various scholars [Czarnowski, Neubauer, Schwörer 1990: 169-173; Kurzweil,Todtenhaupt 1991: 63-79; Weiner 1991: 15-19]. In „Chirurgia parva", Lanfrancus Mediolanensis instructs: „*…make fire around the vessel, let the vessel be suspended above the ground, so that distilled oil may flow down into the receiver beneath…*" [Piotrowski 1993: 57]. A similar description is provided by Albertus the Great (ca. 1200-1280) in his „De vegetabilibus" which constitutes an interesting and important tribute to the history of pine tar. Based on his own observations, Albert the Great describes a dedicated double stove to produce wood pitch [Anzulewicz 1997: 221-230].

It is, however, „Buch der Natur" (1350) by Konrad von Magenberg (1309 – – 1374) that provides a specialist description of a juniper oil manufacturing process. „Buch der Natur" is also the first in German literature to describe double-pot dry distillation of wood. In his report, von Magenberg relies on earlier sources, referring to „Liber de natura rerum" by Thomas Cantimpratensis (1200 – 1262). The 16th and 17th centuries saw an increase in interest for destructive distillation of wood and bark. This is reflected, among others, in the work by Georgius Agricola (1494 – 1555) on minerals and mining, which compiles all wood and bituminous substance processing techniques Agricola was aware of, and highlights the unique role of pyrolysis. Equally important was „De la Pirotechnia" where Vannoccio

Biringuccio provides a detailed description of wood-pitch production process in a two-compartment container sunk in the ground. Further information on the 18th-century birch bark tar manufacturing methods is provided by Friedrich Mager [Kurzweil, Todtenhaupt 1990: 73-74; 1991: 71-72; 1992: 252-253; 1996].

Some time later, various types of piles were used to obtain wood tar, a technique strictly connected with metallurgy, using solely charcoal for smelting metals from ores [Barthel 1967: 195-203; Szydłowski 1968: 154-158; Rajewski 1970: 46--53; Todtenhaupt, Kurzweil 1994: 201-206]. Piles allowed the partial use of liquid products of distillation, including sour water and wood pitch. It was already Pliny the Elder to report in his „Historia Naturalis" that Egyptians used sour water as one of components to mummify dead bodies and pitch to maintain their sea vessels [Rosumek 1997: 273-277].

I.2.2. APPLICATION EVIDENCE

Wood tar and pitch served many various purposes. First relevant descriptions of tars and pitches come from the Holy Bible [Arnold, Mendez 2002]. Noah did not use anything else but wood pitch for caulking his ark [Gen. 6, 14). Pitch was also used for mortar in the walls of the mythological Tower of Babel [Gen. 11, 3) and as an impregnator in a basket carrying Moses and thus rescuing him from inevitable death from the cruel Pharaoh [Exod. 2, 3]. One of the earliest written sources to mention pine tar is the aforementioned „Historia Naturalis" by Pliny the Elder (1st century AD). The use of dry distillation products is ascertained for ancient Greece where, mixed with resins and blood, these served to seal wine amphorae. It is conceivable that they were also used for ritual and magic purposes [Piotrowski 1993: 53-61]. Traditional medicine used these to heal various skin or lung diseases and recognized their antibacterial and antiseptic properties in treating humans and animals [Kurzweil, Todtenhaupt 1996]. Good examples of how these qualities were recognized are mentions by Pedanios Dioscurides of Anazarbos (1st century AD) in his „De Materia Medica" translated by Berendes [1902: 94]. Dioscurides believes that liquid pitch is „*…an effective antidote for lethal poisons and a medication for leanness, lung ulcer, cough, asthma, heavy lung discharge (…). Pitch ointment is good for swollen tonsils and inflamed internal laryngeal muscles (angina), (…) for snake bites if applied together with finely-ground salt. (…) It has a beneficial action also if added to antiseptics*".

This range of applications proves that disinfectant and preservative properties of pitch were already recognized in the times of Dioscurides. There is also a mention by Jan Długosz in his „The annals or the chronicles of the glorious Kingdom of Poland [Annales seu cronicae incliti regni Poloniae]" ascertaining the use of pitch for its flammability properties as an essential component in liquids poured onto heads of aggressors penetrating defensive walls. Długosz reports that, during the siege of Głogów in 1109, defenders were pouring boiling pitch onto aggressors, causing irreversible tissue necrosis, deep scald injuries by long exposure, or even permanent disability. Extensive scalding could lead to death from hyperthermia, respiratory distress, or heart attack. Mentioned above, Długosz was the first Polish historiographer to report the use of pitch for defensive purposes. Much later (1650), Siemonowicz, in his „Great Art of Artillery, Part One" [Artis Magnae Artilleriae pars prima], confirms that pitch was a main component of incendiary bullets and missiles of any type [Sikorski 1997: 235-247].

Since ancient times, wood tar was widely used in boat and vessel construction, for its hydrophobic properties. Along with other natural materials (grass, moss, animal hair), wood tar was an excellent caulking agent. It conserved structural wooden elements of boats and vessels, protecting them against adverse effects of humidity [Cristensen 1968; Prehn 1991: 59-61; Pohlandt 1997: 253-255].

Some scholars also report wood tar having been used in leather tanning [Kossakowski 1891: 797-799; Szafrańscy 1961: 72]. A finely tanned top quality product or Russian leather was impregnated with nothing but liquid wood tar. Both the product and its Polish name presumably originate in Russia where production of, and trade in such leather have a long history. Russian leather as well as clothing made from it were extremely durable, impermeable, and resistant to continuous bending. Undoubtedly, wood tar was the agent to ensure leather durability, flexibility, and impermeableness [Moog 1997: 265-268].

It is evident that wood tar had a wide array of uses, including those that are likely to remain untraceable in written sources. The purpose of wood tar was, among others, to treat brittle and friable hooves, impregnate fishing nets, lubricate wagon axles and wheel hubs, and reduce friction between surfaces of wooden wagon parts [Wężyk 1872: 123; Szafrański 1958: 330-343; Wrębiak 1972: 28; Kośko, Langer 1986: 587-600]. In folklore, wood tar played an essential role of a magic preventive measure against illnesses. In the opinion of Moszyński, in Slavic lands, people used to cheat imminent illnesses by writing with wood tar upon doors: „*Nobody is home! Come yesterday!*" [Moszyński 1967: 315-316]. Newborn babies were fumigated with wood tar smoke to prevent or repel evil influence. They were also protected by an eggshell filled with wood tar and placed at the bedhead. With wood-tarred heads and backs, the cattle was believed to be safe from illnesses. For the same reason, adders were nailed to stable doors and pots containing wood tar were placed in each corner of a room [Pierzchała 1896: 337].

Enumerated above, the applications are far from exhausting all the roles of wood tar. This is because, failing any other suitable substance, ancient people deemed wood tar to be a cure-all. It should be highlighted that the written records referred to the above date to later periods in prehistory, i.e. from the Iron Age onwards, and as such are only to a small extent capable of helping interpretation of Neolithic and Bronze finds. Furthermore, very few mention wood tar technological formulas or application methods, or those practices that are likely to be untraceable by archaeological methods. For this reason, the specificity of written sources imposes considerable limitations on our study of periods preceding the Iron Age. Thus, this section is meant to signal rather than exhaust, the roles of wood tar.

I.3. LINGUISTIC EVIDENCE

This section attempts to investigate the feasibility of examining the archaeological record of wood tar based on linguistic evidence, following the linguistic archaeology approach [Sherratt,Sherrat 1988; Renfrew 1989; 1992; 1994; 2001; Mallory 1991; Breschini, Haversat 1997; Nyland 1997; Kowalski 1998]. Linguistic archaeologists structure their hypotheses following comparative analysis of both grammatical structures of sentences in various languages, and miscellaneous associated mythological plots, referring to the older Nostratic speech community [Kaiser, Shevoroshkin 1988; Bomhard, Kerns 1994; Mallory, Adams 1997; Kowalski 2000; 2001]. This section focuses on two issues of primary importance. On the one hand, it attempts to trace back the origin of the Polish terms *dziegieć* and *dziegciarstwo* meaning wood tar and wood-tar production, respectively. On the other hand, it examines symbolic dimension of words used to denote prehistoric wood tar applications. However, drawing conclusions about prehistoric processes based on linguistic evidence, which often considerably post-dates the processes, has definite limitations dictated by modern cognitive abilities. Nevertheless, despite the limitations, the examples below show that, in certain cases, it is feasible to provide an explanation for some linguistic links using archaeological and linguistic evidence.

A. Origins of the word *dziegieć*. The linguistic evidence demonstrates that *dziegieć* derives from the Indo-European language family which comprises the Balto-Slavic language group, the latter including a Baltic language sub-group [Mańczak 1999: 25]. Belonging to this sub-group are East Baltic languages which comprise Lithuanian; in Lithuanian, the word *degùtas* is used to designate wood tar [Šlapelio 1940: 45; Brückner 1974: 109; Bańkowski 2000: 324]. Combined with negative evidence for any significant migration between late antiquity and emergence of Baltic tribes, this link might point to a long tradition of wood-tar production in this part of Europe [Józwiak 2003: 234]. Similar words for wood tar appear also in the East Slavic language group: *dzjogac*' in Belarusian [Orębska-Jabłońska, Biryła 1962: 133], *djogot*' in Russian [Hessen, Stypula 1988: 183], and *d'ogot'* in Ukrainian [Bańkowski 2000: 324; Iwczenko 2003: 143]. Somewhat similar nomenclature has been also developed in West Slavic languages: *dehet* in Czech [Vydra 1952: 73; Brückner 1974: 109; Oliva 1994: 239] and *decht* in Slovakian [Stano, Buffa 1988: 68].

Inseparability of practices associated with wood-tar, pitch, and grease production is also ascertained by other linguistic examples. In the South Slavic language group, e.g. in the Bulgarian influence zone, where wood pitches are still being produced today, wood tar is referred to as *katrán* [Sławski 1987: 366], while wood tar production activities are designated with the term *pitch production* instead of the expected *katrán production*. Similar naming patterns are traceable for wood tar in many languages of the Indo-European language family. In Serbo-Croatian [Frančič 1987: 511] and Macedonian [Pianka, Topolińska, Videski 1990: 111], both of which belong to the South Slavic language group, and in Albanian [Mann 1957: 383], which is an Illyrian language, the word for wood tar is *kàtran*. A very similar word, i.e. *catrán* [Reychman 1970: 90], designates wood tar in Romanian which belongs to the Eastern Romance language group, *catrame* [Meisels 2004: 282, 471] in Italian which belongs to Western Romance language group, or *katrámi* [Jurewicz 2000] in Greek which belongs to the Hellenic branch. The interchangeable use of terms for wood tar and pitch in many different language groups, i.e. Illyrian (Albanian), Eastern Romance (Romanian), Western Romance (Italian), West Slavic (Czech, Slovakian), South Slavic (Macedonian), and East Slavic (Russian), may indicate that the two substances were equally meaningful, which once again supports the idea formulated in Chapter I.1. that wood-tar production and pitch production were inseparable in prehistory.

Related words for wood tar exist also in Turkish (*katran*) which belongs to the Oguz subgroup of Turkic languages, whose sub-group is included in the Altaic languages of the Ural-Altaic linguistic family [Antonowicz-Bauer, Dubiński 2005: 304]. A noteworthy fact is that the Turkish language does not distinguish between wood tar [Antonowicz-Bauer, Dubiński 2005: 304] and pitch [Antonowicz-Bauer, Dubiński 2005: 413]. Hungarian representing the Ugric language group, or a branch of the Ural-Altaic linguistic family, uses the word *kátrány* to denote wood tar [Reychman 1980: 563], whereas Arabic (Southwest Semitic group), which belongs to the Semitic language family, uses the word *qatrānum* [Danecki, Kozłowska 2001].

B. Analysis of the symbolic dimension of words used to denote wood tar applications. The existence of the close relationship between wood tar and fire-related activities (kindling fire, keep fire burning, or firing) is evidenced by the Lithuanian (Baltic language subgroup) word *dègti* which exhibits some sound correspondence with *degùtas* [Šlapelio 1940: 45; Brückner 1974: 109; Bańkowski 2000: 324]. Accordingly, it does not seem unreasonable to advance the hypothesis that wood-tar production, pitch production, and other activities, which inherently involve fire to process wood and bark, were originally treated collectively as a group of certain activities rather than individually. Moreover, the relationship appears to have existed between the wood-tar production process and fire, the latter being recognized in Indo-European symbolic environment as a purifying and basically transforming agent. A raw material (wood or bark) ceases to exist as a material and becomes processed or „transformed" into wood pitch [Kopaliński 1990: 136; Kempiński 1993: 315].

The linguistic evidence proves a strong relationship existing between wood tar and birch bark, and ceramic decorative art. The Indo-European nomenclature perceives **peukā* or a pine as a tar-providing tree [Gamkrelidze, Ivanov 1984: 631]. Also, there is a close relationship between the word pine and the lexeme **peik^*, the latter meaning 'painting, dying, or writing'. These observations prove that prehistoric producers were using pine tars as black plant-based paint for decorative purposes. This use is also confirmed by archaeology [Langer, Kośko 1992; 1999; Langer, Pietrzak 2004b; 2004c]. Once painted with organic wood-tar colorants, ceramic vessels became more attractive for their oily- and shiny-looking surfaces [Kowalski 2003: 11]. Likelihood of using wood tar for aesthetic purposes, e.g. for painting ceramics, appears to be confirmed also by a somewhat distant example of the Arabic word *qatara* which denotes the activity of 'painting, dying, or covering with wood tar' and echoes the word *qatrānum* meaning wood tar [Danecki, Kozłowska 2001].

There is also a similarly sounding Hebrew (Northwestern Semitic language) word *qətār* meaning „incense" [Marek 1929: 194]. As such, the word points to the possibility that, for its purifying, healing, and magic properties, including specifically apotropaic powers, wood tar may have been used for incense. Both the ethnographic [Pierzchała 1896: 337; Moszyński 1967: 315-316; Wrębiak 1972: 35] and archaeological record [Kośko,Langer 1997; 2000; Gumiński 1989: 164] confirm the use of wood tar in medicine or practices designed to repel evil or protect against spells, demons, and spirits of the dead [Gryglewicz, Łukaszyk, Sułkowski 1985: 838]. The incense was also burnt during funeral rites to ease the soul's passage to the afterworld [Kopaliński 1990: 135-136].

There was also **leipo* or 'modelling, attaching, affixing, and bedaubing with grease', with its related lexeme **loipos* meaning 'appropriate, suitable' or 'decorative', included among essential activities that bore aesthetic value and were reflected in the Indo-European language [Sławski 1970: 168, 271; Mallory, Adams 1997: 528]. Both words describe activities of a potter lubricating vessel bodies with tars and ornamenting vessel surfaces with coloured motifs or applied bark or bast elements. Both lubricating and ornamenting should be perceived as reflecting the concept of durability and life inherent in the creation process. Characterizing wood tar, viscosity and smoothness used to form an indissoluble whole among aesthetically important qualities. Rubbing greasy substances into vessel bodies can be related to conservation of earliest leather containers [Kowalski 2003: 12].

Identification of bark with leather and bark containers with leather containers is clear in traditions of many European communities whose languages are rooted in the older Nostratic speech community that predated the earliest agrarian cultures [Bomhard, Kerns 1994]. In pre-ceramic times, containers made from bark or leather might have been deemed capable of continuously increasing their volume as is the case for bark and skin covering trees and animals, respectively. This idea was probably behind later ornamenting ceramic vessels with applied bark elements or covering vessel bodies with tars [Langer, Kośko 1999; Langer, Pietrzak 2000; 2004a]. However, it should not escape attention that, so prepared, the ceramic containers were perceived by users as exhibiting also high aesthetic value ('beautiful and attractive'). What immediately presents itself is the comparison between an ornamented, painted, or bark-covered surface of ceramic vessels and tattooed or painted skin (verbal communication by Kowalski, for which we are thankful). In this context, **korā*, or the Indo-European word for bark, was a synonym for protective coating, covering, or skin [Bomhard, Kerns 1994]. Birch bark was highly appreciated particularly for aesthetic qualities attributable to its light colour identified with glare, shine or beauty.

This specific connotation can be exemplified by such Indo-European words as **bherəgos* and **bherəgā* meaning a birch or birch species, respectively, or by their Nostratic equivalents ***bar-/ **bər-* meaning 'to shine/glitter' [Bomhard, Kerns 1994]. Some scholars believe that the colour white was the reason why many Indo-European traditions perceive birch bark as possessing strong ritual and magic properties, and a birch tree as symbolizing magic purity [Kowalski 2003: 12-14]. A birch tree was also deemed to protect against evil powers and witchcraft [Kopaliński 1990: 35]. Cutting or tearing bark, and subsequent attaching bark with wood tar to ceramic vessels, should be interpreted as activities to add durability, impermeableness, and shine to ceramic containers. Based on Germanic derivatives of **leub(h)-ō*, Kowalski points to the relationship existing between birch trees, birch bark, and substances contained on the one hand, and healing magic and preparation of medicinal extracts on the other [Kowalski 2003: 15]. This relationship is confirmed by archaeological finds datable to the Neolithic or early Bronze Age [Baczyńska, Lityńska-Zając 2005].

Many linguistically meaningful names in Slavic languages confirm the use of ceramic vessels with decorative birch bark elements applied upon the surface. These names prove that birch bark and wood tar were used both to repair damaged ceramic vessels, and to fix birch bark upon the vessel surface [Langer, Rola 1997: 35-40; Vogt 1949: 50]. These practices are strongly related to the 'vessel healing' process by which vessels were consolidated, i.e. repaired (verbal communication by, for which we are thankful); they also reflect healing properties of birch tar otherwise used to heal people and animals [Moszyński 1967: 315-316; Wrębiak 1971: 35]. The Russian language (East Slavic language group) provides similar and indirect linguistic evidence for a tradition of using wood tar to seal or decorate ceramic vessels [Kowalski 2003: 16].

A noteworthy fact is that wood tar was also used for wheeled transportation to eliminate friction of wooden parts of wagons. This specific application is confirmed by relevant words occurring in Czech, Serbo-Croatian, or Macedonian which, in addition to already mentioned terms for wood tar, utilize the popular name *kolomaz*, or wheel grease [Vydra 1952: 73; Frančič 1987: 511; Pianka, Topolińska, Videski 1990: 111], that is likely to describe one of original uses of wood tar as a lubricant. This information is further supported by the ethnographic record for territories with a long tradition of wood-tar production and trade [Wrębiak 1971; Brylak-Załuska 1983].

Yet another type of finds, which deserves a mention here, is wood tar lumps discovered in the barrow graves of the Proto-Pit Grave and Catacomb cultures [Kośko, Langer 1986]. Wood tar remains are usually found near a head or on a calotte of the dead. Originally, they formed a layer of a plastic binder on the head of a deceased warrior, applied most probably during the funeral rite of attaching hair or scalps back onto the warrior's head [Vazmitina *et al.* 1960: 62, Fig. 46; Klejn 1961; Kośko, Langer 1986; Otroščenko, Pustovalov 1991]. According to some scholars, including Klejn, this practice was to provide the dead with all elements required for his 'afterlife' [1961: 105-109]. However, in his interpretation efforts, Klejn transplanted ritual practices of North American Indians directly into a specific prehistoric situation, which might raise some doubts. North American Indians believed a scalp to have been one of a warrior's main attributes that expressed his strength and liveliness. Therefore, if scalped in battle, warriors were prevented from living in the afterworld. Following the presented concept, it was essential for the dead to have total 'completeness' in afterlife ensured; the role of hair was thus vital [Ślusarska-Michalik 2005: 153]. As far as mythological symbolism is concerned, hair was identified with vegetation on the one hand and with the death on the other hand. Noteworthy are also mythological references to immortality and to a source of life-giving and resurgent power symbolized by long and abundant hair [Kempiński 1993: 454-455]. In many cultures, hair was regarded as a seat of the soul and life, and as embodiment of youth [Kopaliński 1990: 469-473]. The importance of hair transpires from written records evidencing funeral rites which involved the cutting and burning off the hair as a sign of mourning and distress after the death of loved ones. Therefore, it is reasonable to assume that the act of covering the head of the dead with wood tar to reattach the scalp might have represented a healing act actually meant to restore vital forces and ensure immortality [Ślusarska-Michalik 2005: 154].

Thus information about tar remains identified in Catacomb culture graves might indicate that wood tar was also a material to make death masks covering the face of the deceased [Kruc *et al.* 1991: 51-53; Pustovalov 2000: 98, 109, Fig. 5]. As far reconstructing skulls with wood tar (death masks) is concerned, an intended healing effect of this post-mortem practice was essential. Sealing eyeholes as well as the frontonasal suture, mandible, and temporal bone areas might have been meant to reflect progressive stages of dying with successive deterioration of particular senses, i.e. sight, smell (breath), speech, and hearing. It is particularly the filling of eyeholes with tar that may be interpreted as an act of depriving the deceased of ruling or controlling powers since eyes were perceived as order-givers or dominance-imposers. For Indo-Europeans, eyes symbolized a source of knowledge and the act of ‘seeing or knowing’: **woid-/ *weid-/ *wid-*. By contrast, depriving anyone of eyesight (e.g. by sealing eyes) caused his or her soul to journey to the afterworld and made the deceased harmless [Kempiński 1993: 312-313]. In many cultures breath epitomises the soul, vital powers as well as immortality and assimilation of spiritual powers. Stopping breathing leads to death and allows passage into the afterlife [Kopaliński 1990: 262]. A mouth represents the source of life, creative powers, and the base of the soul. At the same time, the mouth also symbolises the passage from life to death and a border between internal life and external life, and between earthly life and the world beyond. If sealed, the mouth illustrates an obligation to remain silent, and death [Kopaliński 1990: 441-442]. Needless to say that what we are dealing here with is a well-known model of a rite of passage: a man departs this world to live in the afterworld. The above-described find (funeral mask made of wood tar) was to ease the deceased into the afterworld, and, at the same time, might have protected the living from the dead.

II. TECHNO-ARCHAEOLOGICAL FUNDAMENTALS OF WOOD-TAR STUDIES

Understanding the chemical structure of wood and bark, which were the chief raw materials in prehistoric tar production, and more generally issues of forestry and chemical wood technology, is essential for the purposes of this study. Knowledge of the chemical composition of these raw materials is important for the interpretation of archaeological preparations subjected to physico-chemical analyses (identification of the initial material, that is, wood and bark species) (Chapter V). Substances referred to as 'molecular markers' characterized by a carbon skeletal structure can be isolated and identified in laboratory research [Brown and others 1993; Evershed 1993; Loy 1993; Briggs, Eglinton 1994: 910]. On these grounds, organic substances may be identified and attributed to certain plants, including wood pitch preserved in a fossil record on archaeological sites [Philp, Oung 1988; Evershed and others 1997; Petit-Dominguez, Martinez-Magato 2000; Martin and others 2001; Regert and others 2003].

Based on this data, it is also possible to conclude on the raw material preferences of prehistoric societies for the purposes of the production as well as use of wood tar. The following discussion of raw material in terms of properties and chemical composition of wood and bark is based on general data available in the literature on the subject.

II.1. RAW MATERIAL USED IN WOOD-TAR PRODUCTION

The chemical composition of wood and bark, and especially of birch and pine as the main raw material used in prehistoric tar-making, has long generated interest in terms of properties and pitch-making potential. Understanding the general chemical composition with emphasis on the extractible substances in these materials, especially the characteristic ones, is essential as they can be used to identify archaeological materials of organic origin, including wood tar.

Birch wood is characterized by a highly uniform anatomical structure, revealing certain differences with regard to macroscopic characteristics of particular types of wood. It is white in colour, in some cases yellowish (silver birch – *Betula pendula Roth.*) or yellowish-red (downy birch – *Betula pubescens Ehrh.*) [Galewski, Korzeniowski 1958: 50-54; Milewski 1965: 88; Skrzypek 1972: 26]. Its natural durability is relatively low; subjected to atmospheric factors, especially if it has not been debarked, it decays completely within five years and in a water-logged environment within about 40 years [Prosiński 1984].

Pinewood is easily worked owing to the resin in it, is highly durable and is resistant to moderate humidity in the air. Its colour ranges from pinkish to red-brown. The most common species in Europe is ordinary pine (*Pinus sylvestris L.*). The commonness of this wood and its technical properties made it useful, like birch wood, in many branches of the prehistoric economy, e.g., fuel and raw material for thermal decomposition. Pine wood is characterized by average natural durability [Galewski, Korzeniowski 1958: 34-41; Milewski 1965: 84; Skrzypek 1972: 23].

Depending on the species, origin, age of the tree and climatic zone and habitat, particular woods can be differentiated considerably in terms of properties, as well as chemical substances. The organic substances in wood can be divided into two groups: high-molecular components building cell walls, referred to as structural substances, and low-molecular ones filling cell walls, referred to as non-structural or minor constituents. Structural components make up about 95 per cent of the wood structure, whereas non-structural ones are represented usually in small amounts. In the case of some wood species, the number of the latter can rise up to about 40 per cent [Prosiński 1984: 127; Surmiński 2000: 31; Kokociński 2002: 52-58].

The wood substance is made up of lignin and cellulose, which contain structures of a fibrous nature. This fibrous structure of cellulose is linked to the molecular structure, as well as the supra-molecular one which leads to the areas of considerable systematic order being formed [Nikitin 1955: 144-148; Surmiński 1978: 113-118; Krzysik 1978: 117-120].

Chemical wood components referred to as structural substances (lignin, cellulose, hemicellulose) are interconnected by a variety of chemical bonds, e.g. oxygen bridges, ester bonds or short tricarbon chains, as well as interaction between molecules. Non-structural substances are bonded less strongly than the structural ones. Often there are no chemical bonds or molecular interaction between these substances, hence the ease with which they can be distinguished. Wood is a complex chemical conglomerate, meaning it is a material in which there are different chemical and physical bonds or none at all between the components [Browning 1963: 103-142]. Wood tissue on the other hand is composed mainly of dead cells of diverse type, while the structural substances forming it belong to the carbohydrate–lignin complex. Most components of this complex are characterized by high molecularity. Carbohydrate compounds, known as holocellulose (cellulose, hemicellulose), constitute 68 – 75 per cent of wood mass, whereas lignin, that is, the aromatic substance, accounts for 21 – 28 per cent of the wood mass [Surmiński 1978: 114; Prosiński 1984: 51; Kokociński 2002: 52-58].

Cellulose, which is a poly-saccharide built of ß-d-glucose remainders, makes 41 – 50 per cent of birch wood [Surmiński 1978: 115, Pl. I; Prosiński 1984: 56, Pl. 24] and about 54 per cent of pine wood [Galewski, Korzeniowski 1958: 36]. Its linear homopolymer structure gives wood cell walls mechanical strength and anisotropic properties [Nikitin 1955: 138-148; Prosiński 1984: 52; Surmiński 1989: 12]. Cellulose is accompanied by carbohydrates from the poly-saccharide group, called hemicellulose; there is less hemicellulose in coniferous wood than in deciduous wood (pine 21%; birch 28%). Their composition includes hexosans, pentosans and polyuronides. Polysaccharides composed of pentose (pentacarbon sugar radicals) are called pentosans; their content in birch wood is 26 – 32 per cent [Nikitin 1955: 272-283; Krzysik 1978: 121; Kin 1980; Prosiński 1984: 249], in pine wood, it is about 13 per cent. Xylan is a pentosan occurring in considerable quantities in deciduous trees (22 – 25%) and in lesser amounts in coniferous trees (10 – 12 %); it is made up of ß-d-xylopyranose remainders [Nikitin 1955: 282; Kin 1980: 18-20; Prosiński 1984: 249-254; Winandy, Green 2001; Kokociński 2002: 52-58].

Araban is another common pentosan, its main chain being made up of α-I-arabinose remainders [Surmiński 1978: 116; Prosiński 1984: 254; Curling, Clausen, Winandy 2002: 34]. Coniferous tree wood has less of it (2%), compared to deciduous tree wood (4%). On the other hand, hexosan, estimated content in birch wood being about 5 per cent and in pine wood about 13 per cent, is a polysaccharide composed of hexoses (hexacarbon sugar radicals). The most commonly encountered substances from this group include mannan, galactan, fructan and glucan [Surmiński 1970: 310; Krzysik 1978: 121; Kin 1980: 18-39; Prosiński 1984: 255-259]. On hydrolysis these substances join with cellulose, hence their designation as cellulosans. The remaining part of hemicelluloses in the form of galactans make up polyuronides; the chief role here is played by polyuronic acid bonded with lignin.

Pectin substances, plant gums and mucilages from phloem fibre, all more easily hydrolyzed (compared to the above), also belong to the hemicellulose group [Nikitin 1955: 296-302; Krzysik 1978: 120; Surmiński 1996: 29; 2000: 69]. The chemical structure of pectin substances departs from the typical carbohydrate in that it contains more carboxylic and methoxylic groups with their main component, which is polygalacturonic acids. The methyl ester of this acid is called pectic acid [Surmiński 2000: 68]. Lignin is made of pectin substances, demonstrating an average content of 3 per cent in wood, which is connected with a drop in their amount in wood at the end of the vegetation period. Polyglucuronic acid is the basic component of wood gums and plant mucilages, forming viscous drippings on the bark of diverse wood species [Surmiński 2000: 69].

Non-fibrous high-molecular lignin is, unlike cellulose, a heteropolymer of three-dimensional structure with a two-part phenylpropan arrangement. Direct bonds between lignin and cellulose are believed not to exist, while lignin is bonded chemically with the hemicelluloses in the wood. Lignin contains about 20 per cent of aromatic compounds and methoxyl groups OCH_3, which are changed into methyl alcohol under high temperatures in the process of wood thermolysis [Nikitin 1955: 103; Krzysik 1978: 122].

The structure of lignin of coniferous and deciduous tree species differs. Lignin in coniferous trees is mainly built of aromatic guaiacyl radicals, that of deciduous trees of aromatic syringyl radicals [Nikitin 1955: 101-123; Kin 1971: 11-47; Surmiński 2000: 72]. Lignin also contains aliphatic remainders: glicerine, hydroxyaldehyde and hydroxy-ketone ones. Its content in birch wood is smaller than in pine wood, 20 per cent and 26 per cent respectively [Galewski, Korzeniowski 1958: 36; Prosiński 1984: 269].

Minor constituents of wood (non-structural substances) are for the most part low-molecular compounds relatively easily soluble in organic solvents and sometimes also in water. For this reason they are referred to often as extractible substances. Both the chemical structure of these substances and their content in wood of different species varies [Hejnowicz 1973: 22-23; Surmiński 2000: 77-95]. Wood of deciduous tree species has less non-structural substances compared to coniferous species secreting resin, which is a mixture of aromatic terpenes built of isoprene fragments, resin acids, fatty acids and their esters [Prosiński 1984: 338; Pollard, Heron 1996: 241]. The resin substance content falls most often in the 3 – – 10 per cent range. Among the terpene compounds making up resin of deciduous tree species the more important ones are bicyclic terpenes (α-pinen, δ-3 and δ-4 karen and borneol), along with the monocyclic (limonene and sylvestrene). Sesquiterpenes are formed when three isoprene molecules are bonded [Nikitin 1955: 336-352; Pollard, Heron 1996: 242; Elias, Simoneit, Cardoso 1997: 305-309; Surmiński 2000: 79-84]. Non-volatile primitive resin acids (1- and d-pimarine acids) and secondary ones (abietene acid) occur together with them.

Fatty substances occur in major proportions in the wood of some deciduous trees, like birch and linden, whereas the bark of some trees, especially the young shoots (willow, for example), contains plant waxes. The principal fatty acids in wood, beside saturated palmitic acid, include unsaturated acids like oleic and linolenic as well as linolic acid which occurs in large quantities [Prosiński 1957]. A substantial role is played by polyphenols occurring in wood and bark of many tree species. These substances include mainly hydrolyzing and condensed tannins and different kinds of colorants and glycosides (Chapter II.3.1).

Tannins are antiseptic in character, protecting against bacteria and fungi. The bactericidal function of tannins is confirmed by insoluble compounds formed of tannins bonding with protein substances. Tannins, like tannin acid, for example, inhibit the growth of protein-based bacteria, proving the medicinal properties of these substances [Nikitin 1955: 375; Surmiński 2000: 86-90]. Also present in wood in small quantities (0.2 – 1.0 %) are mineral substances occurring in the form of silica and oxalates.

II.1.2. CHEMICAL STRUCTURE OF BARK

The chemical structure of bark differs from that of wood both quantitatively and qualitatively. Beside the principal structural substances like lignin, cellulose and hemicelluloses, bark contains extractible substances, of which some are specific of a given species or related group of species [Blaim 1973: 13-20; Surmiński 1996: 39-51; Antkowiak 1997: 13].

One of the principal chemical constituents of the bark of deciduous trees is lignin, which makes up 25 – 30 per cent and so exceeds the amounts noted for the wood of the species (20 – 22 %). In pine bark, lignin presence is estimated at more than 50 per cent [Surmiński 1970; Filipek, Drogosz 1977]. The chemical structure of lignin in bark differs from that of its counterpart in wood; this is expressed by a different quantitative share of phenol groups, like guaiacyl and syringyl ones[Andersson and others 1973: 191; Surmiński 1996: 31; 2000: 72]. Bark lignin is also distinguished by strong bonding with polyphenols of the likes of bi-, tri- and oligo-flavonols, products of their decomposition (protocatechuic, catechuic and vanillin acids, and phlobaphens).

Bark lignin bonds with suberine, a substance specific of bark [Surmiński, Dziurzyński 1976: 228; Ekman 1983: 205-211; Fengel, Wegener 1989; Surmiński 1996: 34-38]. Suberine is a biopolyester of suberine acids, constituting a complex mixture of aliphatic acids C_{18}–C_{22} uni- and dicarboxylic, saturated and unsaturated, oxy- and epoxyacids, which occur partly in esterified form [Ekman 1983: 205; Kislitsyn 1994; Moire and others 1999: 1142].

Suberine is made up of a number of acids, the most important of which are:

- phenolic acid: $C_{21}H_{42}(OH)COOH$,
- suberine acid: $COOH(CH_2)_6COOH$,
- phloinic acid: $COOH(CH_2)_7(CHOH)_2(CH_2)_7COOH$,
- phloinolic acid: $CH_2OH(CH_2)_7(CHOH)_2(CH_2)_7COOH$,
- phloionic acid: $HOCH2(CH_2)_7(CHOH)_2(CH_2)_7COOH$,
- phloionolic acid: $HOOC(CH_2)_7(CHOH)_2(CH_2)_7COOH$.

Similarly as in the case of lignin, phenol acids in suberine testify to its aromatic nature [Surmiński, Dziurzyński 1976: 228]. Birch bark contains sizable amounts of suberine (up to 38 %), tannins, colorants, resin acids, fatty substances, waxes and other substances of a phenol character [Ekman 1983: 209; Pollard, Heron 1996: 255-257]. Suberine content in pine bark is much smaller, only about 3 per cent [Prosiński 1984: 63, Tab. 33].

Cellulose is another important structural substance in wood bark. Its content in birch bark reaches about 20 per cent, in pine bark about 30 per cent. Bark is also characterized by a smaller content, compared to wood, of hemicelluloses which occur in the form of hexosans (glycomannan) and pentosans (araban) [Surmiński 1970; Prosiński 1984].

Extractible substances in birch bark are represented among others by glycosides occurring in the form of betulin, betuloside and glyco-vanillic aldehide, which is present mainly in the bark of young birches [Surmiński, Dziurzyński 1976: 227--231; Cole, Bentley, Hua 1991: 265-268; Surmiński 1996: 45-46; 2000: 92-93].

Depending on growth conditions, age, season and even habitat, the outer bark of birch contains 10 – 30 per cent betulinol responsible for its white colouring and other related triterpenes [Jääskeläinen 1981: 599-603; Cole and others 1991: 265--268; Surmiński and others 1995: 158;] with antiseptic properties which determine the medicinal properties of birch tar [Berendes 1902: 94; Hayek and others 1989: 2237; Surmiński 1996: 55; Antkowiak 1998: 107, 111]. The inner bark contains less than 2 per cent betulinol, whereas there are only trace quantities of the substance in the wood. The bark of different species of birch growing in Eurasia as well as North America contains, beside betulinol, a whole series of triterpene compounds. Derivatives of lupanon, such as betulinic, ursolic and allobetulinic acids, are the main ones among these.

Triterpene substances are for the most part pentacyclic compounds occurring mainly in the form of alcohols, hydroxyacids and ketones. Their content in birch bark falls in the range of 38 – 40 per cent. Triterpenes are present also, although in smaller quantities, in the bark of other tree species, like beech, hazel and alder [Ludwiczak, Szczawińska 1965; Surmiński 1996: 50]. Substantial betulinol content is attested among others for the outer core of *Betula pendula*. Betulinol is also characterized by considerable thermal stability (melting point – 261 °C); it is to be expected then that its chemical structure remains unchanged during pyrolysis [Hayek and others 1989: 2229; Kislitsyn 1994]. The systematic name of betulinol is lup-20(29)-ene-3.28-diol and its molecular weight is 442.7. The substance is soluble in pyridine and tetrahydrofuran, and only poorly soluble in dichloromethane and chloroform. It is entirely insoluble in water and petroleum benzin.

Birch bark is characterized by particularly good insulation properties, which made it extremely useful to the prehistoric societies of Europe [Clark 1957: 249]. It also contains mineral substances (3 – 5%), mainly in the form of silica and oxalates. Together, these substances determine the high natural durability of birch bark.

Polyphenols, including phenol hydroxyacids, phlobaphens, tannins and glycosides, are characteristic constituents of birch bark. Among the glycosides one should mention coniferin, which is typical of pine [Surmiński 2000: 93]. The most common colorants in birch bark are flavons, represented foremost by quercetin and its derivatives and catechin, which is polymerized together with leukocyans to form condensed tannins. Birch bark also contains considerable amounts of resin and wax substances which become oxidized leading in effect to the resins containing secondary resin acids beside the primary ones, as well as a number of products of the oxidizing of terpene compounds. The barks contains also much larger amounts of mineral substances compared to wood [Surmiński 1970: 325; 1996: 39-51; Antkowiak 1997: 12-19].

In prehistoric Europe birch was one of the most important deciduous woods. It was quite common in the area under discussion, making way only for coniferous complexes with pine and deciduous oak and beech forests. Birch wood, like pine wood, was used as fuel because of the highly caloric fatty and terpene substances in it [Milewski 1965: 84; Surmiński 1996]. It was also used in cooperage, cartwrighting and production of charcoal for the needs of primitive metallurgy. The considerable natural durability of birch bark made it a material of choice for insulating wooden architecture. Foremost, however, the wood and bark of both birch and pine were used to produce wood tar, which had extensive applications, among others, as an antiseptic, binder and colorant (Chapter II.5).

II.2. TAR MAKING PROCEDURES

II.2.1. THE ARCHAEOLOGICAL PERSPECTIVE

A reconstruction of the tar making process is possible on the grounds of archaeologically recorded finds of lumps of the petrified product and layers of a black tarry substance adhering to the surface of vessels used in the production or secondary processing of wood tar. The physical and chemical properties of tar are dependent on a set of factors on which its production depends. The most important of these include the kind and quality of the raw material, the production method and the temperature of the process. The structure and properties of the product of wood and bark pyrolysis may be modified depending on circumstances and changes introduced in each of these factors.

Data on the destructive distillation of wood indicate a two-phase process composed of chemical changes of the raw material caused by the action of high temperatures and the division of products of the distillation. Depending on the degree of control exercised over temperature growth the process of pyrolysis could have proceeded in a single stage, without fractionating volatile substances, or it could have resulted in the creation of a number of fractions with different physical properties and chemical composition (Chapter I.1). Always, however, there was a volatile fraction and remains (e.g. charcoal) [Langer 1989: 14]. The separation of the distillate from the remains is dependent mainly, as said above, on the temperature. The same compounds can be obtained in the form of a distillate when the temperature is appropriately high or as a pitch substance when the temperature is lower. Therefore, it was possible to obtain pitch instead of a gaseous substance in a process resembling the rendering of fat. The product obtained with this method was contaminated with remains of the raw material and less homogeneous. Technological simplicity is an advantage in the case of primitive apparatus (one vessel) and low efficiency in controlling the temperature. Thus, wood tar should be understood as the distillate, as well as a product of the above described simplified technology (Chapter I.1). The difference between the two is easy to observe owing to the possibility of the presence of remains of unprocessed raw material.

Considering the long time span from the Neolithic to the Bronze Age, there are relatively few known unquestioned remains of production features and vessels associated with wood-tar making by prehistoric communities. This situation may be due to researchers frequently overlooking these kind of archaeological sources during fieldwork as unimportant from a research point of view or improperly interpreting the finds as, for example, food remains. Another possibility is that ‘tar workshops’ were usually situated by prehistoric communities near forests and at a distance from habitation settlements, making them easy to miss in the excavation record which is concentrated foremost on the economic and dwelling zones. The distance from human settlements is one reason why such features are found only incidentally. Despite this there has been enough archaeological research on tar-making features to indicate that different technologies were used for tar production in prehistoric Europe.

Archaeologically confirmed wood tar finds indicate that one of the most common ways of making tar, in Europe as well as in the Polish lands, was ‘melting’ in a single vessel (Fig. 1) [Kośko, Langer 1986: 587-600; 1997: 25-28; Chachlikowski 1994: 161; Pollard, Heron 1996: 257-269]. The process carried out in a single vessel, in temperatures of 220 – 280 °C, gave a certain amount of the heavy fraction, the tarry distillate, with considerable amounts of unprocessed raw material (wood or bark). Heavier tar fractions were possible to obtain thanks to the gradual evaporation of easily volatile pitch substances in high temperatures. The product obtained in this way was characterized by short usability as it petrified rapidly.

None of the recorded finds from the given time period from the Dnieper and Elbe interfluve can be considered with certainty as a production feature reflecting processes of tar making [compare Wojciechowski 1969: 29-39; 1972: 265-276]. Instead, excavations have uncovered ceramic vessels used to make or store the

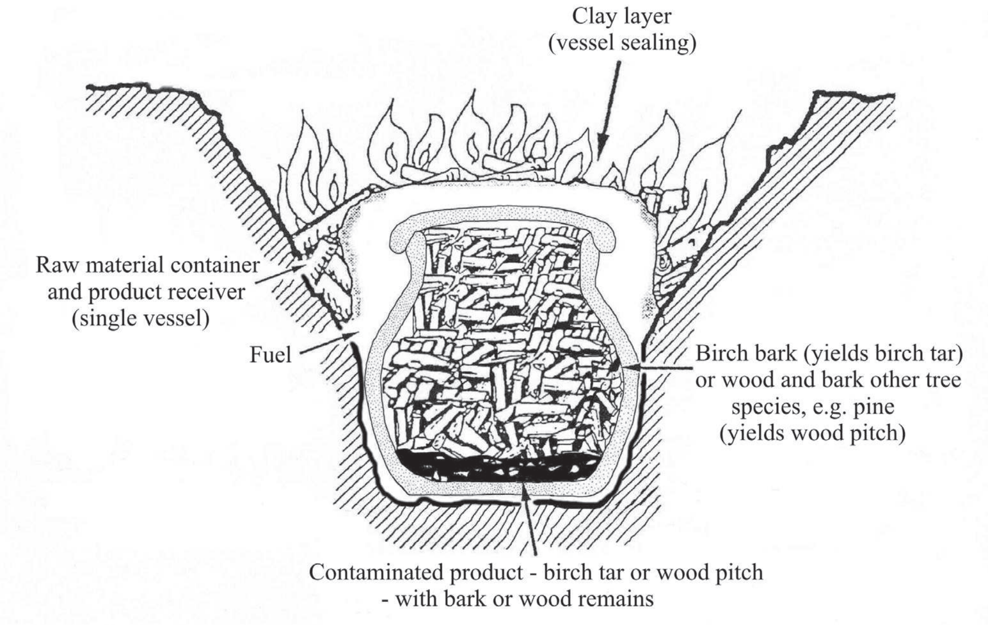


Fig. 1. Diagram of a single-chamber tar kiln

product; these are small ceramic forms about 10 cm in diameter at the base [Kośko, Langer 1986: 592; Langer 1994: 180-181]. These observations have gained in credibility in the face of the effects of experimental archaeology designed to obtain wood tar in a single-chamber kiln [Czarnowski, Neubauer, Schworer 1990: 169-173; Neubauer-Saurer 1997: 41-44]. In these experiments, ceramic vessels were filled with birch bark and covered with a flat pebble. The gap between the rim of the vessel and the pebble was sealed with clay creating a kind of production reactor, which was placed in glowing charcoal. The effectiveness of the process is determined by the tightness of the vessel, allowing no air inside, and raising the temperature to about 400 °C inside the vessel and maintaining it for some time at this level. Several experiments with this method have shown that the technology may have been used in the past despite relatively few finds of the type attested to in the archaeological record [Kośko, Langer 1986: 592; Chachlikowski 1994: 161].

A more developed and effective way of producing wood tar called for a procedure separating the remains of the raw material (wood or bark) from the final product (tar). This required an additional container to receive the product (Fig. 2) [Kośko, Langer 1997: 25-28; Langer, Pietrzak 2004a; Langer, Pietrzak 2004b]. Archaeological finds indicate that vessels with perforated bottom were used as reactive chambers [Gumiński 1989: 113, 164; Dobrzańska and others 2005; Kubica-Kabacińska and others 2005]. The tar kiln was carefully coated with clay

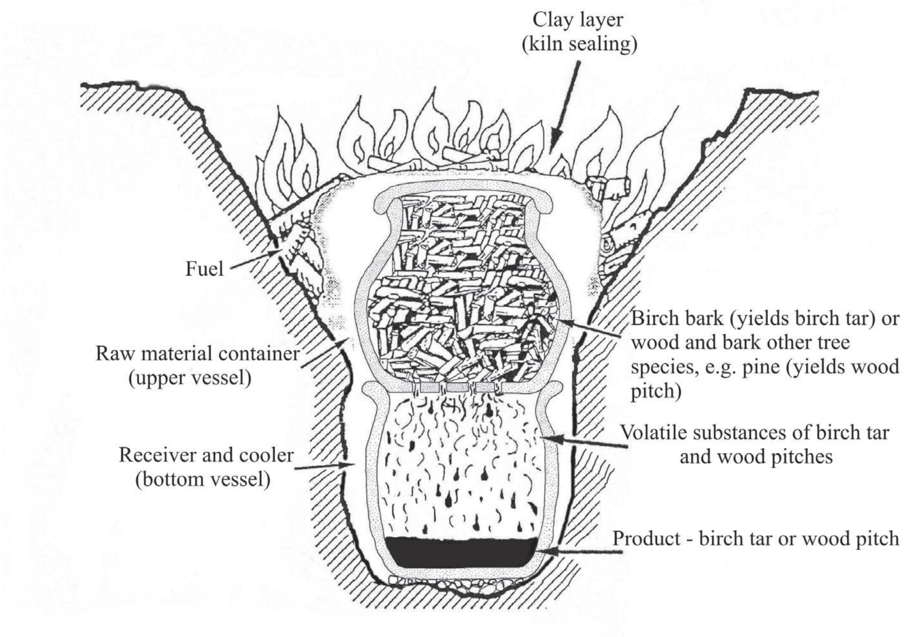


Fig. 2. Diagram of a double-chamber tar kiln

all around and placed at one third of the height of a funnel-like pit which was also lined with clay. A fire was ignited around the production site, and the wood and bark released, in conditions of high temperature without oxygen access, wood tar which flowed down into a container set up underneath.

Experimental distillation of wood and bark by various researchers has confirmed these observations [Szafrański 1949–1950; Czarnowski, Neubauer, Schworer 1990; Kurzweil, Todtenhaupt 1991]. The *büt – bär – büt* method, which calls for descending distillation (*destillatio per descensum*) [Kurzweil, Todtenhaupt 1992], produces a distilled tarry product that is not polluted, as technoarchaeological research has shown, with pieces of unprocessed wood or bark [Langer 1994: 180-181].

Remains of tar kilns from the Bronze Age attest to an important technological-production breakthrough, which was based on a tripartite reactor (Fig. 3) [Langer, Pietrzak, Cichocka 2004]. In similarity to the double-chamber tar kiln, a vessel was used to receive the product and another vessel was placed as an intermediary container between the reactor chamber and the proper receptacle. This kind of tar kiln with a vessel as a kind of ‘filter’ purifying the pitch substance flowing into the receptacle below was supposed to guarantee a very pure (without any remains of the raw material) product of the destructive distillation of wood and tar [Langer, Pietrzak, Cichocka 2004].

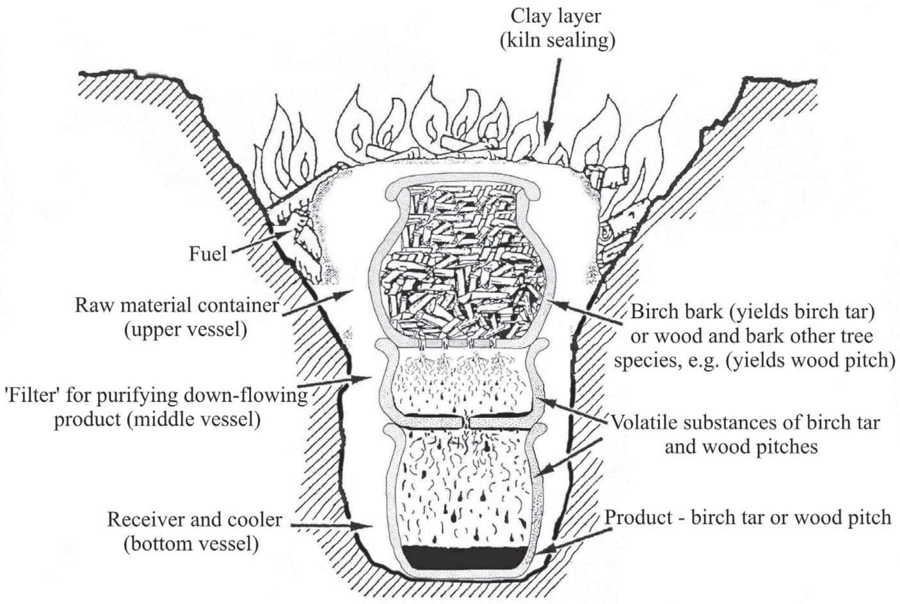


Fig. 3. Diagram of a three-chamber tar kiln

In later times, tar was also produced in piles, which should be associated with metallurgical activities using charcoal exclusively for smelting ore [Bielenin 1992].

The relative rareness of tar among archaeological finds does not help in understanding the method of its production, but its broad application and relatively simple technology should be reflected in an abundance of related artefacts. At the same time there should be many more production sites known. The evidence to date indicates that the methods and equipment used for tar production have not changed significantly from antiquity into the modern age.

General conclusions concerning the dry distillation of wood and bark, formed on the grounds of currently available information, indicate that a tarry fraction was the primary intended product of primitive tar-making, differentiated only by the share of contaminants and preservatives. The substance is observed in the archaeological record as petrified post-production remains (of the product or technological residues) characterized by extensive contamination with fragments of the raw material. It has already been noted above that there exist containers for secondary processing of tar or its storing (along with remains of the raw material) and even distinct lumps [Kośko, Langer 1986: 592; Szmyt 1992: 77; Chelidonio 1997: 45-50].

Archaeological evidence for the theory that wood tar was produced by destructive distillation of wood and bark in ceramic reactors is recorded in excavations in the form of shards of ceramic vessels used in this production [Kośko, Langer 1986; Langer, Pietrzak, Cichocka 2004]. These are as a rule fragments of ceramic containers with traces of a dark pitch substance, mostly on the inside surface and mostly in the bottom parts. These vessels may have been used to store tar or for secondary processing of tar [Weiner 1991: 15-19]. There are also examples of ceramic containers with a perforated bottom, which can be associated indisputably with tar production [Langer, Pietrzak, Cichocka 2004]. It should be emphasized, however, that production vessels discovered in an appropriate archaeological context would constitute the only form of indisputable evidence in this matter. Relevant to Paleolithic and Mesolithic finds of tar remains, one should ask whether dry distillation of wood and tar is possible without a ceramic reactor [Mania, Toepfer 1973: 119-120, Pl. 11; Larsson 1983: 75-76; Nuzhnyi 1990: 114; Sulgostowska 1991–1992: 45-49; 1997: 19-23; Aveling, Heron, Larsson 1996; 1997; Aveling, Heron 1998; 1999]. Certain researchers are of the opinion that tar from the Neolithic and Bronze Age was produced just like its Paleolithic and Mesolithic counterparts without any difficulties or restrictions [Weiner 1988: 329-334; Czarnowski, Neubauer 1991: 11-13]. One should assume therefore the possibility of a tar-making technology without the use of vessels.

This purely hypothetical assumption is supported by the results of experimental archaeology [Weiner 1991: 15-19; Osipowicz 2004: 54-59]. A pit in the ground was filled with stones fired red-hot and birch bark. Tightness was achieved by laying successive layers of red-hot pebbles until the bark was covered completely. Stones and sand mixed with clay and grass tightened the sealing of the installation. Pyrolysis of birch bark proceeded in much the same way as inside a ceramic container, but the quality of the tar was not as high as when using a ceramic reactor. It is possible that ancient farmers and pastoralists may have had sufficient contacts to learn this ancient technology of tar-making and to consider it as more effective. In effect, despite extensive archaeological excavations, we are still faced with very little available data on methods of tar production.

It is impossible to establish at the present state of research whether there existed a single technological formula in the basins of the Dnieper and Elbe, but it does not seem very likely that there was one. Specific information on how tar was produced is supplied by the earliest tar samples. A better understanding of the technological processes was the result of archaeological experiments which recreated the production cycle peculiar to a particular technique. An analysis from this angle should help in straightening out the chronology of discovered organic substances and tracing their mutual relations. It can also help to some extent in determining when tar started to be produced on a bigger scale.

To sum up, it can be said that prehistoric tar makers in Europe of the period in question very probably used different methods from the simplest one, which used either one ceramic vessel or none, to more elaborate ones based on double- or triple-chamber kilns. Some of these procedures were based on local traditions of tar-making, whereas others could have been borrowed from other regions of Europe. Developments in this field were presumably the effect of contacts with other parts of Europe, which escalated especially in the first half of the 4th millennium BC. This intensification of contacts is manifested by a greater number of finds from the area in question compared to other periods.

Archaeological finds from the region in question from the 6th–2nd millennium BC indicate that prehistoric tar-makers were well aware of the utilitarian properties of the available raw materials and the processing technology. Knowledge of the temperature of decomposition, antiseptic properties and considerable natural durability of wood and bark was internalized through practice. Judging by the quality of ready products, producers were capable of evaluating the suitability of raw materials for pyrolysis, either to obtain the final product or to prepare material for further processing through the addition of various substances (Chapter II.4). An analysis of samples of prehistoric tar from the Dnieper and Elbe interfluve in terms of technological procedures applied for their production has shown that all the basic ways of processing wood and bark were used [Kośko, Langer 1986: 587-600; Langer 1989: 14; Czarnowski, Neubauer 1991: 11-13; Weiner 1991: 15-19; Langer, Pietrzak, Cichocka 2004].

II.2.2. THE TECHNOLOGICAL AND CHEMICAL PERSPECTIVE

Wood and bark processing involves either mechanical treatment, which does not change the organic structure of the raw material, or chemical treatment. The latter is of greater interest from the point of view of this study. Chemical treatment results in a complete change of the physical and chemical structure of the wood. Tar is obtained in just such a process. Destructive distillation or wood pyrolysis as the process is called, otherwise known as dry distillation or thermolysis, involves the carbonization of wood. High temperatures without air access lead to the decomposition of wood, in effect of which water is released first, followed by non-condensing gasses and a water distillate or acetic acid. Charcoal and tar are produced as well.

Pyrolysis should be understood as a process intended to release the chemical compounds in wood and bark, in the effect of which the raw material is decomposed and ceases to exist as such. Both wood and bark are used, of deciduous trees (mainly birch) as well as coniferous ones (primarily pine).

Wood pyrolysis, the product of which is tar, is a technological process in which wood or bark is subjected to heating in a non-oxygen environment, resulting in a number of different products. Tar includes more than 200 organic chemical compounds, both aliphatic and aromatic. Aliphatic compounds are the products primarily of the destructive distillation of cellulose and hemicellulose, whereas aromatic compounds are the effect of thermolysis of lignin [Kozłow, Korolewa 1960: 305]. Changing the conditions of the chemical reaction taking place in high temperatures during the dry distillation process affects the end products. Owing to its considerable differentiation, the process of tar-making can be divided into stages.

Up to temperatures of 170 °C, heating dries the wood and releases water. The thermal decomposition of wood or bark is minimal at this stage. The chemical composition of the raw material is not changed. At this stage of the production process wood and bark absorb the thermal energy supplied by an outside source of heat (fire) in the course of evaporating water [Jiang 1999].

In the 170 – 270 °C range, a preliminary reaction of charring of wood and bark begins with the chemical composition also changing gradually at this stage. Decomposition of hemicellulose, mainly pentosans, begins at this stage of the process. Volatile substances are formed and gasses are released (CO_2 and CO); small amounts of liquid substances containing acetic acid and methanol are produced. Distillation of wood tar begins. These reactions are endothermic in nature, that is, they use heat supplied from outside.

Further heating (270 – 280 °C) speeds up the wood decomposition process, which takes on an exothermic character, meaning that heat is now released. At this stage decomposition of cellulose begins and the degradation of hemicellulose is continued. The cellular stability of cellulose is diminished as it enters in reaction with hemicellulose cells. The content of the latter remains stable despite the loss of pentosans. This is linked to the rising number of hexosans, which are a product of cellulose comminution [Beall, Eickner 1970: 45; Statheropoulos, Kyriakou 2000: 203-214; Ball, McIntosh, Brindley 2002: 1-17]. The release of distillates increases very rapidly:acetic acid, methanol and pitch. Lignin content falls, its decomposition being connected with the reaction with hemicellulose. Charcoal is also produced, even as the amount of carbon oxide and dioxide falls.

The temperature range of 280 – 450 °C (wood carbonization) is characterized by the strongest release of hydrocarbon and the beginning of the process of hydrogen formation. In this phase polymerization and condensation take place in the reactive chamber, having an influence on the formation of compounds that are more resistant thermally. The amount of released easily flammable gasses, such as methane, grows.

The last stage takes place in temperatures of 450 – 500 °C (wood roasting). In this stage volatile components are removed from charcoal and the amount of liquid constituents drops. Substances resembling hydrocarbon are formed and secondary reactions of polymerization and condensation occur [Davidsson, Pettersson 2002: 270].

The resulting mix of gasses and vapours of the volatile substances is the effect of chemical reactions taking place in strictly determined conditions. The character of these reactions is dependent mainly on the distillation temperature, the amount and quality of the gasses that are formed and pressure. The catalytic action of the formed charcoal is not without significance, as it is very active [Wojciechowski 1955: 75; Prosiński 1957: 605-612; Monkielewicz, Pflaum 1967: 306-308].

The slow course pyrolysis affects output and allows for the processing of small fragments of wood and bark. The output of liquid products rises in temperatures up to 360 °C, after which it drops [Surmiński 1996: 55]. The above discussion indicates that reactions taking place in the reactive chamber starting from a temperature of 270 °C are exothermic. This stage of the reaction requires no heat from outside to proceed; it even releases heat. For this reason, the fire around a tar kiln needs to be kept going until this point in the process is reached (270 °C), after which it can be extinguished. The heat of the reaction is sufficient for the distillation to be completed. Obviously, the process of pyrolysis is chemically quite complex. Wood and bark do not possess the components that are produced from them in the process of destructive distillation. The products of this process are the effect of not one, but a series of complex reactions, each one of which depends on the factors of time, pressure and temperature – the fundamental parameters of all chemical changes.

In the opinion of Klason, wood pyrolysis in temperatures of about 400 °C followed this reaction [Prosiński 1984: 605-620]:

$$\begin{aligned} &2\,\underset{\textit{wood*}}{C_{42}H_{60}O_{28}} \xrightarrow{>400\,^{\circ}\mathrm{C}} 3\,\underset{\textit{charcoal*}}{C_{16}H_{10}O_2} + 28\,\underset{\textit{water}}{H_2O} + 5\,\underset{\substack{\textit{carbon}\\ \textit{dioxide}}}{CO_2} + 3\,\underset{\substack{\textit{carbon}\\ \textit{oxide}}}{CO} + \\ &+ 2\,\underset{\textit{acetic acid}}{CH_3COOH} + \underset{\textit{methanol}}{CH_3OH} + \underset{\textit{wood pitch}}{C_{28}H_{22}O_4} \end{aligned}$$

* Averaged elemental composition

Pyrolysis in temperatures under 400 °C yields (%):

Table 1

Product quantities of the dry distillation of wood [Prosiński 1957: 607].

Charcoal	34.7%
Water	24.9%
Gasses	15.0%
Acetic acid	5.9%
Methanol	1.6%
Wood pitch	17.9%
Total	**100. 0%**

II.3. PHYSICAL AND CHEMICAL PROPERTIES OF WOOD PYROLYSIS PRODUCTS

The chemical formula of tar obtained by wood and bark pyrolysis is neither constant nor strictly defined. It is directly connected to how different chemical compounds react in the process of pyrolysis: some are completely decomposed, others undergo polymerization when heated [Kozłow, Karolewa 1960: 305]. Both birch and pine tar are characterized by similar physical properties, manifested by similar viscosity and an opalescent dark brown colour. Both are lighter than water (density: $\rho = 0.8 - 0.9$ g/cm^3) and have a characteristic turpentine smell. In both cases, they demonstrate good solubility in different organic solvents, such as chloroform, methylene chloride and tetrahydrofuran. Their hydrophobic properties make it insoluble in water.

II.3.1. PHYSICAL AND CHEMICAL PROPERTIES OF BIRCH TAR

Following years of research, scientists have isolated among the many different compounds making up birch tar and identified characteristic glycoside components. Glycosides are constituents of hydrolizing tannins and are derivatives of monosaccharides, formed from the joining of a sugar radical with the hydroxylic non-saccharide aromatic component, aglycone [Surmiński 1996: 45; 2000: 93]. Betulin, a glycoside is characteristic of birch tar; it is composed of D-glucose and aglycone, which is a methyl ester of salicylic acid. Other important glycosides include betuloside and glyco-vanillic aldehide [Surmiński 1979: 362; 1996: 49; Surmiński, Kasprzyk 1997: 93; Pollard, Heron 1996: 252-257; Sauter and others 1987: 1151-1152; Browning 1963]. Betulin occurs also, although in smaller amounts, in the bark of beech trees (*Fagus silvatica* L.) [Ludwiczak, Szczawińska 1965: 584].

Birch tar is characterized also by a substantial terpene content, foremost pentacyclic triterpene:betulinol, which is responsible for the white colour of birch bark [Surmiński 1979: 362; Jääskeläinen 1981: 599; Surmiński, Kasprzyk 1997: 93]. Betulinol and the other triterpenes with the lupanon and olean skeletons belonging in this group [Shiojima and others 1992; Scholichin and others 1980; Sauter and others 1987; Protiva and others 1981; Ogunkoya 1981; O'Connell and others 1988; Mahato, Nandy, Roy 1992; Lindgren, Svahn 1966; Lin, Nes, Heftmann 1981; Lehn, Vystrcil 1963; Hayek and others 1989; Hejno, Jarolim, Sorm 1965] are biologically active substances with antiseptic properties which are responsible for the medicinal properties of tar [Bruckner, Kovacs, Koczka 1948; Surmiński and others 1995; Jääskeläinen 1981; Budzikiewicz, Wilson, Djerassi 1963], produced in the process of thermolysis. These observations have been confirmed in recent biomedical studies, which have demonstrated positive results of using substances contained in tar for the treatment of HIV virus [Pînzaru, Leopold, Kiefer 2002; Guidoin and others 2003: 153] and in cases of skin cancer [Kim, Pezzuto, Pisha 1998; Kim, Koo, Kim 2001; Patočka 2003]. Triterpenoid glycosides, also called saponins, are also distinguished by a wide spectrum of properties:bactericidal, fungicidal, antiviral, cytotoxic, painkilling, anti-inflammatory, anti-cancerous, improving blood circulation and antiallergic [Zdzisińska and others 2003; Patočka 2003].

R1	**R2**	**Group 20(29) of Lupanon**	**Group of 12-olean**
OH	CH_3	Lupeol	ß-amyrin
OH	CH_2OH	Betulinol	Erytodiol
OH	CHO	Betulinic aldehide	Oleanolic aldehide
OH	COOH	Betulinic acid	Oleanolic acid
OH	$COOCH_3$	Methyl betulinian	Methyl olean
O=	CH_3	Betulonic aldehide	–
O=	CHO	Betulinic acid allobetulin	–
O=	COOH	–	Acetyl-oleanic acid
O=	CH_2OH	Betulin	

Tar also contains derivatives (monomers) of suberin, which is one of the basic constituents of birch bark: 9,10-epoxy–18-hydroxyoctadecanoic acid and 22-hydroxyeicosenoic acid [Ekman 1983: 210, Pl. 1; Bolmgren, Norin 1981: 742; Reunanen, Holmbom, Edgren 1993: 177, Pl. 1]. The predominant acid among fatty acids in birch tar is linolic acid.

Cellulose is depolymerized during pyrolysis and is further degraded leading to the production of a number of products, of which the most important is cellulose carbon, acetic and formic acids, formaldehide, furfural, phenols, furans, toluen [Prosiński 1957]. Non-condensing gasses include carbon dioxide, carbon oxide, methane and ethane. Lignine is decomposed in high temperatures, producing aromatic compounds like coniferyl alcohol, vanillin, methanol, formic aldehide, acetic acid, creosol and guaiacol [Monkielewicz, Pflaum 1967: 307].

II.3.2. HYSICAL AND CHEMICAL PROPERTIES OF PINE TAR

The most important constituents of pine tar are phenols and derivatives formed from lignin decomposition, such as pyrocatechol and pyrogallol. Like the triterpenes in birch tar, these substances are strongly antiseptic (bactericidal and fungicidal). Pine tar contains considerable (approximately twenty times more than coal tar) amounts of phenol compounds, derivatives of guaiacol, hence capable of forming bicyclic links of the dihydroxydiphenylmethan type [Wajszczuk 1967: 120; Flodin 1978: 12-13; Antkowiak 1997: 29].

Pine tar also contains substances referred to as monoterpenes (C_{10}) and sesquiterpenes (C_{15}), which despite their volatile nature can survive for millennia in favourable conditions. Monoterpenes, saturated hydrocarbons, are a constituent part of terpene oil, which is a product of pine resin distillation [Surmiński 1994: 46-64; Pollard, Heron 1996: 242]. Sesquiterpenes on the other hand, such as calamenene and cadalene occurring in products of pine wood pyrolysis, can survive in an anaerobic environment, waterlogged for instance [Robinson and others 1987: 641; Elias, Simoneit, Cardoso 1997: 308].

The chemical composition of tar from coniferous trees is characterized by the presence of diterpenes, which occur among others in pine wood [Gough 1965; Enzell, Wahlberg 1969; Pollard, Heron 1996: 243-245]. Diterpenes have the structure of abietene, pimarine and labdane. Abietine and pimarine dominate in resins containing non-polymerized structures, such as those in pine. Wood tar from trees from the *Pinaceae* family, especially pine (*Pinus sylvestris* L.) are characterized by a high content of abietine acid [Edwards, Farwell, Daffner 1996: 1640; Petit-Dominguez, Martinez-Maganto 2000; Martin and others 2001], pimarine acid [Robinson and others 1987: 641; Edwards, Sibley, Heron 1997: 2375], as well as oleic and palmitic acids [Holmbom, Avela 1971: 12; Fox, Heron, Sutton 1995: 371] and the products of their thermal transformation, e.g. retene.

Pine tar contains in considerable amounts bicyclic terpenes and their derivatives. The high importance of this group of hydrocarbons depends on their fundamental role in the chemical composition of aromatic oils characteristic of coniferous woods. Thus, these substances are the main components of turpentine. δ-3 carene is a characteristic component of pine tar, responsible for the pleasant aroma of pinewood; equally characteristic are α-pinene and ß-pinene, the content of which in turpentine reaches 60 – 95 per cent [Petit-Dominguez, Martinez-Maganto 2000; Gough 1965: 2059]. The latter two substances are characterized by similar physical properties and a similar chemical structure [Surmiński 2000: 82]. Camphene, an important volatile substance smelling like turpentine, whose derivative is borneol, is another important constituent of pine tar.

Substances like creosol and guaiacol are also produced in the process of pyrolysis. Wood tar, whether birch or pine, contains substances resistant to high temperatures and the environment (they are not biodegradable), which allows them to be treated as 'molecular markers' characterizing archaeological samples of tarry materials.

Components which largely preserve their original properties in birch tar include betulin and suberine. Betulinol, a pentacyclic triterpene, is distinguished by considerable thermal stability. Suberine, which is a biopolyester composed of hydroxy and epoxy acids and dicarboxylic acids, is responsible for bark properties like elasticity, non-permeability, thermal isolation, resistance to water, alcohol and other organic solvents.

Diagnostic substances for pine tar include among others:abietine acid, pimarine acid, and reten, a high-temperature product of the thermal transformation of resin with a very durable aromatic structure. It occurs in relatively large quantities in fossil pine tar discovered during archaeological excavations. The remaining compounds are transformed to a different extent or completely degraded, also biodegraded, under the influence of temperature and external factors.

The chemical composition of wood tar, like the composition of any other product of dry distillation, is dependent not only on the quality of the processed raw material, but also on the method of production and to a large degree on the temperature and time of the process as a whole.

The transformation that occurs in wood and bark, the main raw materials for making wood tar in the past, as a result of chemical processes to which they are subjected, changes the very essence of these materials. The new substances that are produced do not occur in the initial material [Krzysik 1978: 22].

II.4. PREPARING TAR AND PROCESSING TECHNIQUES

As discussed elsewhere in this study, prehistoric producers of tar obtained different products depending on the raw material they used in the destructive distillation of wood and bark. Finds of petrified tar indicate that birch and pine wood and bark were the preferred materials used in the thermolysis.

An integral part of the tar-making process is the processing formula and later modifications largely determined by the intended use. Prehistoric tar producers had a whole range of preparatory procedures depending on the conceived use. Remains of pitch substances recorded during fieldwork demonstrate that tar makers controlled the composition by choosing the proper raw materials (mainly birch and pine wood and bark) in appropriate proportions, for example, 2:1, in order to obtain the desired effect, that is, the desired property of tar [Kośko, Langer 1986]. With no proper, meaning tight containers to protect from uncontrolled degradation (petrification), the substance had only a short utility span. Means were found, however, in the form of fatty substances added to the mix, to counteract these processes [Kośko, Langer 1997: 25-28; Szafrański, Szafrańska 1961: 70]. Nineteenth-century ethnographic observations stand in confirmation of conclusions based on physico-chemical analyses [Brylak-Załuska 1983; Wrębiak 1971]. According to this information, in order to make the tar thicker and to prolong its usability makers would „*cook it (...) with cattle or mutton tallow, adding 200 g of fat per each kilogram of pitch*" [Wrębiak 1971: 34]. The procedure allowed prehistoric tar makers to form the processed tar into lumps or rolls weighing 100 – 150 g for storage purposes. Lumps of similar shape have been recorded on many archaeological sites, e.g., Ca Nove di Cavaion (Verona – I) connected with the Bronze Age Polada culture dated to 1800 – 1500 BC [Chelidonio 1997: 45-50]. Fingerprints of either producers or users of the tar have been preserved on the rolls discovered at this site; they were modelled by hand and used perhaps to smear ceramic vessels (as repairs or conservation). Vessels repaired with a similar substance were also discovered at this site to confirm this idea.

Tar used in medicine and folk veterinary medicine had aromatic herbs added beside the fat in order to raise its value. Prepared in this way the tar was used as incense around sick people and animals and had wide application in medicinal and prophylactic magic [Brylak-Załuska 1983: 28], which also finds reflection in the archaeological material [Baczyńska, Lityńska-Zając 2005].

Thermal processing was also needed for efficient application of the product. Wood tar hardens to a solid once it cools and can be processed only when heated at high temperatures. Finds of tar as binder reveal smooth and even surfaces, which is due to its properties of plasticity and good adherence. According to Czarnowski and Neubauer-Saurer, the substance could be spread on the surface to be glued, heated and spread with a damp hand [1991: 11-13], but the end result was less than satisfactory owing to the rapid cooling of the pitch substance which did not allow the binder fragments to coalesce fully. An experiment with a heated pebble, conducted by Czarnowski and Neubauer-Saurer, showed that the source of heat acted as a kind of soldering tool. The heated end of the pebble moving against the tar softened the material enough to allow it to be smoothed to an ideal state [Weiner 1988: 329-334]. This method proved much more effective than the previous one discussed above.

Unsuccessful cases of binding have also been recorded with the repaired vessel breaking apart at the point of reparation [Langer, Pietrzak 2000]. The reason for this is believed to be excessive loss of volatile elements, the tar having been heated too strongly either during the production process or as a result of secondary thermal processing [Czarnowski, Neubauer, Schwörer 1990: 169-173]. These ingredients, which are responsible for the plasticity and flexibility of tar, escape with each secondary heating of the binder, resulting in deteriorating quality of the product. Lowered plasticity diminishes the sticky properties of the substance. Product quality deteriorates also with excessive charring, which lowers plasticity and consequently limits economic usefulness. Progressive thermal degradation of complex organic substances making up tar can lead to the creation of heat-resistant polymers of low volatility, due to a lack of control over temperature at the production stage or produced intentionally in extreme thermal conditions. In extreme cases they took on the form of pure carbon. Prehistoric tar makers were aware of the effects and applied technology deliberately, modifying the tar layer on vessel surfaces to suit their needs. The objective was to achieve higher resistance of the pitch substance used either as a colorant (for aesthetic reasons) or insulation (longer maintenance of heat) to high temperatures, such as those encountered while using a vessel in a hearth, for example [Langer, Kośko 1992; 1999]. The effect of post-depositional conditions on tar structure and thus on its properties should not be overlooked in this case.

Samples of pitch substance from the settlement in Talianki (Tomaszów group of the TrC, phase CI) and from barrows in the cemetery in Obloj (PYC – extended burial horizon) in modern Ukraine have demonstrated the extremely homogeneous nature of tar produced from birch and pine wood in proportions of 2:1. The substance from Talianki had little if any mineral or organic admixtures (e.g. remains of wood or bark which have been frequent in samples analyzed to date) [Kośko, Langer 1986]. The only departure in this respect was a colloidal suspension of carbon particles to be interpreted as evidence of soot, which could mean that soot was used potentially as a pigment, applied either directly or as an element of a more complex kind of paint [Langer, Kośko 2000]. As for tar finds from the cemetery in Obloj, they should be linked to a posthumous ritual of attaching the scalp to the head using a kind of wood grease prepared according to a strictly followed recipe [Klejn 1961; Kośko, Langer 1986]. In this context one should consider the possibility of a special category of tar being produced, one that had its own special and unique purpose. This kind of birch-pine tar would have had its own production or preparation recipe, different from the others and intended specifically for magic and medicinal treatment. The interpretation, however, raises certain doubts and requires more analytical substantiation before it is accepted.

Physico-chemical analyses have also helped to identify the procedures involved in preparing tar colorants applied to pottery surfaces. Traces of mineral components frequently present in organic colorants are interpreted as contaminants introduced in the post-depositional process, but they can also be considered as intentional mineral admixtures added by the prehistoric makers, especially in view of their even distribution and their presence solely in the organic layer. The producers' objective was to ensure better adherence, durability and mechanical resistance to wear of the ceramic surface on which the pitch substances were observed [Hadzi, Orel 1978: 51-62; Langer, Kośko 1999; Langer, Pietrzak 2004a].

Methods of application to pottery surfaces have also been identified. The way in which the organic layer adheres to the walls of ceramic vessels indicates that the substance was applied in liquid form using implements as if they were brushes. Recording iron compounds in the form of a purposeful addition to tar, used as a colorant, is a curiosity to some extent because their spatial distribution has been interpreted as evidence of blood cells, although no characteristic haemin (blood colorant) was discovered [Langer, Kośko 1992: 61-68; Kośko, Langer 1997: 25--28]. Use of blood suggests knowledge of its colouring properties, especially after the discovery had been made that colour could be fixed in the process of firing of the pottery. Finds of this kind (with traces of iron compounds as an addition to the tar) have been recorded in Polish territory [Piotrowski 1993: 53-61; Pollard, Heron 1996]. Certain preparatory treatment of organic colorants were mentioned also by Jira with regard to Neolithic finds from Böhmen [1911: 239].

An unusual form of tar use was recorded on a number of archaeological sites from the Neolithic and Bronze Age in western and northern Europe. Fieldwork at Hornstaad-Hörnle I in Germany [Rottländer 1981; Schlichtherle 1981: 65; Evans, Heron 1993: 446; Heron and others 1989: 330] and Seefeld in Switzerland [Schoch 1995], as well as Spjald in Jutland [Becker 1990; Hayek and others 1990] uncovered lumps of petrified tar with human bite marks. These finds have been interpreted by researchers as proof that wood tar was a prototype for modern chewing gum. Owing to its antiseptic properties, wood tar when chewed could have released large amounts of disinfecting substances which could have acted as a painkiller and cleared the respiratory tract (inhalation) and mouth and teeth [Rajewski 1970; Schlichtherle, Wahlster 1986]. Similar finds were made recently on a site from the Mesolithic in Freisack (Germany) [Gramsch 1985: 57-67], as well as in Scandinavia [Larsson 1983: 75-76]. It remains to be seen whether this is indeed a case of tar being used as a stimulant. It is also possible that chewing tar was a form, incidental to be sure, of softening the product in preparation for further processing.

The observations presented above have demonstrated that preparatory treatment was an important part of the tar-making process and the choice of procedure depended on the application (whether as binder, colorant or magical and medicinal substance). Further recipes and formulas are entirely possible, although untraceable in the archaeological record at present. Archeometry is the sole field of science which can help in finding answers to these questions.

II.5. RESIDUES OF WOOD TAR – ARCHAEOLOGICAL DATA

This part of the study is dedicated to a presentation of the current body of evidence on ‘hypothetical wood tar’, showing at the same time a broad range of applications. The task of distinguishing wood tar among remains of organic materials from the Lowland is only apparently easy and the undoubted uniqueness of these finds compared to other artefacts is helpful only to some extent. Finds of ‘hypothetical wood tar’ are commonly recorded by archaeologists macroscopically alone and even more frequently they are interpreted wrongly or overlooked as insignificant for research. Meanwhile, tar residues discovered in the area chosen for this study indicate a diversity of functions of the product in the economy and rites of prehistoric societies. It would be incorrect therefore to assume a single interpretative variant for finds of this type. Tar residues should be considered in four main categories, based on criteria of form and also function in consequence: (Chapter II.5.1) lumped tar substance, (Chapter II.5.2) tar substances on pottery, (Chapter II.5.3) tar substances on utilitarian objects and (Chapter II.5.4) carbon deposits. The source base for these four main categories of archaeological finds is abundant, although finds representing applications of tar in prehistory less easily reflected in the material have also been considered (Chapter II.5.5).

II.5.1. LUMPED TAR SUBSTANCES

Lumped organic substances is a fairly diverse category as regards function. Residues of products of destructive distillation of wood and bark are often recorded in the form of black or brown-black lumps of either mat or glossy surface, often revealing unprocessed material, clearly distinguishable in the fractures. Wood and bark can thus be isolated already at the level of macroscopic observation of finds of this sort and distinguished from other organic materials with similar external appearance. A considerable differentiation of the size of observed tar substances has a direct influence on excavation procedures.

II.5.1.1. LARGE FRAGMENTS LUMPED TOGETHER

In this case we are dealing with large, easily distinguished samples of differentiated functionality (Fig. 4). Materials from this category may represent post-production residues, binders and substances of medicinal and magical properties. Good examples of this category have been recorded at archaeological sites in Polish territory [Krzak 1961: 72; Wojciechowski 1972: 265-267; Kośko, Langer 1986: 592; Szmyt 1992: 77; Duday, Kowalewska-Marszałek 2003], as well as in Ukraine [Kośko, Langer 1986: 593; 2000: 135-138] and countries of Western Europe [Heron and others 1989: 330; Evans, Heron 1993: 449].

Organic materials discovered in a palafitte settlement of the Altheim culture in Ergolding Fischergasse, Bavaria, dated to 3700 – 3340 BC, in 1982 – 1987 [Evans, Heron 1993: 446-449; Heron, Nemcek, Bonfield 1994: 266] belong in this category. One should also consider the finds from site 6A in Łąck [Domańska 1995: 10], where a clay ladle filled with the products of the thermal decomposi-

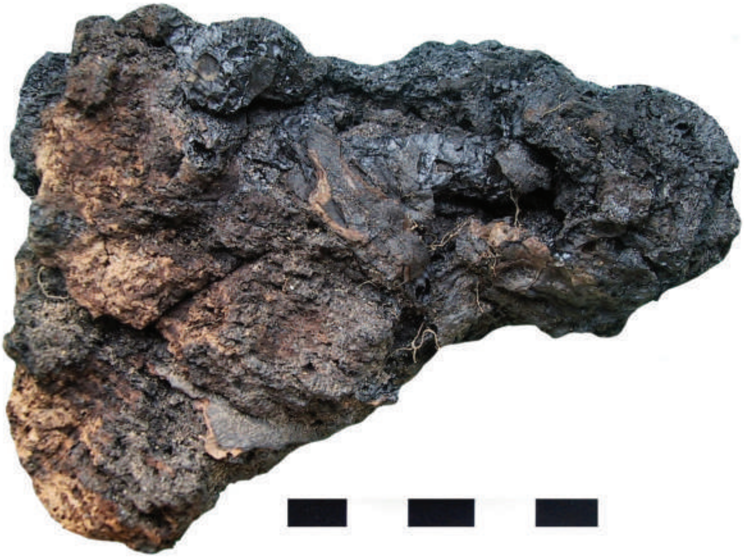


Fig. 4. Example of a large fragment of wood tar

Fig. 5. Example of small fragments of wood tar

tion of birch bark was found, among other artefacts, at the bottom of a cult feature near a grave from the Sarnowski phase of the FBC. The residues of pyrolysis were radiocarbon dated to 3940 – 3700 BC (OxCal 3.9, 1 sigma).

II.5.1.2. SMALL FRAGMENTS

Organic substances are seldom found on archaeological sites owing to the specific conditions required for their preservation, such as, for example, an oxygen-free environment (bog sites or palafitte settlements). In the case of small tar fragments the limitations of the excavation methods are obvious, hence the need to consider flotation (Fig. 5). The technique has been proven for sites like the multicultural site 13 in Żuławka, Wyrzysk commune, Piła district, Wielkopolska province, recording among others a substantial amount of pitch substances [Dmochowski 2002: 88-91; Pyżewicz 2003].

Incorrect interpretation is another issue when recording small fragments of tar at excavations. This concerns in particular organic material occurring in the form of small black lumps which often resemble lumps of charcoal externally.

II.5.2. TAR SUBSTANCES ON POTTERY

Ceramic vessel shards are the most abundant archaeological category preserving traces of organic substances, including tar. Organic compounds could be absorbed by the porous microstructure of fired pottery or preserved on the vessel surface. Tar residues can be distinguished on the grounds of a set of macroscopically distinguishable characteristics of colour, gloss, and surface as well as fracture texture (Chapter I.1).

II.5.2.1. POST-PRODUCTION RESIDUES

The group is relatively abundant and diverse in character. Organic post-production residues are also of considerable significance for research on production technologies (shards of vessels used in production containing residues of wood tar or used for secondary processing and storage of tar) as well as for identifying the material used for wood-tar production (product residues containing unprocessed

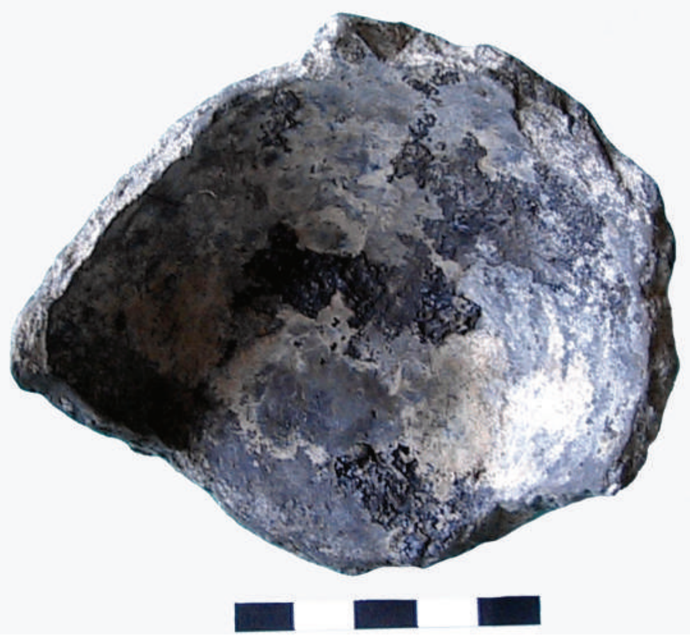


Fig. 6a. Fragment of a single-chamber tar kiln

Fig. 6b. Fragment of a vessel used for wood-tar production (fragment of the reactive chamber)

wood or bark). The potential informative value of this group of finds in the corpus of archaeological petrified wood tar residues is unquestioned (Fig. 6).

This category is well exemplified by tar residues associated with communities of the Funnel Beaker culture, recorded in excavations in, e.g. Dąbrowa Biskupia, site 21 [Kośko, Langer 1986: 592]; Podgaj, site 6A [Chachlikowski 1994: 103-105]; Kuczkowo, site 1 [Langer, Pietrzak 2000], and the Lusatian settlement in Kuczkowo, site 1 [Langer, Pietrzak, Cichocka 2004]. Samples qualified in this category of archaeological sources occur usually as layers of petrified tar on the inside or outside surfaces of the walls of ceramic vessels, mainly in their belly and bottom parts (Fig. 7). Frequently the substance is heavily charred, demonstrating advanced graphitization, due to high temperatures, and consequently not easy to identify. In some cases pottery can be identified with considerable certainty as production vessels [Chachlikowski 1994: 160; Kośko, Langer 1986: 592; Gumiński 1989: 113, 164; Langer, Pietrzak, Cichocka 2004; Heron, Nemcek, Bonfield 1994: 266].

A high melting point (more than 250 °C) and extensive graphitization and polymerization of the substance in the layer immediately adjoining the vessel walls, as well as actual residues of the raw material (wood or bark) suggest post-production residues. Tar on the outside surface of ceramic pots could have been applied intentionally (as colorant or binder) or been unintended, the effect of the vessel coming in contact with the substance (post-production residues). Vessels used to roast wood and bark were of course subjected to the action of high temperatures, serving sometimes as a container to collect the ready product. It should be emphasized, however, that it is extremely difficult and frequently impossible to ascertain whether recorded tarry residues can be classified as post-production residues or are evidence simply of a vessel being heated over a fire. The 'humanistic' approach of many researchers to source material can be countered in this case by archeometric analyses, which can help to resolve such issues.

II.5.2.2. BINDING AND SEALING MATERIAL

This group is large and characteristic, as well as distinct from both a formal and functional points of view. Therefore, it merits separate treatment. The degree of inner differentiation of the materials is insignificant and their ubiquity among other tar finds substantial. Good counterparts can be found from territories outside Poland, occurring almost everywhere in Europe, from the Paleolithic through the Middle Ages.

Wood tar and bituminous substances were widely used in prehistory, the former as a widely accepted binder. Specific uses include pot repairs from the Neolithic [Kośko, Langer 1986: 593; Gumiński 1989: 164; Chachlikowski 1993: 161; Langer,

Fig. 7a. Fragment of a double-chamber tar kiln (inside surface)

Fig. 7b. Fragment of a double-chamber tar kiln (outside surface)

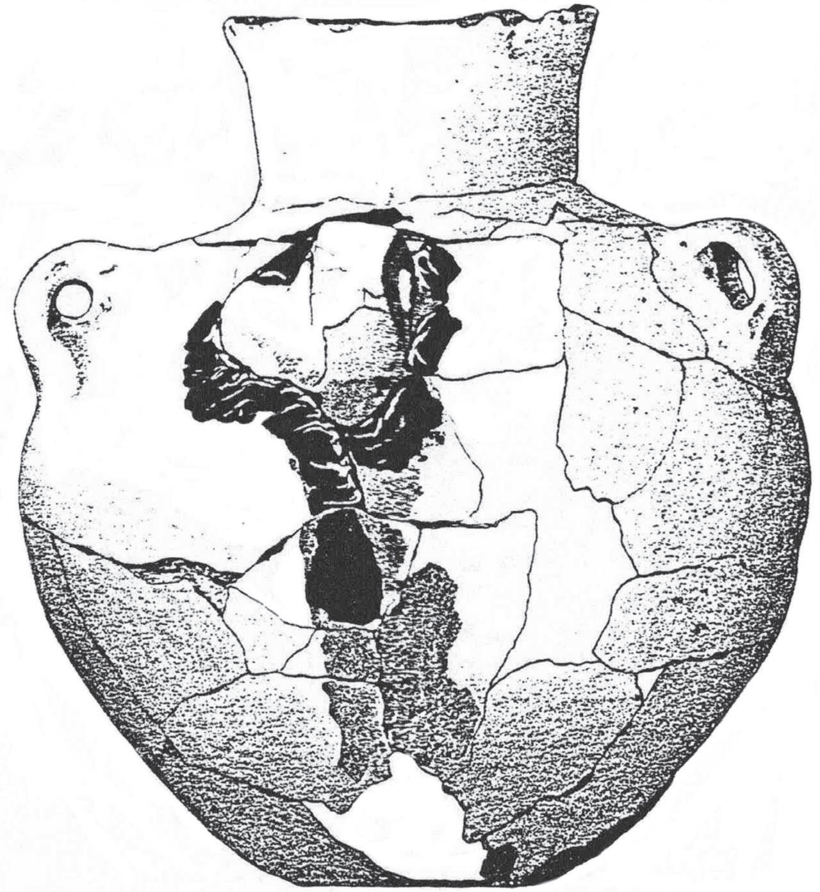


Fig. 8. Example of repairs to a ceramic jar using wood tar as binder [Schwabedissen 1979: 170, Fig. 3: 1]

Kośko 1999], which find parallels from sites in Western Europe [Schwabedissen 1979: 167-172; Heron and others 1989: 325-331]. Schwabedissen described a jar attributed to the Rosenhof group of the Funnel Beaker culture from a site in Schleswig-Holstein, in the case of which a large fragment of the belly had been broken off and reattached using tar as a binder (Fig. 8) [1972: 1-8; 1979: 170]. An analogous find from a later age was recorded in Great Britain, suggesting a lasting tradition of using tar as binder in pottery repairs over large parts of Europe well into the Iron Age [Novotný 1952: 275-278; Sauter 1967: 27-29; Rottländer 1974: 95-98; Bunny 1993: 17; Charters and others 1993: 91-101; Regert and others 2003: 101-120].

Fig. 9. Examples of ceramic vessels decorated on the outside with cut-out bark ornaments attached with tar binder [Gonzenbach 1949, Pl. 5]

A common practice in the Neolithic was to decorate the outer surface of vessels with birch bark attached with an organic binder (Fig. 9) [Gonzenbach 1949, Pl. 5,12,13; Vogt 1949: 50-51]. That tar was used as a binder in these cases (as a base for the ornament cut from birch bark) is indicated by the fact that the substance can be found solely on the outside walls of ceramic vessels [Kośko, Langer 1992: 67; Langer, Kośko 1999; Langer, Rola 1997: 35-39]. Tar must have been applied in vertical bands about 3 cm wide and approximately 0.5 – 1 mm thick, which suggests this kind of intentional use when one takes into consideration the substantial natural density of the substance. These observations are confirmed by further evidence for the use of tar as binder for a cut-out bark ornament in the form of ceramic pots from Jezuicka Struga, site 17, preserving on the outside surface evident bands of tar documenting the presumed bark ornament. This particular site from the Kujawy region is attributed to Phase 2I A of the FBC [Kośko, Langer, Szmyt 2000].

The use of tar for sealing porous walls of ceramic vessels has been attested by both archaeological [Chachlikowski 1993: 160; Langer, Pietrzak 2004a] and ethnographical data [Foster 1956: 732-733]. Pottery has a tendency to absorb the organic content it comes in contact with owing to the porous and permeable character of ceramics as a material, hence tar with its hydrophobic properties was a virtually ideal means for sealing this porous microstructure on both the inside and outside of pots used for cooking, drinking and storing of liquids [Rice 1987: 163-164; Schiffer 1990]. The use of plant (organic) wax in similar capacity has been recorded in archaeological excavations at the Neolithic site of the Altheim culture in Ergolding Fischergasse (Bavaria, Germany) [Heron, Nemcek, Bonfield 1994: 266-269; Bonfield, Heron, Nemcek 1997: 203-212;].

Archeometric analyses have demonstrated layers of tar and resin on pot walls to possess excellent thermal conductivity properties (quicker temperature growth inside heated pots) [Schiffer 1990; Foster 1956; Langer, Pietrzak 2004a; 2004b]. With some caution the use of organic substances including tar can be linked to prehistoric milk economy. Storing milk and its processed products in pottery containers would have necessitated a sealing of the vessel surfaces to counter the inherent permeability of clay walls. An alternative interpretation of archaeological finds of this kind is the potential use of tar on the inside surface of pots as a sort of antiseptic against bacteria and fungi which could have spoiled food, including dairy products. Further analytic research in this field should help to confirm or reject ideas presented in this section.

II.5.2.3. COLORANTS

Colorants constitute the next category of recorded archaeological presence of tar on pottery (Fig. 10). The scope of their function is difficult to determine due to destructive post-depositional conditions on most archaeological sites on the Lowland, not to mention the fact that few organic compounds have the capacity

Fig. 10a. Examples of vessel surface being decorated with a thin layer of tar colorant

Fig. 10b. Example of a vessel surface coated with a relatively thick layer of tar colorant

Fig. 11. Example of a vessel with engraved band ornament filled with a painted tar colorant

to survive heating in high temperatures (most materials of this type are charred in a temperature of about 400 °C). Some polymers, which could be formed in effect of pyrolysis of complex organic substances, are resistant to high temperatures (up to 800 °C). These substances of complex composition and a brown-black or black colour can even take on the form of pure carbon in extreme cases as a result of complete charring or even graphitization. The end effect is a resistant black colour on the surface of clay pots. Vessels covered with material of a similar nature could have been used in high temperatures, for example, for cooking over a fire. Wood pitch was one of the materials which could have been used for this purpose on ceramic vessels. Polymer components of low volatility in these substances resulted in a permanent colour forming on objects during the process of annealing, this being permitted by the sufficient liquidity of these substances.

The proper identification of ceramic colorants, that is, proper distinguishing of this category among other, often accidental tar residues, is another issue. Microscopic observation may help in this question, revealing intentional application of a layer of the product and excluding accidental forming of tar deposits as a result of burning wood and bark in the fireplace. The appearance of the surface and the thickness of the applied coat only on the external surface of a pot may be considered in evidence. Even spreading and a fairly uniform thickness of less than

1 mm of a black organic substance on the surface of a pot is proof of intentional application for aesthetic purposes. A frequent use of mineral ground to modify (smoothen) pottery as well as observable brushwork are also construed as proof of intentionality (Fig. 11) [Langer, Pietrzak 2000; Pietrzak 2010].

An even distribution of mineral admixture on the surface of organic colorants leads to the conclusion about intentional modification of the properties of the tar coat. The addition of mineral substances increased the mechanical durability of the organic layer and its resistance to wear, and resulted in better adherence of the tar substance to the clay fabric. The pitch layer on the surface of a vessel could have been subjected to a process of heat setting, also increasing the thermal durability of the surface of the colorant. This was important from the point of view of safe use of a decorated vessel in a hearth, for example, without fear of damaging the colorant [Langer, Pietrzak 2004b; Pietrzak 2010].

II.5.3. TAR SUBSTANCES ON UTILITARIAN OBJECTS

European finds from the Stone Age illustrate many different applications of tar for mounting stone and flint inserts on tools made of organic materials like wood, bone and horn [Aveling, Heron, Larsson 1996; Hayek, Krenmayr, Lohninger 1991: 153-156; Sulgostowska, Hoffmann 1993: 75-88]. It seems that mounting of tool or weapon elements, like arrowheads and bone points with stone inserts, without tar was not sufficiently strong, whereas their tying would not have been practical in the case of knife blades and sickles (Fig. 12) [Behm-Blancke 1962: 110, 154-159, Fig. 15-23; Barfield 1994: 14-15, Fig. 3-4; Bahn 1995; Werther and others 1998; Sauter and others 2000: 736]. Tar binder was used in such cases, but in combination with other forms of joining. The points were placed in appropriate crevices or hollows and fixed with an organic binder (wood pitch) [Winiarska-Kabacińska 1993: 89-93]. There are examples, however, were tar was the sole binder used to mount the working elements of a tool [Hayek, Krenmayr, Lohninger 1991: 153-156; Larsson 1983: 95-96].

Bituminous substances appear to have been used on a par with wood pitch as a binder in prehistoric times. Evidence for such practice has been supplied from the Near East as well as other regions [Boëda and others 1996: 336-338; Pollard, Heron 1996: 293-368], from the Middle Paleolithic in Syria [Holdaway 1996: 288-289] and the Eighteenth-Dynasty Tell el D’aba in the Eastern Nile Delta in Egypt [Endlicher, Tillmann 1997: 333-342]. Flint inserts in this case were mounted in a handle of organic material using a bituminous binder. In Europe, substances of this type were used, according to Koller and Baumer, to mount a knife blade in a handle originating from excavations of an Early Bronze Age site at Xanten-

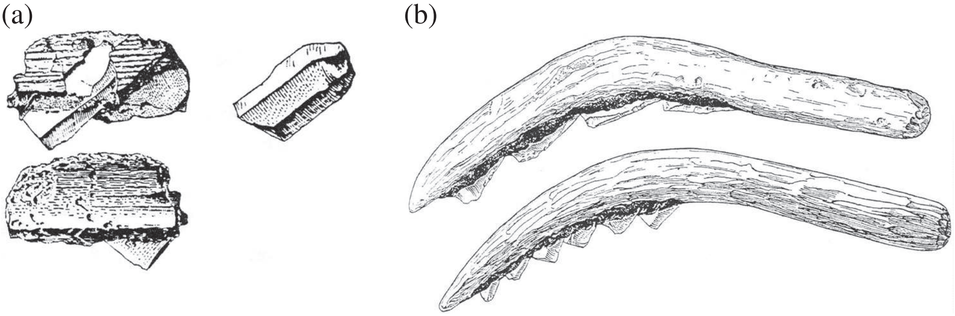


Fig. 12. Example of mounting using tar binder:(a) flint inserts, (b) in a wooden haft [Behm-Blancke 1962: 154, Fig. 15]

Wardt, Germany [1993: 117-131]. Archaeological finds indicate that even as tar binder was being used in one region (Upper Austria, Denmark, Germany, Poland, Sweden, Ukraine), bituminous substances were used elsewhere (Egypt, Syria). In the Near East there are natural outcrops of the material, which were being exploited on a mass scale from the Middle Paleolithic. In Europe at this time (Germany), the use of bituminous substances as binders was an alternative to tar.

II.5.4. CARBON DEPOSITS

All the processes taking place in ceramic vessels, especially preparation, storage and cooking of food as well as other production activities involving plant and animal products, leave chemical traces on the pottery. Relevant activities include, among others, brewing beer, tanning, processing and storage of dairy products, dyeing and salting. Distinguishing among these substances and their identification has been made possible by considerable advances in techno-archaeological research. The nature and distribution of layers of organic residues could reflect ways in which they were formed, as well as ways in which food, for example, was prepared [Andersen, Malmros 1984; Hastorf, DeNiro 1985; Hally 1986]. The presence of burning and soot helps to determine ways in which vessels were heated [Skibo 1992].

The most frequently encountered organic remains are those of food, which is only natural considering the ubiquitous connection of ceramic vessels with food preparation and consumption. Cooking and baking freed organic substances which either escaped or were absorbed into the walls of the pots. Charred remains (carbon deposits) often recorded on ceramic surfaces, are presumed to represent food which was being prepared or stored in the given pot and which, burnt as a result of high temperatures, adhered to the walls of this vessel.

Remains of organic substances could be deposited on the walls of ceramic vessels also as a result of a broad range of other activities connected with other spheres of life of prehistoric societies than food preparation [Rice 1987: 210; Dunnell, Hunt 1990]. They can also be a side effect of processes, however, of tar making and processing. In this case it is important to be able to distinguish between remains linked to food and those that are the effect of other processes. At the level of microscopic observations, decisive evidence in favour of food remains is the presence of unprocessed plant cells or animal tissues, which differ from typical tar material. The different nature of such food-related remains is reflected also in the physico-chemical characteristic recorded in technoarchaeological research (FTIR, TLC, NMR, MS). The results of relevant analyses permit precise identification and distinguishing of food remains from the remains of other organic materials [Pollard, Heron 1996].

II.5.5. OTHER

Issues brought up by analyses of materials not included in the above discussed groups of finds can be helpful in evaluating the role of prehistoric tar making as a supra-cultural and supra-regional phenomenon. The set of finds of analogous nature, as well as observations presented in this sub-chapter, referring to finds from other areas of Europe and the world, are inspirational for further investigations.

In prehistoric times which knew no crude oil products and where bituminous substances and other chemical means were no competition for tar obtained through processes of dry distillation of wood and bark, the product must have been well sought-after, in Polish territories as much as in all Europe as we know it.

II.5.5.1. BOAT AND SHIP CAULKING AND PRESERVATION MATERIAL

Many natural product analyses have concentrated on organic materials from shipwrecks, well preserved and conserved in a marine environment [Egenberg 1996; Robinson and others 1987: 637-644; Reunanen, Ekman, Heinonen 1989: 33--39]. Curt Beck from Vassar College in New York examined many shipwrecks from the Mediterranean, dated from the 4th century BC through the 7th century AD

[Beck, Borromeo 1989: 51-58; Beck, Smart, Ossenkop 1990: 369-380]. Samples consisted of sealants forming a protective layer on vessel ceramics used for transportation of goods and caulking material found in the structure of ship wood. The substance was identified as pine tar. The authors explained the production process as pyrolysis of pine wood or resin roasting. Pine resin was also used as a condiment for wine, making the wine today referred to as *retsina* in Greece.

Langer identified and analyzed Viking ship caulking from the 11th century, sampled in cooperation with the National Museum in Szczecin. At the present stage of research the substance used to seal the early medieval boat has been identified as pine tar mixed with considerable amounts of hair or fur and plant fibres [Cichocka 1999]. Analogous finds come from Norway (Oseberg, Gokstad, Tune), where Viking boats used to be caulked with wood pitch mixed with natural materials, such as grass, moss and animal fur [Egenberg 1999].

II.5.5.2. SUBSTANCE USED IN MUMMIFICATION

Archaeologists and a broader group of specialists have been fascinated by Egypt and by the mummification technique for years. Science is using ever more elaborate analytical techniques to identify archaeological materials, including natural substances used in the mummification process [Hairfield, Hairfield 1990: 41A-45A]. The most recent study by Mark Proefke and his co-authors from the University of Illinois, concerning mummification of the dead in Roman-period Egypt uses mass spectrometry combined with gas chromatography (GC-MS) and a tandem technique of coupled mass spectrometry (MS-MS) to identify coniferous resin and bituminous substances used in liquid form for mummifying the dead [Proefke and others 1992: 105A-111A]. In earlier studies chromatographic techniques were used to analyze the substances with which bandages were saturated; wax and galbanum (gum resin) were among the identified substances, as well as bituminous products and an extract from tamarind fruit. Outer wrappings turned out to be preserved with animal glue despite historical sources to the contrary, saying that products of animal origin were never used in the mummification process.

Polish scientists have contributed to the research on mummification in Ancient Egypt. In 1995 the staff of the Mediterranean Archaeology Department of the Archaeological Museum in Kraków, in association with Egyptologist Andrzej Niwiński from the University of Warsaw, undertook a project to examine the mummy of Iset – Iri – Hetes dated to the Ptolemaic age. Modern analytical techniques combined with a series of specialist research methods, including those from the natural sciences, were applied. Understanding the technical side of mummification demands a deep knowledge of the chemical substances used on skin tissue as well as body wrappings. Chemical analyses have identified resin among the substances. It has been proven that the Kraków mummy was covered with a mix of cedar-wood resin and bitumen. A closer look at the results of all of the analyses has contributed new information on the mummification process, the technique used and the funerary ceremony as well as the social status of the deceased, which is reflected in the number and quality of the grave goods [Babraj, Szymańska 1998: 4-10].

II.5.5.3. WOOD TAR IN RITES AND PRIMITIVE MEDICINE

Summing up current research one should emphasize the perpetuation into medieval and even modern times of the centuries-old tradition associating wood/birch tar with diverse rituals, attesting to the deeply rooted conviction regarding its role in rites and medicine [Szafrański, Szafrańska 1961: 72ff.; Moszyński 1967: 315-316]. Mentions of magic procedures using wood tar in the beliefs and rites of primitive societies are evidence of this. According to other reports, tar had the power to frighten off demons [Kośko, Langer 1986: 598; Szafrański 1949–1950: 481]. Rituals in which wood tar played a noteworthy role cannot be easily classified owing to their diversity, especially as the surviving information concerns only some of the rites. Links of wood tar with the underworld are reflected, among others, in finds of death masks of the PYC and CaC in Ukraine. The heads of the deceased were coated with a thick layer of 'plastic' tar to prevent their spirits from returning and tormenting the living. Observation of burials of the CaC on the northern coast of the Azov Sea led Klejn to a more functional interpretation, linking the application of wood tar to a pre-burial rite of attaching scalps [1961: 105--109]. A special category of 'ritual tar' can be assumed after Kośko and Langer. It would have been produced ritually, perhaps on specific days of the year, and used in rites that could have been quite distant in time [Kośko, Langer 1986: 598]. It seems that the extensive demand for high quality pure tar in the crafts, folk medicine and prophylactic magic justified the effort put in its production.

New and sometimes spectacular discoveries contribute to the already broad range of birch tar and wood pitch applications in prehistoric times. Lumps of birch bark tar with human bite marks (Fig. 13) from archaeological sites in Germany, Switzerland as well as Sweden and Denmark are among such finds [Larsson 1983; Schlichtherle, Wahlster 1986: 92; Heron and others 1989: 330; Evans, Heron 1993: 449; Aveling, Heron, Larsson 1996]. These Mesolithic and Neolithic finds are obvious proof of chewing or biting off bits of tar. Similar evidence has originated also from other Western European sites [Becker 1990; Hayek and others 1990] and recently also from Polish sites. Lumps of 'hypothetical tar' with human bite

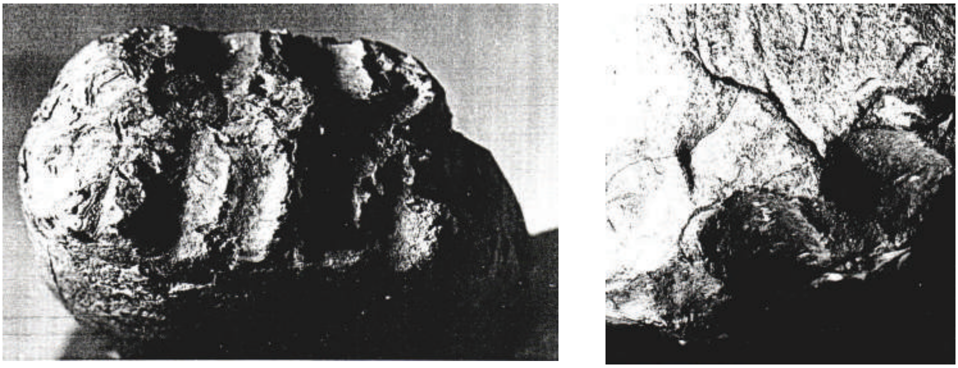


Fig. 13. Lumps of wood tar with human bite marks [Hayek and others 1990: 219-220. Fig. 20-21]

marks recovered from excavations at the multi-cultural site Żuławka 13, Wyrzysk commune, Piła district, Wielkopolskie province, were among the 70 artefacts with traces of tar substances (ceramic vessels, flint tools, lumps of pitch), most probably birch tar, including the pieces with bite marks [Dmochowski 2002: 88-91].

Birch tar may have been used as a kind of primitive ‘chewing gum’ in prehistoric Europe. Chewing this kind of tar releases large amounts of disinfecting compounds, possibly of use in clearing the respiratory system and maintaining oral hygiene. It is very likely that chewing lumps of tar, possibly together with herbs of medicinal properties, brought relief from aching throats and teeth, and it may have also had a whitening effect on teeth [Aveling 1997: 2; Aveling, Heron, Larsson 1996].

An alternative interpretation for lumps of tar with human bite marks from all over Europe, from the Mesolithic through the Bronze Age, is their use by children (aged 6–15) to extract milk teeth and reduce teething pains. It is also possible that it may have been used as a pacifier for small children [Nordqvist 1994].

II.6. RESEARCH PROCEDURES – SAMPLING

Owing to the specificity of organic materials, such as tar substances and carbon deposits, the manner in which this category of sources is treated during excavations and subsequent studies is greatly related to the condition in which the substance is preserved and consequently the way in which it may be interpreted. Routine tasks linked to documenting finds include washing and drying of archaeological artefacts, their inventorying, possible mending and reconstruction, and conservation. At each stage there is a real threat of losing significant data as a result of improper treatment of organic substances.

At the first stage, washing especially of ceramic vessels, could damage or remove from the walls of pots all traces of organic substances, particularly thin layers of pigment coating the surface. Merely scratching the surface of interest to us could largely compromise any conclusions regarding how the substance was applied and its links with the ceramic ground.

At the second stage one should take care not to damage potential tar substances by avoiding inking any marks on surfaces coated with unidentified organic material. Another frequent procedure is to apply a thin coat of white correction fluid or polish in order to be able to write on remains of tar substances covering a ceramic vessel on either side. In many instances this prevents credible physico-chemical laboratory analyses of organic material. To protect pigment on a ceramic surface a protective layer of varnish is often applied, ruining any chances for conducting archaeometric analyses. Inattention on the part of those registering artefacts may result in the loss of sometimes invaluable data on organic substances found on these objects.

Repairs or reconstruction of an artefact, pottery included, leads to mending of potshards with different kinds of adhesives, especially organic ones, which either destroy or severely damage any organic substances on the surface. This excludes or at least hampers later physico-chemical analyses of the artefact. Use of detergents or conservation agents in the case of elements of wooden structures can have the same effect. Samples intended for archeometric research should not be heated or even exposed to the action of the sun's rays.

Organic substances preserved on archaeological artefacts may also be degraded by such actions, as bathing the surface of flint tools with organic solvent in order to carry out functional traseological analyses. The use of organic solvent is essential on the one hand to remove contamination from the surface, allowing analyses to be carried out. On the other, it causes irrevocable damage to organic substances present on archaeological artefacts, whether binders like resin and wood pitch used to mount flint inserts in wooden, bone or antler tools, or other organic substances, remains of plant or animal tissues and traces of blood, which could bring light to bear on ancient diet and activities like hunting associated with procuring food.

The described factors may all significantly compromise any examination of organic samples, hence they should all be taken into consideration when selecting samples for analyses. Foremost, one should keep in mind the proper sequencing of research procedures, permitting the full research potential of artefacts with preserved organic substances to be taken advantage of.

III. RANGE AND METHODOLOGY OF LABORATORY TESTS

Many organic substances recorded in the course of excavations show extensive structural changes hindering credible identification of their original form and function. It is crucial to identify correctly examined substances as any further, more specific laboratory tests and archaeological interpretations would not otherwise be possible.

Physico-chemical methods are used in the examination of vegetable materials surviving on archaeological sites in the form preventing their identification using standard microscopic observations. Such a situation is encountered as a rule in the case of highly comminuted food remains [Heron, Evershed 1993: 247-286; Kimpe, Jacobs, Waelkens 2001: 87-95] and the remains of wood tar in the form of amorphous pitch mass, adhering to vessels and tools and deprived of any traces of anatomical structure [Kośko, Langer 1986: 587-600; Reunanen, Holmbom, Edgren 1993: 175-177; Koller, Baumer, Mania 2001: 385-397; Langer, Pietrzak 2004a: 100-117; Langer 2005; Pietrzak 2010].

In some cases chemical compounds in a fossil organic material of anthropogenic origin may serve as additional criteria for taxonomic classification of subfossil specimens [Philp, Oung 1988: 887A-896A; Poynter, Eglinton 1991: 725--731; Pollard, Heron 1996].

Physico-chemical methods also help identify vegetable substances such as resins [Langenheim 1990: 16-25; Edwards, Farell, Daffner 1996: 1639-1648; Martin *et al.* 2001: 380-384], amber [Lambert, Beck, Frye 1988: 248-263; Jezierski *et al.* 1999: 201-206; Vávra 1999: 219-230], wood pitch and wood tar [Mills, White 1989: 37-44; Hayek *et al.* 1990: 2038-2043; Heron, Nemcek, Bonfield 1994: 266-269; Beck *et al.*1999; Sauter *et al.* 2001: 21-24] and distinguish them from animal substances [Evershed *et al.* 1997: 402-406; Malainey, Przybylski, Sherriff 1999: 95-103; Mottram *et al.* 1999: 209-221], and geogenic organic materials (asphalt, petroleum, bituminous materials) [Rullkötter, Nissenbaum 1988: 618-621; Connan, Deschesne 1991: 152-159; Boëda *et al.* 1996: 336-338].

To examine the available remains of 'putative wood tar", a broad spectrum of Physico-chemical methods was used to overcome the exceptional complexity of problems to be solved.

The assessment of the degree of similarity and difference between the methods of destructive distillation of wood used in prehistoric times is a major problem faced by modern physico-chemical laboratory analysis. A no less important goal, an attempt to determine the function of 'putative wood tar' is followed by the task of identifying possible admixtures in the examined samples and determining the manner substances (wood tar) were applied to the ceramic substratum.

Setting out to examine fossil objects using physico-chemical methods, it is necessary to remember that their effectiveness is much greater when we have results of relevant analyses of present-day materials to compare with the examined sub-fossil specimens. With the present degree of research advancement, this means in practice examining plant species and their organs that live today with those we intend to compare samples obtained on archaeological sites.

III.1. MELTING POINT MEASUREMENT

One of the major analytical methods in preliminary archaeometric examinations is the measurement of melting point. The melting point is a distinctive characteristic of solids, mainly those which have a crystal structure. Substances of high purity melt in a narrow range of temperatures [Vogel 1984: 183-188]. The more impure a substance, the broader the range is, attaining 10° ÷ 30°C for mixtures. It should be stressed here that the melting point of mixtures, with the remains of petrified wood tar being mixtures no doubt, cannot be precisely determined. What can be observed is the range of temperatures between the commencement of melting and its end. It must be stressed here that the range grows with the increase in the amount of impurities.

Groups of substances of specific properties melt in a similar temperature range, making it easier to preliminarily assign examined preparations to a given group of compounds. This allows researchers to draw conclusions about similarities between the chemical composition of compared preparations and find out whether the examined substance has been subjected to the secondary impact of high temperature. Moreover, it can be found which samples consist of heavy ends of wood-tar pitch (obtained in a higher temperature) and which contain lighter ends [Langer 1989: 17, Langer, Kośko 1999: 74].

All melting point measurements were made using a polarizing microscope coupled with a Boëtius Wagem apparatus, model PHMK 05, with a heating stage (in the temp. range of 0 °C to 300 °C), using unrefined non-homogeneous samples. The results are given in Chapter V.1 (Tables 2-21, pp. 143-153).

III.2. SOLUBILITY TESTS

The method of selective solubility is based on differences in chemical properties of wood pitches, mainly on their different behaviour upon contact with chemical reagents. Next to the melting point measurement, this is another method of preliminary examination of archaeological materials which does not call for the use of complicated apparatus and is suitable for making a series of tests of large sample numbers. Owing to the use of solvents of a different polarity and standard samples, it is possible to correlate the examined substances and determine their organic or mineral chemical nature [Vogel 1984: 113]. This method supplies quantitative data and allows researchers to assess the impact of high temperatures on organic substances. Low or zero solubility of examined materials in organic solvents and simultaneous zero solubility in water and water solutions of HCl and NaOH testify to their advanced thermal degradation. Furthermore, this method is also helpful in determining low contents of some mineral components present in organic materials (composite materials) otherwise undetectable, e.g. a positive colour reaction with ammonium thiocyanate (NH_4SCN) attests to the presence of iron compounds [Langer, Pietrzak 2004a: 100-117; Dobrzańska *et al.* 2005].

The results of these tests tell us about the solubility of examined materials, which can be used in examinations requiring the use of liquid preparations: chromatographic tests (TLC), spectroscopic tests (UV-VIS, IR, GC-MS) and in separating samples by the extraction method.

All examined archaeological preparations were subjected to solubility tests in many organic solvents of various polarities:

- – Hexane (C_6H_{14}),
- – Cyclohexane (C_6H_{12}),
- – Carbon tetrachloride (CCl_4),
- – Methylene chloride (CH_2Cl_2),
- – Chloroform ($CHCl_3$),
- – Ethyl acetate ($C_4H_8O_2$),
- – Methanol (CH_3OH),
- – Acetone (C_3H_6O),
- – Tetrahydrofuran (C_4H_8O),
- – Toluene (C_7H_8),
- – Benzene (C_6H_6).
- – as well as in water and in water acid (1 N HCl), and alkaline (10% NaOH) reaction solutions.

As comparative materials were used standard samples of birch and pine tar produced under laboratory conditions.

The assessments of solubility were made by observing qualitative effects (colour changes of solutions):

- – [+++] very good solubility,
- – [++] good solubility,
- – [+] poor solubility,
- – [–] zero solubility.

Standard sample designations:

- Db – birch tar
- Ds – pine tar

To determine the mineral content (iron compounds) of the examined archaeological preparations, a colour test was performed using ammonium thiocyanate (NH_4SCN). The test was preceded by a blank test or adding ammonium thiocyanate to hydrochloric acid (HCl) used in solubility tests. The results are presented in Chapter V.2 (Tables 22-41, pp. 154-176).

III.3. THIN-LAYER CHROMATOGRAPHY

Owing to the complex chemical composition of examined organic substances, the analysis of samples from archaeological excavations is a complicated task. Laboratory tests performed on such preparations aim, in the first place, at their identification by separating examined mixtures and isolating the components which are diagnostic for a given group of substances.

One analytical method helpful in this task is known as Thin-Layer Chromatography. It is fast and very effective, and has many uses such as identification, analysis and separation of organic substances. This is achieved thanks to differences in the speed mixture components moving across a substratum (silica gel) when a solvent is drawn up a coated plate [Randerath 1966; Opieńska *et al.* 1971; Berthiller 1975; Taber 1982: 1351; Wasiak 1982: 94-97; Witkiewicz 1995].

As it was necessary to have liquid archaeological preparations (solutions), only these preparations were subjected to a TLC analysis which dissolved well in organic solvents (Chapter V.2). In comparative tests, as reference samples, wood-tar standard samples were used obtained from birch, pine, oak, beech, spruce, alder, hornbeam and ash wood under laboratory conditions (Chapter V.3). Chromatograms were performed on 60 F_{254} silica gel layers 0.25 mm thick and coated onto glass, aluminium or plastic foil produced by Merck. For chromatographic analysis, extracts were subjected that had been obtained using pure chloroform or, in the case of less soluble preparations, a solvent mixture of chloroform:methanol (3:1). As mobile phases a number of solvents were used that had different polarities: hexane, cyclohexane, carbon tetrachloride, chloroform, methanol in the form of mixtures of various volumetric ratios:

- hexane (C_6H_{14}) : carbon tetrachloride (CCl_4) 5:1 (v:v),
- hexane (C_6H_{14}) : carbon tetrachloride (CCl_4) 3:1 1 (v:v),
- cyclohexane (C_6H_{12}) : chloroform ($CHCl_3$) 10:1 1 (v:v),
- cyclohexane (C_6H_{12}) : chloroform ($CHCl_3$) 5:1 1 (v:v),

– chloroform ($CHCl_3$) : methanol (CH_3OH) 15:1 1 (v:v),
– chloroform ($CHCl_3$) : methanol (CH_3OH) 10:1 1 (v:v).

By far the best separation results were obtained with the mixture of hexane and carbon tetrachloride in the proportion of 3:1 as a mobile phase. Chromatograms were observed in UV radiation of wavelengths λ=254 nm and λ=365 nm.

Small blots of solution of examined substances were applied to a chromatographic plate about 1.5 cm from its bottom edge. After drying it, the plate was immersed in a mixture of solvents which through capillary action was drawn up the plate, thereby separating substance components. Individual components created separate blots characteristic of each substance. Finally, when the solvent approached the top edge, the plate was taken out and dried. To visualize separated colourless substances, plates were viewed in UV light or were subjected to chemical treatment (development). The location of blots representing the individual components of analytes was described using the retardation factor R_f which expresses the ratio of the distance travelled by a blot to the distance the solvent travelled. R_f oscillates between 0 and 1 and is a distinctive feature of any chemical compound – it is constant under given experiment conditions and may be used for identification. In this way, it is possible to count components in archaeological preparations and identify them especially by comparing with standard samples [Hairfield, Hairfield 1990: 41A-45A; Langer; Pietrzak 2004a: 113; Langer 2005: 428, Pietrzak 2010].

Chromatographic tests are a simple method of distinguishing wood-tar samples from somewhat externally similar modern asphalt products and coal pitch, relying on different chromatographic pictures.

TLC tests also allow researchers to prepare selected (diagnostic) organic material fractions for analysis using gas chromatography coupled with mass spectrometry (GC – MS) [Reunanen, Ekman, Heinonen 1989: 35].

TLC calls for minute samples even considerably below 1 mg, although usually samples of 1 – 3 mg are taken. The results are given in Chapter V.3 (Tables 42-52, pp. 177-182).

III.4. MICROSCOPIC OBSERVATIONS

The observations made use of a polarizing optical microscope (POM) of low magnification (80-350 times) to study the structure of archaeological preparations and to assess preliminarily the function and character of finds. Observations in reflected light allow researchers to determine such physical properties as viscosity and the surface moistening capacity of an organic substance (wood tar) upon contact with a ceramic substratum, as well as help detect remains of a raw material (bark or wood) and possible mineral admixtures. This method makes possible high precision imaging of surfaces of examined materials. Microscopic observations tell us how wood tar was applied to the surface of artefacts (ceramic vessels, tools) and what the impact of secondary thermal treatment was [Langer, Kośko 1999]. Microscopic observations also help to distinguish thin layers of petrified wood tar from black colorants applied to the surface of a vessel, especially inorganic ones, by determining the way they are bound to the substratum [Langer 1989: 16].

On the other hand, scanning electron microscopy helps study the morphology details of materials and identify their chemical composition. An image in a SEM is produced by sampling (scanning) examined material with a beam of electrons. The surfaces of archaeological preparations seen as a microscope image have a ‘three-dimensional’ character, owing to the presence of a shadow. The images obtained have lower resolution, which is sufficient however for the study of the morphology of biological materials and structures [Dobrzański, Hajduczek 1987: 163-185; Dobrzańska *et al.* 2005: 237; Kubica-Kabacińska *et al.* 2005: 258, 259; Langer 2005: 431-434]. Selected archaeological samples or their fragments, having been washed in organic solvents and coated with gold in a vacuum sputter, were examined using a Philips SEM 515 scanning electron microscope, providing magnification of 100-5000 times.

Microscopic examinations moreover, are very helpful in the study of organic materials by providing information on their origin, ambient impact and changes they underwent for instance due to high temperature [Maniatis, Tite 1978-1979: 125-129; Józwiak, Langer, Pietrzak 2001: 403-415; Langer, Pietrzak, Groszewska 2008]. It is also possible to detect inorganic admixtures in organic material and identify its microstructure (blood cells – contour-marked areas of higher iron concentration that are not visible on the surface (SEM) [Langer 1997; Langer, Kośko 1999; Alvarez *et al.* 2001: 457-464].

The maximum magnification is 100,000 times at a resolution of 5 nm.

By using both methods of observation, a series of photographs was obtained, the study of which provided detailed information on the production technology of examined preparations (presence of the remains of unprocessed raw material) and their diverse applications. Further, data were obtained on the original uses of archaeological artefacts on which traces of organic products had survived. What is more, it was possible to identify the microstructure of examined preparations (impact of high temperature), the methods of their modification, including the addition of improvers such as mineral components, and the technique of layer application. The results in the form of SEM and POM photographs are given in Chapter V.4 (pp. 183-224).

III.5. INFRARED SPECTROPHOTOMETRY

Infrared Spectrophotometry is a basic analytical technique in chemical laboratories. A relative facility of making spectra, low analysis costs and highly meaningful results make this technique widely used in many fields [Zieliński, Rajcy 2000: 323-388; Sadlej 2002: 162-258].

Absorption of infra-red light exploits the fact that atoms vibrate and rotate in molecules. They vibrate around their axes while their atoms oscillate around balance points. Absorption of infra-red light induces changes in both rotational and oscillational energy of a molecule [Dyer 1967: 31-67; Szczepaniak 1997: 107-129].

The examinations of wood-tar samples used the basic range of the infrared spectrum, covering the wave number interval of 4000-400 cm^{-1} corresponding to the wave length of 2.5-25 μm (MIR – Mid Infrared), which is characteristic of the vibrations and rotations of most molecules and their constituent characteristic atom groups (functional groups). They are characterized by typical, distinctive vibration frequencies that change little upon moving to other atom configurations, making up other molecules. Spectrum images are closely related to the occurrence of given atom groups and are also dependent on the molecule structure (for pure substances – chemical compounds) and on the proportions of components in a mixture. Thus, IR spectra help identify functional groups and substances by comparing them with a standard spectrum or by analyzing characteristic absorption bands [Janowski 1982: 43-46; Oszczapowicz 1982: 52-58; Robinson *et al.* 1987: 639; Martoglio *et al.* 1990: 1123A-1128A; Casadio, Toniolo 2001: 71-78; Langer 2005: 417-420].

An IR spectrum of a substance is commonly considered to be its ‘fingerprint’ – distinctive and unique for a given compound. The identity of spectra obtained under identical conditions is a proof of identity of chemical compounds. Therefore it is possible to compare archaeological materials with standard samples of wood pitches and to determine the structure of compounds by carefully analyzing spectra [Kośko, Langer 1986: 587-600; Regert, Vacher 2001: 20-29; Regert, Rolando 2002: 965-975; Pietrzak 2010].

With this method it is possible to detect the presence of specific, characteristic atom groups (e.g. NH_2, OH, COOH), determining the chemical properties of a substance, its reactivity and processes to which it was subjected as for instance neutralization or thermal treatment. It is also possible to determine the composition of a given material, distinguish organic materials from inorganic ones [Langer, Kośko 1992: 61-68], and geo- and bio-genous from one another (e.g. waxes, oils, bituminous materials) and from anthropogenic ones (wood tars, wood-tar pitches, wood tar) [Langer, Kośko 1999].

IR spectra also show the degree of degradation (e.g. thermal) of organic materials and the temperature at which a given material was heated. Badly degraded organic substances (e.g. charred) are characterized by poorly readable IR spectra, hindering the identification of the original material [Langer 1997a: 136-138; Langer, Kośko 1999: 63-77; Józwiak, Langer, Pietrzak 2001: 403-415]. On the other hand, such a spectrum is proof of a high temperature action, causing thermal degradation and removal of most functional groups from a molecule. As a result, there are no characteristic vibration frequencies in the spectrum or relevant peaks become much less intensive. Thermal processes differ, in their mechanisms, from others also causing degradation, therefore it is generally possible to distinguish end products by determining which process was dominant using IR spectra.

The measurements of IF absorption spectra of wood-tar samples were made on an FTIR spectrometer Bruker IFS 66v/S, using mainly solid samples (1 – 3 mg) dispersed in potassium bromide (KBr – 200 mg). In a few cases, due to the state of preservation of examined preparations, measurements were performed on sample films smeared on salt plates (NaCl) using chloroform solutions. A small amount of substance needed for reliable examinations makes it easy to collect representative samples free from any impurities. In practice, slightly more material is collected: 10 – 100 mg. Results are given in Chapter V.5 (Tables 53-72, pp. 225-253).

III.6. MASS SPECTROMETRY

The principle of mass spectrometry involves the analysis of masses of fragments produced by the break-up of the examined compound under a strong external impact, e.g. an electron beam (EI – Electron Impact Ionization) whose energy is controlled. Molecules are ionized and fragmented with each ion having a distinct mass-to-charge ratio (m/c) [Płaziak, Golankiewicz 1992; Szczepaniak 1997: 345-358; Zieliński, Rajcy 2000: 436-504].

The examined preparations may be gaseous, liquid or solid – the way a sample is introduced depends on its volatility. This method allows one to identify substances by observing the characteristic spectra of the decay of their molecules, distinctively different for each compound. Two different organic compounds never produce identical mass spectra. Meanwhile, substances belonging to the same group of compounds, owing to a similar fragmentation, produce similar mass spectra. It is also possible to explain the chemical structure of substance molecules. The results obtained by this method in the case of contaminated samples are not entirely reliable. Therefore, in the case of mixtures of various compounds (wood pitches) or when samples are contaminated, as is the case with archaeological preparations, MS must be accompanied by a method of preliminary separation, e.g. gas chromatography coupled with mass spectrometry (GC-MS) or high pressure liquid chromatography coupled with mass spectrometry (HPLC-MS) or tandem mass spectrometry (MS-MS) [Langer 1989: 21; 2005: 424-427].

An obvious advantage of this method is the minute size of samples – a fraction of a milligram of a substance is enough, whereas on the negative side is the fact that samples are destroyed, i.e. the original substance cannot be recovered [Johnstone 1975; Hoffmann, Charette, Stroobant 1998]. In practice, samples of 1-5 mg are collected, taking great care to make them representative and prevent their contamination. Even the smallest amount of impurities may considerably hinder interpretation of results or even falsify them.

All this points to the possibility of effective identification of organic substances originating with archaeological excavations, including wood tar, which is illustrated by many studies (e.g. fats and fatty acids [Evershed, Connolly 1988: 143-145; Evershed *et al.* 1995: 8875-8879; Petit-Domingues, Martinez-Maganto 2000: 727-734], resins [Foster, Zinkel 1982: 89-98; Hairfield, Hairfield 1990: 41A-5A; Proefke *et al.* 1992: 105A-111A; Weser *et al.* 1998: 511A-516A; Schneider, Kenndler 2001: 81-87], beeswax [Wiedemann, Bayer 1982: 619A-628A; Evershed *et al.* 1997: 979-985; Evershed *et al.* 2003: 1-12], wood tar and wood pitch [Kośko, Langer 1986: 587-600; Langer 1994: 182-183; Dudd, Evershed 1999: 359-362; Regert, Vacher 2001: 20-29]).

The GC-MS spectra of archaeological preparations were recorded on a Hewlett Packard II 5890 chromatograph, DB-1 column, coupled with an AMD-Intectra GmbH-Harpstedt D-27243 mass spectrometer, Model 402. The results in the form of GC-MS spectra are given in Chapter V.6 (pp. 254-255).

III.7. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

This method is based on measuring the absorption of radio waves by a sample placed in a strong magnetic field. Most often, use is made of the interaction between radio waves and the nuclei of a hydrogen atom (^{1}H – NMR). The recorded spectrum form (number and shape of signals) depends on the molecule structure of a compound and allows one to assess the number and kind of hydrogen atom groups comprised by the molecule [Oszczapowicz 1982: 52-58; Zieliński, Rajcy 2000: 67-202; Sadlej 2002: 337-414].

Nuclear magnetic resonance serves to identify compounds and examine molecule structure. In the examination of archaeological materials, NMR helps to describe and identify them [Cassar *et al.* 1983: 238-239; Cunningham *et al.* 1983: 965-968; Lambert, Beck, Frye 1988: 248-263; Martinez-Richa *et al.* 2000: 743-750]. NMR may be also indirectly helpful in assessing the degree of degradation of organic materials, determining the mechanisms of degradation processes and gauging the effect of the environment on the samples of wood pitches [Langer 2005: 422-424].

With the increase in thermal degradation, ^{1}H-NMR spectra contain increasingly more intensive signals corresponding to aromatic compounds (7 – 9 ppm) at the expense of saturated group signals (0 – 3 ppm). In the extreme case of the advanced graphitization of organic materials, ^{1}H-NMR signals fade away even when magic angle spinning (MAS NMR) is used.

This is caused by, on the one hand, decrement of hydrogen atoms responsible for ^{1}H-NMR resonance and on the other, increase in interactions between atomic nuclei and free electrons found in badly charred materials. Such interactions result in a very considerable broadening of resonance lines observed on NMR spectra.

This analytical method is a very effective research tool which can be used best with uncontaminated substances. NMR examinations produce also good results with the analysis of mixtures (e.g. wood pitches), for they allow researchers to detect the presence of certain classes of chemical compounds (e.g. saturated and unsaturated, including aromatic and olefin ones) and determine their proportions [Dyer 1967; Janowski, Dąmbska 1982: 47-51; Szczepaniak 1997: 132-143].

The amount of substance necessary to perform a test depends on the method used and usually stays between 5 and 100 mg.

Thus ^{1}H NMR spectra were recorded on a Varian Gemini 300 VT (300 MHz) spectrometer in deuterated chloroform while chemical shifts were given in δ values [ppm]. The results in the form of ^{1}H NMR spectra are given in Chapter V.7 (pp. 256-258).

III.8. ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Electron paramagnetic resonance is a very sensitive technique of detecting organic radicals, inorganic structures and ions with magnetic properties [Kobiela 1982: 59-65; Stankowski, Hilczer 1994: 54-74; Sadlej 2002: 415-430].

The technique consists in studying configurations with unpaired electrons. EPR measurements are made against a standard (1,1-diphenyl-2-picrylhydrazyl, DPPH) to determine the spectroscopic splitting factor (g) of the examined sample and calibrate the intensity scale. Its principle of operation takes advantage of paramagnetic centres – configurations related to the presence of unpaired electrons of a stable magnetic moment. Factor g specifies the energy of interaction between the total magnetic moment of the configuration and the magnetic field. For most paramagnetic centres in a molecule, the factor oscillates around the value of 2.

For a given radiation value, the resonance of various paramagnetic centres is observed at various values of the external magnetic field. In effect, an EPR spectrum is obtained.

All the EPR spectra of archaeological preparations were recorded on a Radiopan SE/X 2547 spectrometer. The calculations of gyromagnetic ratio (*g*) of an electron were performed according to the following formula:

$$g = \left(\frac{1}{1.3996} \right) \times \left(\frac{b}{B_0} \right) \Big/ 10000$$

b – mean of frequency modulation [Hz]

B_0 – magnetic field strength, [mT], and the width of resonance line (ΔH) was determined as well.

EPR spectra supply information on the immediate vicinity of a paramagnetic centre in a molecule. The dependence of spectroscopic factor (g) and line width (ΔH) on the temperature of production or treatment of examined material reflects its thermal history. Samples showing greater line width ΔH and a higher value of factor g were subjected in the past to treatment in lower temperatures and, vice versa, recorded lower values of ΔH and g attest to the action of higher temperatures. The older the preparations, the higher the factor g.

In the study of archaeological preparations, the technique of EPR, thanks to its high sensitivity, is used to confirm conjectures about the organic origin of samples subjected to high temperatures (organic radicals) and to determine the thermal conditions they were in previously (‘thermal history’) [Robins *et al.* 1978: 703-704; Hillman *et al.* 1983: 1235-1236; Hillman *et al.* 1985: 49-58; Sales *et al.* 1987: 103-109; Krzyminiewski, Langer, Kośko 1998: 131-137; Langer 2005: 421, 422]. With this technique, it is possible to determine the age of samples too [Grün *et al.* 1997; Marsh, Rink 2000; Grün, Beaumont 2001: 467-482; Hoffmann, Mangini 2003].

The advantage of the EPR is the possibility it offers to study composite materials composed of an organic portion, having the nature of a binder, and a mineral portion, which is greater by volume and acts as a filler. Moreover, it is also possible to examine very thin layers of organic materials (below 1.0 mm) badly contaminated by inorganic substances coming from the ceramic substratum (e.g. organic colorants on outer vessel surfaces) [Bensimon *et al.* 2000: 1623-1632; Józwiak, Langer, Pietrzak 2001: 403-415; Langer, Pietrzak 2004b].

Tests call for very small samples (usually 1-100 milligrams, depending on the intensity of the observed signal), which can be solid, liquid even gaseous. A sample is not destroyed during measurement – it can be preserved or used in other tests. The results are given in Chapter V.8 (Tables 73-111, pp. 259-279).

IV. INTERPRETATION OF PHYSICO-CHEMICAL EXAMINATIONS

Most organic archaeological finds, including tar (Chapter IV.1.1) and bituminous (Chapter IV.1.2) substances as well as composite materials (Chapter IV.1.3), subjected to standard analytical procedures, (Chapter IV) demonstrate considerable structural changes. In some cases the changes prevent a credible identification of the material of the finds and make the determination of their original form and function much harder. The question of material identification (Chapter IV.1) and technological variation, including an attempt to determine raw material species, was given priority because it is prerequisite to finding answers to other problems raised here. These include identification of the types of wood tar (Chapter IV.1.1) bituminous (Chapter IV.1.2) and composite (Chapter IV.1.3) substances and the ways they were applied (Chapter IV.2). Furthermore, the modification techniques of the products of wood and bark dry distillation will be discussed together with a general outline of technological and functional varieties of examined materials. Finally, an attempt will be made to identify raw materials, technologies and application of wood tar in various times and cultures (Chapter IV.3).

IV.1. IDENTIFICATION OF PRODUCTION TECHNOLOGY OF EXAMINED SUBSTANCES

Laboratory tests show that all examined samples can be identified with either wood-tar, bituminous and composite substances and can be divided into six major technological groups according to their properties. The six groups were distinguished relying on the common properties of the samples: the content of esters (COOR), carboxylic acids (COOH) and their salts (carboxylates, $RCOO^-$), presence of mineral components, behaviour in organic solvents and under thermal degradation. The division of examined materials presented below follows earlier works [Langer, Pietrzak 2000; 2004; 2004a] and experience gathered by the Archaeometric Laboratory, AMU Faculty of Chemistry, Śrem. The model, however,

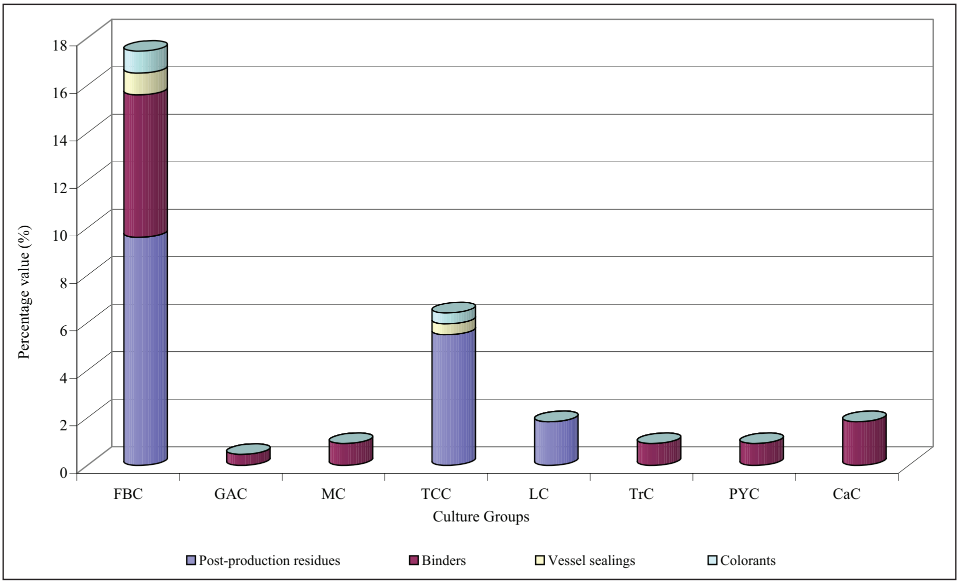


Chart 1. Percentages of Technological Group I materials according to particular functional categories

has been slightly modified and expanded to suit the special character of examined preparations.

IV.1.1. EXAMINATION RESULTS OF WOOD-TAR SUBSTANCES

IV.1.1.1. TECHNOLOGICAL GROUP I

Wood-tar substances comprised in this technological group form a set of 67 preparations coming from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and from one of comparative territories (*Cycle of cultural systems of the steppes and forest-steppes of Eastern Europe*) which accounts for 30.7 per cent of all examined materials. The percentages of wood-tar substances from Technological Group I in the inventories of particular cultural units are shown in Chart 1.

Technological Group I is represented by typical wood-tar materials (Fig. 14) with a high content of saturated compounds and hydrocarbon substituents consisting chiefly of CH_2 and CH_3 groups (fatty acids and alcohols; FTIR: ~ 2926 cm^{-1}, ~ 2854 cm^{-1}, ~ 1456 cm^{-1}, ~ 1376 cm^{-1}), including carboxylic acids (COOH – satu-

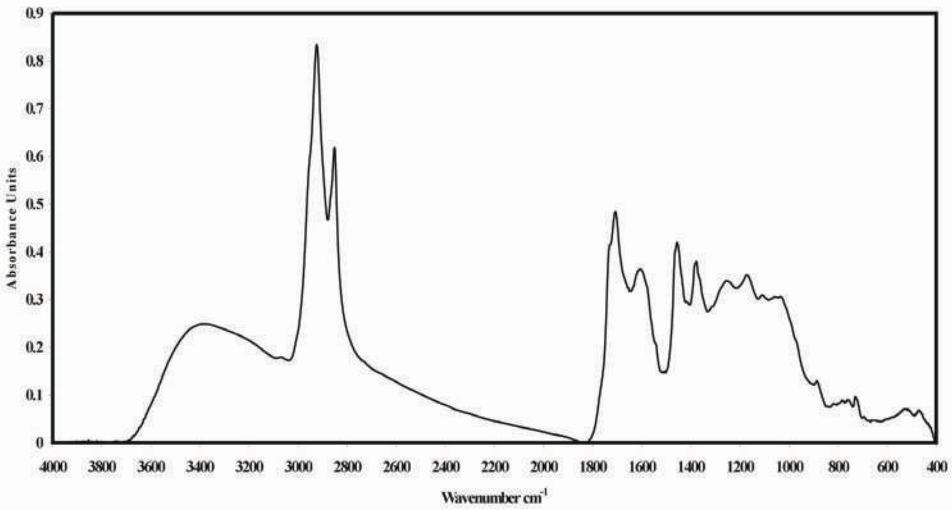


Fig. 14. A typical infrared spectrum of wood-tar substances of technological group I

rated and unsaturated fatty acids; FTIR: ~ 1710 cm^{-1}) and their esters (COOR – fats; FTIR: ~ 1733 cm^{-1}) and a low content of carboxylic acid salts (RCOO^{-}; FTIR: ~ 1600 cm^{-1}) as well as random admixtures of mineral substances FTIR: 1100 – – 1000 cm^{-1}). The last-mentioned substances were also found in EPR tests (paramagnetic substances – g is about 1.8485 – 2.9804 and ΔH is about 36.42 – 167.33 mT – Chapter V.8). Small amounts of unsaturated compounds are recorded as well, containing double bonds in a molecule (FTIR: ~ 3065 cm^{-1}). The content of free organic acids allows researchers to distinguish three sample types in the examined materials (Chapter V.5), according to which acids dominate in them:

- aromatic acids (FTIR: ~ 1700 cm^{-1}),
- unsaturated acids (FTIR: 1703-1710 cm^{-1}),
- saturated acids (FTIR: 1711-1718 cm^{-1}).

Wood-tar substances assigned to this group are the lightest and medium ends of wood tar obtained by dry destructive distillation of wood or bark (a much higher content of, respectively, esters – FTIR: ~ 1733 cm^{-1} and carboxylic acids – FTIR: ~ 1710 cm^{-1}). Wood as a raw material for producing some samples is indicated by a much higher amount of esters in relation to carboxylic acids caused by a high cellulose content (cellulose of a different composition and a higher molecular mass than in bark) in the products of wood pyrolysis [Surmiński 1996]. Whereas a high amount of carboxylic acids, in relation to their esters, attests to the use of bark for producing wood tar (Chapter V.5).

Most archaeological preparations included in this group are products obtained from birch wood or bark (FTIR: ~ 884 cm^{-1} and ~ 730 cm^{-1}; TLC: R_f

about 0.24 – 0.28 in the mobile phase of hexane – carbon tetrachloride 3:1). A noticeable absence of diagnostic fractions – low-polar of R_f of about 0.80 and medium-polar of R_f from about 0.42 to 0.46 and from 0.52 to 0.56 – precludes the identification of these substances as pine, oak, spruce, hornbeam or ash tar (Chapter V.3). A marked similarity to birch tar is revealed by the tests of high polarity fractions using a solvent composed of chloroform and methanol in the proportion of 10:1 or 5:1. Under other separation conditions (Merck silica gel, hexane – carbon tetrachloride 3:1), a diagnostic substance for the preparations under examination is the substance that is also present in the standard sample of birch tar the value of R_f of which varies from about 0.24 to 0.28 and which is not found in any other standard sample (Chapter V.3). Fewer samples were obtained from pine or birch-pine raw material, which is evidenced by FTIR absorption: ~ 860 cm^{-1} and the presence of both birch-tar diagnostic substance of a higher polarity and R_f from about 0.23 to 0.29 and medium polarity fractions characteristic of the pine standard sample with the value of R_f varying from about 0.36 to 0.39 and from 0.46 to 0.48 (Chapter V.3).

Group I materials stand out from the others because of their partial or complete solubility in organic solvents (Chapter V.2) and softening and melting points below 300 °C (Chapter V.1). In most cases, melting point values confirmed that the archaeological preparations had not been heated above the temperatures of their decomposition (they must have been applied in low temperatures away from the source of intense heat, for instance, a hearth). Among the examined preparations, some substances and out owing to their softening and melting points that are lower than those normally observed, confirmed solubility in low-polarity solvents (e.g. hexane, cyclohexane) and strong infrared absorption (FTIR) caused by saturated compounds with hydrocarbon substituents built of long chains composed of CH_2 and CH_3 groups: ~ 2926; ~ 2854; ~ 1456; ~ 1376 cm^{-1}, that surpasses in intensity normal values observed for standard samples (Chapter V.5). These characteristics point to the possibility of intentional modification of wood tar by adding vegetable and/or animal fats in order to lower its softening and melting points. The organic character of all examined materials in this group is confirmed by the detection of carbon radicals (EPR: g about 2.0025 – 2.0035 and ΔH about 0.4 – 0.61 mT) (Chapter V.8). Curiously enough, this group was found to contain examples of all the distinguished categories of wood-tar application: post-production remains, binders, vessels sealings and colorants (Chapter IV.2).

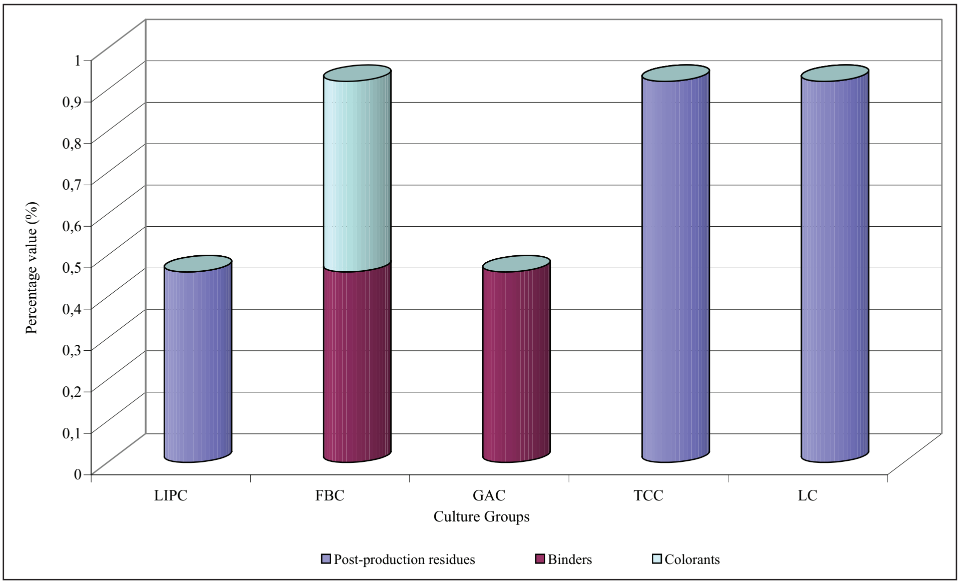


Chart 2. Percentages of Group II tar substances in particular functional categories

IV.1.1.2. TECHNOLOGICAL GROUP II

The group consists of only eight preparations originating solely from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and accounts for 3.7 per cent of all pitch substances examined. The percentages of Group II tar substances in the inventories of particular cultural units is shown in Chart 2.

The group comprises tar substances (Fig. 15) having a similar content of esters (FTIR: ~ 1733 cm^{-1}), carboxylic acids (FTIR: ~ 1710 cm^{-1}) and their salts (carboxylates RCOO-, FTIR: ~ 1600 cm^{-1}), a much lower amount of saturated substituents consisting of CH_2 and CH_3 groups (FTIR: ~ 2926 cm^{-1}, ~ 2854 cm^{-1}, ~ 1456 cm^{-1}, ~ 1376 cm^{-1}), a very low content of double bonds in molecules or a total absence thereof (FTIR: ~ 3070 cm^{-1}) and a small addition of mineral components (FTIR: ~ 1030 cm^{-1}). The tar substances contain only two types free organic acids:

– aromatic acids (FTIR: ~ 1700 cm^{-1}),
– unsaturated acids (FTIR: 1703-1710 cm^{-1}).

The raw material used to produce the preparations was birch wood or bark, which is shown by infrared absorption (FTIR) of about ~ 884 cm^{-1} and ~ 730 cm^{-1} observable also in the birch standard sample (Chapter V.5, Table 53). Whereas no absorption at about ~ 860 cm^{-1}, characteristic of the pine standard sample, precludes the use of pinewood or bark to produce the preparations (Chapter V.5, Table 53).

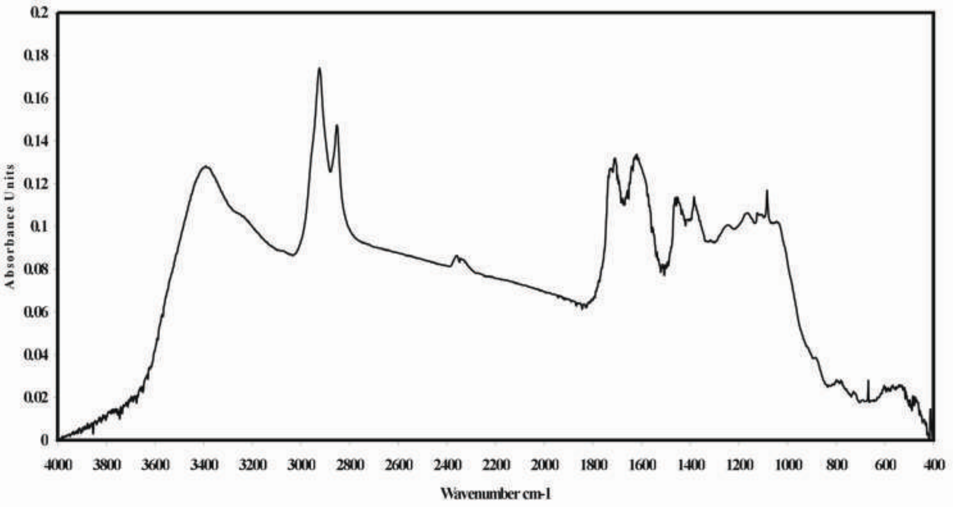
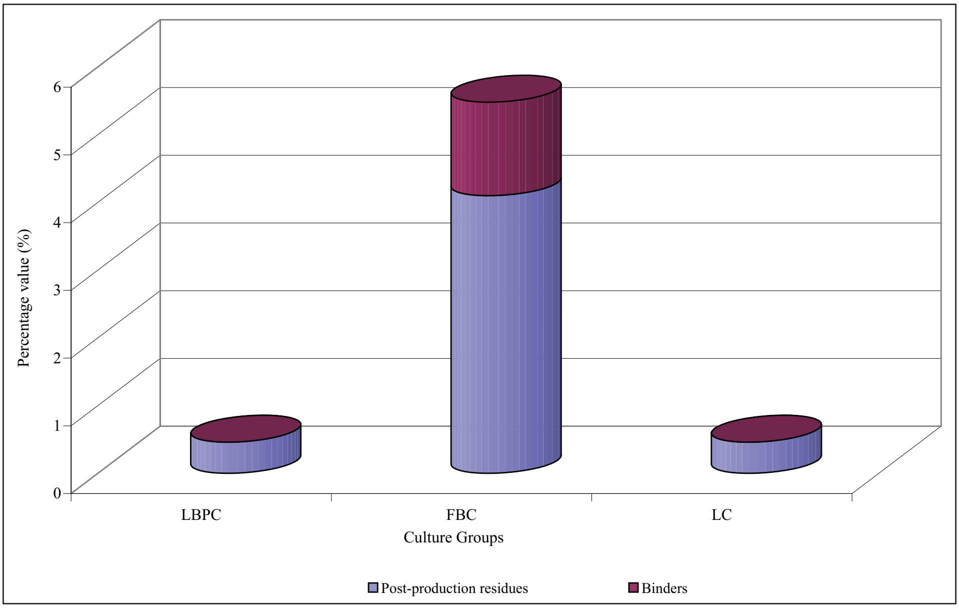


Fig. 15. A typical infrared spectrum (FTIR) of Group II wood-tar substances

The samples in this group are characterized by an increased thermal resistance, in comparison to Group I tar substances, which is seen in melting points above 300 °C (Chapter V.1) and limited solubility in organic solvents (Chapter V.2).

Detected in chromatographic tests (TLC), a diagnostic fraction with R_f from about 0.24 to 0.26 (hexane – carbon tetrachloride 3:1), corresponding to the standard birch sample (Chapter V.3), as in the case of Technological Group I, testifies to the birch origin of the samples. These are medium and heavy wood tar fractions and tar materials subjected later to thermal modification. This is true for both post-production remains (re-processing) and binders and colorants (thermal stabilization of wood-tar substances). The presence of organic radicals ascertained in EPR tests (g of about 2.0022 – 2.0042 and ΔH of about 0.45 – 0.85 mT) confirms unequivocally the organic nature of the samples (Chapter V.5). The similar intensity, location and width of EPR lines, corresponding to the presence of organic radicals in all the archaeological preparations, prove that the wood tar was produced under similar conditions and its samples share a thermal history [Krzyminiewski, Langer, Kośko 1998: 131-137; Józwiak, Langer, Pietrzak 2001; Langer, Pietrzak, Cichocka 2004]. Whereas signals of the following parameters: g of 1.9842 – 2.4648 and DH of 45.41 to 130.13 mT, correspond to the presence of paramagnetic components (mineral substances left by inadvertent contamination of samples) (Chapter V.8).

Deserving separate attention, wood-tar substances of a mixed character, combining the characteristics of Technological Groups I and II, have physico-chemical properties making them close to Group I materials while failing to melt below



C h a r t 3. The percentages of Group I/II tar substances in particular functional categories

300 °C or displaying very low solubility in organic solvents. The latter property, in turn, is characteristic of the preparations included in Technological Group II.

As these preparations are so similar to both groups, no description of them is given. They make up a small assemblage of pitch substance finds, counting altogether 14 samples originating solely from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and accounting for 6.4 per cent of all source materials examined. The percentages of Group I/II tar substances in particular functional categories are shown in Chart 3.

IV.1.1.3. TECHNOLOGICAL GROUP III

Technological Group III comprises pitch substances represented by a set of 30 preparations coming from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and one of the comparative territories (*Cycle of cultural systems of Eastern Europe's forest zone*) which account for 13.8 per cent of all materials examined. The percentages of Group III tar substances in the inventories of particular cultural units are shown in Chart 4.

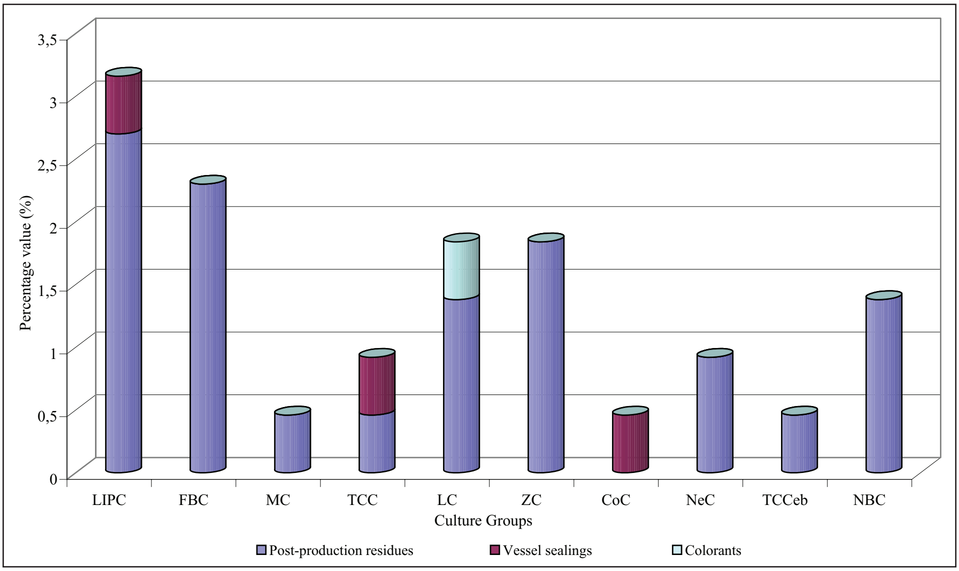


Chart 4. The percentages of Group III tar substances in particular functional categories

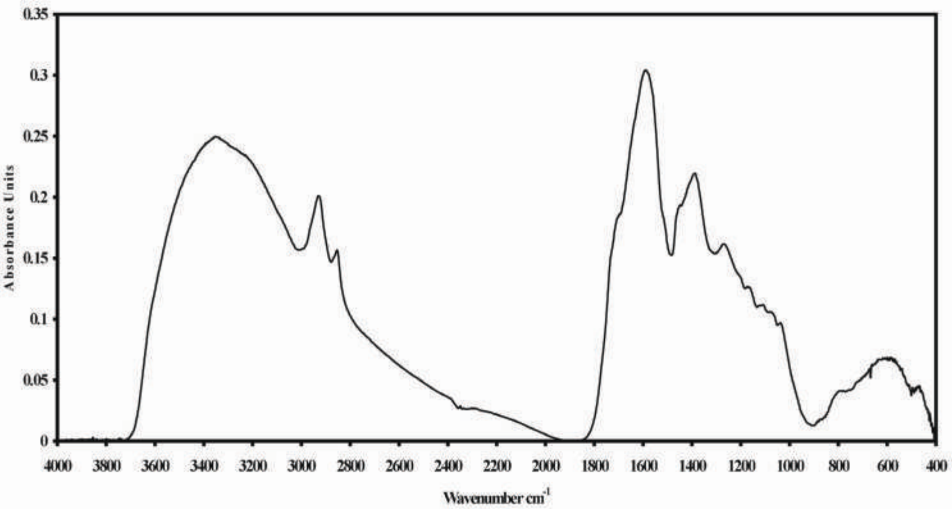


Fig. 16. A typical infrared spectrum of Group III wood-tar substances

The materials comprised in this group are organic substances (Fig. 16) with a clearly dominant content of carboxylic acids (RCOO-, FTIR: ~ 1600 cm^{-1}), as well as saturated substances but containing even fewer CH_2 and CH_3 groups (FTIR: ~ 2922 cm^{-1}, ~ 2851 cm^{-1}, ~ 1442 cm^{-1}, ~ 1376 cm^{-1}) in molecules (Chapter V.5).

The dominating amount of carboxylic acids may result from a random contact of the examined materials with basic environment components (soil or ceramic substratum). It cannot be excluded, however, that wood-tar substances were purposefully modified by neutralizing organic acids to bring their aggressive action to a minimum. Purposeful neutralizing of acid while producing wood-tar substances is very likely as it greatly lowers the reactivity of the wood-tar layer with the substratum, especially so when the substratum has a high content of calcium carbonate (limestone, calcite).

The samples in this group are wood-tar substances mostly thermally degraded which neither melt below 300 °C (Chapter V.1) nor dissolve in organic solvents (Chapter V.2), which prevents identification of the material they were made from (diagnostic substances were removed under the influence of high temperature). This conclusion is borne out by the absence of ester functional groups and a low content of acid ones ascertained by infrared tests. The organic character of samples was confirmed by the presence of organic radicals in EPR tests (g of about 2.0025 – 2.0041 and ΔH of about 0.38 – 0.84 mT – Chapter V.8). A contact with a source of high temperature, in the case of post-production residues, could have taken place when producers neglected to control the secondary processing of wood-tar substances (heating). Whereas vessel sealings and colorants were purposefully subjected to annealing, which increased the network density of the samples. The annealing made wood-tar substances adhere more strongly to ceramic vessel surfaces and made them more heat resistant. This, in turn, enabled such ceramic vessels to be used in high temperatures, for instance, in a hearth.

IV.1.1.4. TECHNOLOGICAL GROUP IV

This is a relatively numerous group of pitch substances counting 49 samples coming from both the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and one of the comparative territories (*Cycle of cultural systems of Eastern Europe's forest zone*) which account for 22.5 per cent of all substances examined. The percentages of Group IV tar substances in the inventories of particular cultural units are shown in Chart 5.

The tar substances included in this group (Fig. 17) are characterized by a negligible content of organic compounds consisting of saturated hydrocarbon radicals CH_2 and CH_3 (FTIR: ~ 2925 cm^{-1}, ~ 2850 cm^{-1}). What sets this group of materials apart is the strong charring of organic substances, which differ greatly in their properties from typical wood-tar samples (archaeological and modern). Group IV samples do not melt below approx. 300 °C (Chapter V.1) nor do they dissolve in

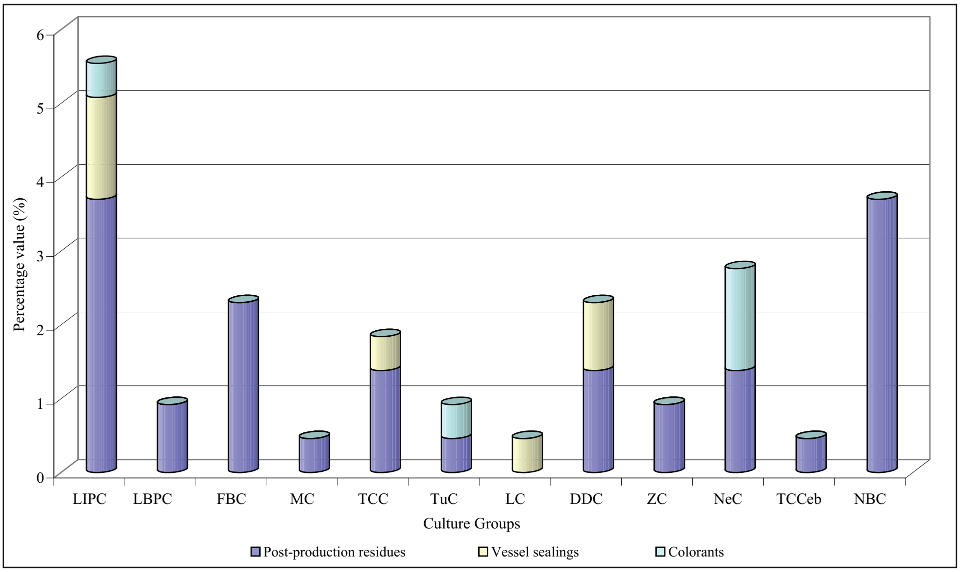


Chart 5. The percentages of Group IV tar substances in particular functional categories

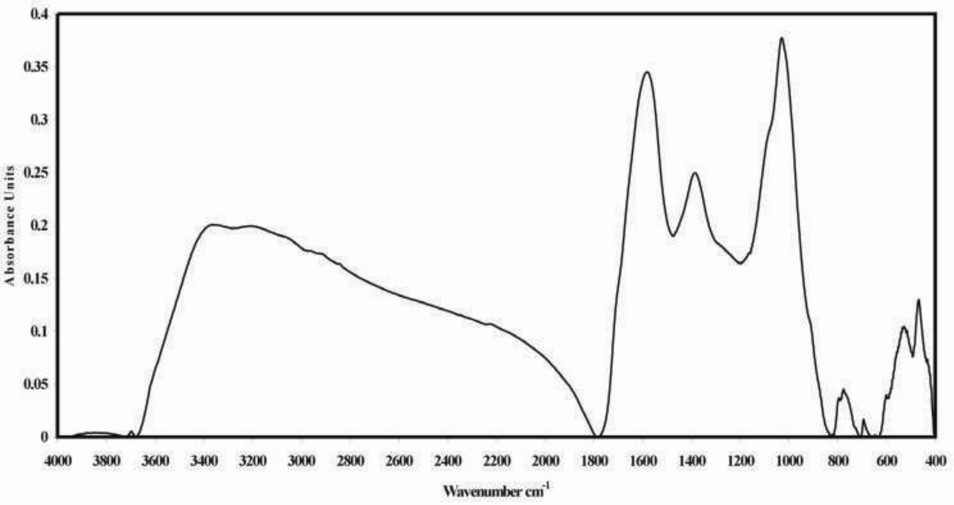


Fig. 17. A typical infrared spectrum of Group IV wood-tar substances

organic solvents (Chapter V.2) and their infrared spectra (FTIR) (Chapter V.5), although characteristic, consist of few broad, high-intensity absorption bands with their maxima around: ~ 3300 cm^{-1}, ~ 1600 cm^{-1}, ~ 1390 cm^{-1} and ~ 1030 cm^{-1} and very low absorption at ~ 2925 cm^{-1} and ~ 2850 cm^{-1}. By these properties they resemble inorganic materials. Whereas absorption observed around ~ 1030 cm^{-1} is related to the presence of mineral substances being random contaminants, which was borne out by EPT tests finding paramagnetic components (g of about 2.0018 – 2.2900 and ΔH of about 0.33 – 1.59 mT – Chapter V.8). The organic nature of samples is confirmed by the presence of organic radicals (g of about 2.0030 – 2.0033 and ΔH of about 0.45 – 0.56 mT – Chapter V.8).

Interestingly enough, Group IV samples were found to have had many uses in the past. They occur as post-production residues on the inner surfaces, sealing layers on inner and outer surfaces or thin colorant layers on outer surfaces of ceramic vessels.

Noticeably strong thermal degradation of samples (greater than in the case of Technological Groups II and III) could be a result of a failure to control temperature during the technological process or a leak (crack) in part of the production set. In the case of some samples (sealings and colorants), the technology of thermal stabilization of wood-tar layers on vessel surfaces was used. The action of high temperature could have triggered, after it exceeded 400 °C, the process of carbonization of organic compounds which, with temperatures rising further, ultimately leads to almost pure coal being produced, whose properties resemble those observed. Hence, any possibility to identify the raw material (wood and bark species) from which the samples were produced is precluded.

IV.1.2. EXAMINATION RESULTS OF BITUMINOUS SUBSTANCES

IV.1.2.1. TECHNOLOGICAL GROUP V

Technological Group V includes a single sample of a colorant, having the nature of geogenous substance, coming from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*), which accounts for 0.5 per cent of all materials examined (Chart 6).

In this technological group, a different category of organic substances was included, namely bituminous materials (Fig. 18) which show a dominating content of saturated hydrocarbon derivatives (large amounts of CH_2 and CH_3 groups, FTIR: 2924 cm^{-1}, 2854 cm^{-1}, 1457 cm^{-1}, 1377 cm^{-1}) with high melting points (above 300 °C) and negligible contamination with mineral components. Small amounts of aromatic hydrocarbons (FTIR: 3027 cm^{-1}, 1532 cm^{-1}, 1483 cm^{-1}, 989 cm^{-1}, 763 cm^{-1} i 720 cm^{-1}) were detected as well.

In this group, geogenous materials of hydrophobic properties were included (which is attested by the negligible absorption of OH groups, FTIR: 3300 cm^{-1}). Substances of this kind are not produced by ‘dry distillation’ (pyrolysis) of wood or

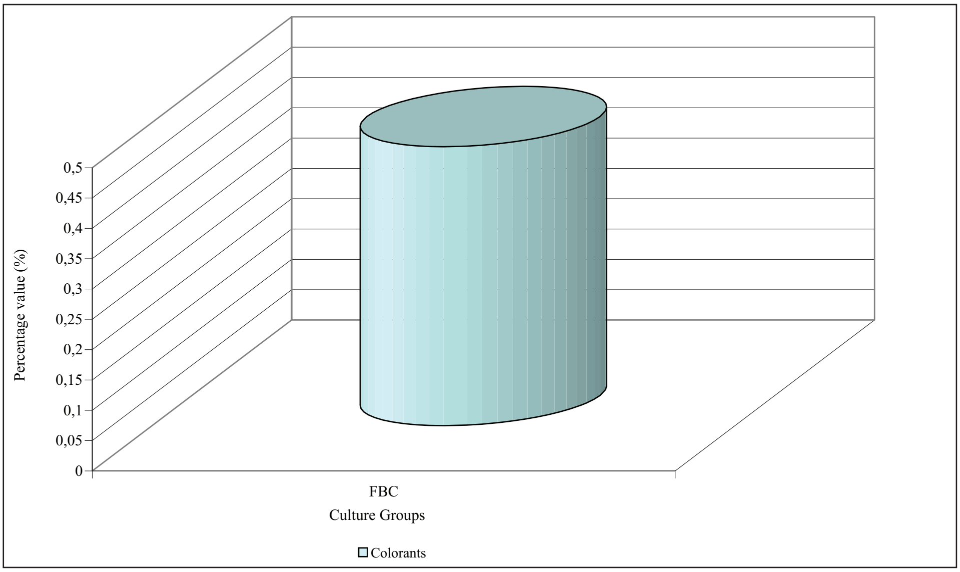


Chart 6. The percentages of Group V materials in particular functional categories

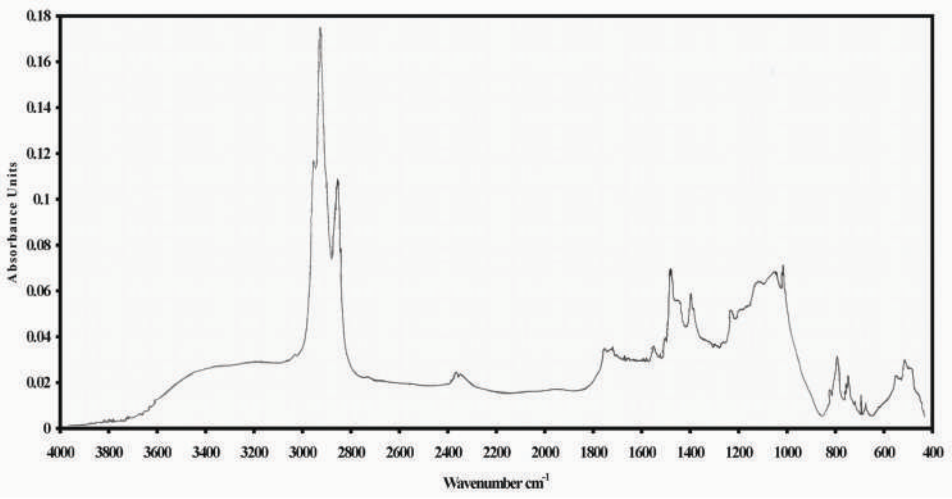


Fig. 18. A typical infrared spectrum of Group V bituminous substances

bark. They were also found to be absolutely insoluble in organic solvents. (Chapter V.2). The organic nature of the bituminous substances, included in Group V, was borne out by carbon radicals detected in the samples (g of about 2.0024 and ΔH of about 0.5 mT – Chapter V.8). Until now, the use of bituminous materials for applying a thin layer onto the outer surface of pottery has been recorded only as vessel ornamentation among FBC societies in Kujawy [Langer, Kośko 1998: 72].

IV.1.3. EXAMINATION RESULTS OF COMPOSITE SUBSTANCES

IV.1.3.1. TECHNOLOGICAL GROUP VI

The pitch substances of Technological Group VI are represented by 49 samples coming from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and two comparative territories (*Cycle of cultural systems of Eastern Europe's forest zone* and *Cycle of cultural systems of the Carpathian Basin*). They account for 22.5 per cent of all source materials examined; a share comparable to that of Technological Group 4. The percentages of Group VI composite substances in the inventories of particular cultural units are shown in Chart 7.

Technological Group VI, comprising composite materials (wood-tar derivatives) (Fig. 19), is characterized above all by the dominating content of purposefully-added mineral components (FTIR: ~ 1085 cm^{-1}, ~ 1030 cm^{-1}) in contrast to a very low amount of saturated compounds with hydrocarbon substituents primarily made up of CH_2 and CH_3 groups (FTIR: ~ 2929 cm^{-1}, ~ 2854 cm^{-1}, ~ 1455 cm^{-1}, ~ 1387 cm^{-1}) and carboxylic acid salts (RCOO-, FTIR: ~ 1600 cm^{-1}). Infrared spectra (FTIR) show also a small share of OH groups (~ 3400 cm^{-1}). The absorption bands of mineral substances (FTIR: ~ 1085 cm^{-1}, ~ 1030 cm^{-1}) and (FTIR: ~ 798 cm^{-1}, ~ 777 cm^{-1}, ~ 726 cm^{-1}, ~ 694 cm^{-1}, ~ 645 cm^{-1}, ~ 565 cm^{-1}, ~ 467 cm^{-1}) indicate the presence of silica (SiO2) and sulphates, phosphates and carbonates. A pitch (wood-tar) substance served as an organic binder while mineral components were used as a filler. As a result of these modifications, an externally homogeneous material was produced, with the borders between conglomerate components macroscopically visible. Despite a dominating amount of mineral substances observable in FTIR (~ 1100 – 1000 cm^{-1}) and EPR spectra (paramagnetic components with g of about 1.8150 – 2.4892 and ΔH of about 27.06 – 130.7 mT) carbon radicals were detected as well (g of about 2.0020 – 2.0048 and ΔH of about 0.45 – 1.97 mT) (Chapter V.8), testifying to the organic origin of the samples.

Considering the hybrid character (organic-mineral) of the composite substances, it can be claimed that their producers attached great importance to the increased durability of the materials so modified (abrasion-resisting layers). They were used solely as colorants on outer vessel surfaces and as layers sealing the microporous structure of ceramic container walls. Some samples in this group were subjected to the heat setting of layers, which is attested by their absolute insolubil-

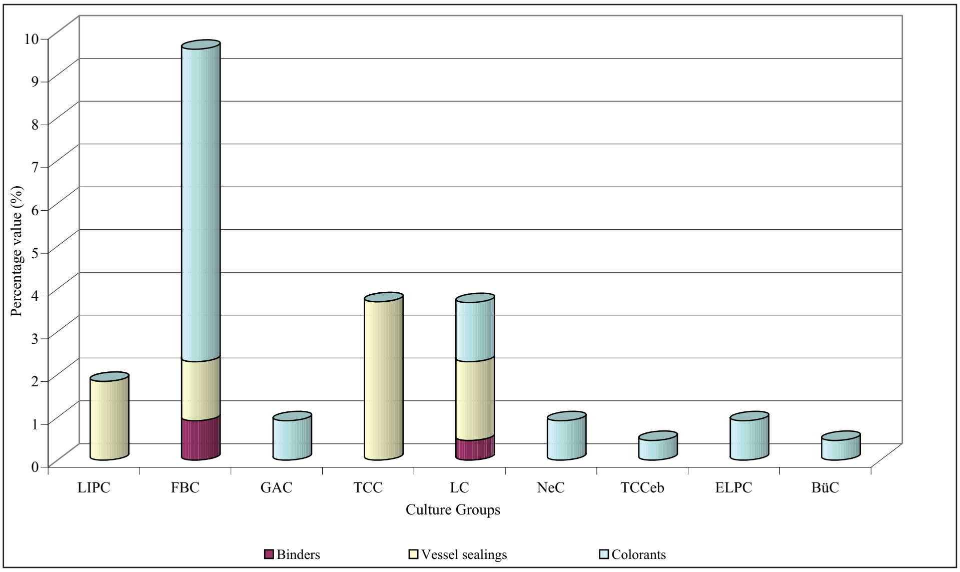


Chart 7. The percentages of Group VI composite substances in particular functional categories

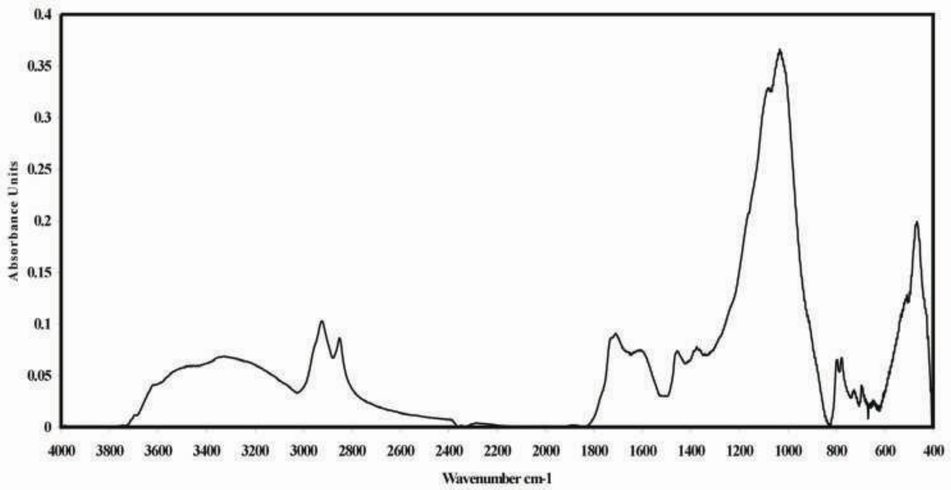


Fig. 19. A typical infrared spectrum of Group VI composite substances

ity in organic solvents and a failure to melt below 300 °C. This, in turn, prevents researchers from drawing any conclusions as to the raw material (wood or bark) used to produce the substances.

Among composite materials, one can also distinguish other substances whose physico-chemical properties (good solubility in organic solvents, melting point below 200 °C) indicate a considerable similarity to typical wood-tar samples. The similarity is reinforced by a large share of saturated compounds, with hydrocarbon substituents consisting mainly of CH_2 and CH_3 groups (FTIR: ~ 2929 cm^{-1}, ~ 2854 cm^{-1}, ~ 1455 cm^{-1}, ~ 1387 cm^{-1}), a smaller amount of carboxylic acid salts (RCOO-, FTIR: ~ 1600 cm^{-1}) and a dominating amount of inorganic substances (FTIR: ~ 1085 cm^{-1}, ~ 1030 cm^{-1}). The preparations were obtained from birch wood or bark (FTIR: ~ 884 cm^{-1} and ~ 730 cm^{-1}, which is also seen in the birch standard – Chapter V.5, Table 53; TLC: a diagnostic fraction of R_f from about 0.24 to 0.26, hexane – carbon tetrachloride 3:1 – Chapter V.3), as well as from pine or birch-pine raw material. This is also attested to by the presence of the high-polarity birch-tar diagnostic substance of R_f of about 0.24 and a medium polarity fraction characteristic of the pine standard of R_f of about 0.36 and about 0.48 (Chapter V.3).

IV.2. IDENTIFICATION OF APPLICATIONS

The investigations towards identification of applications for all and any materials subjected to physico-chemical analysis have shown the necessity for grouping the tars into four fundamental functional categories, i.e. post-production residues, binders, vessel sealing agents and colorants. The properties ascribed to each of the categories are functional and ascertained primarily through macrographic observations and microscopic examinations, the latter supported by other physico-chemical methods (Chapter V). A wide range of physico-chemical analysis has been a requirement to precisely identify the uses for the organic materials, including specifically the applications that sometimes fail to be clearly identifiable by microscopy. Presented below and split up into categories, the tested materials include mostly wood tar residues on walls of ceramic vessels, with wood-tar lumps and wood-tar deposits on flint tools being represented infrequently and incidentally, respectively. For a complete list of organic finds subjected to laboratory testing, see Catalogue of Finds.

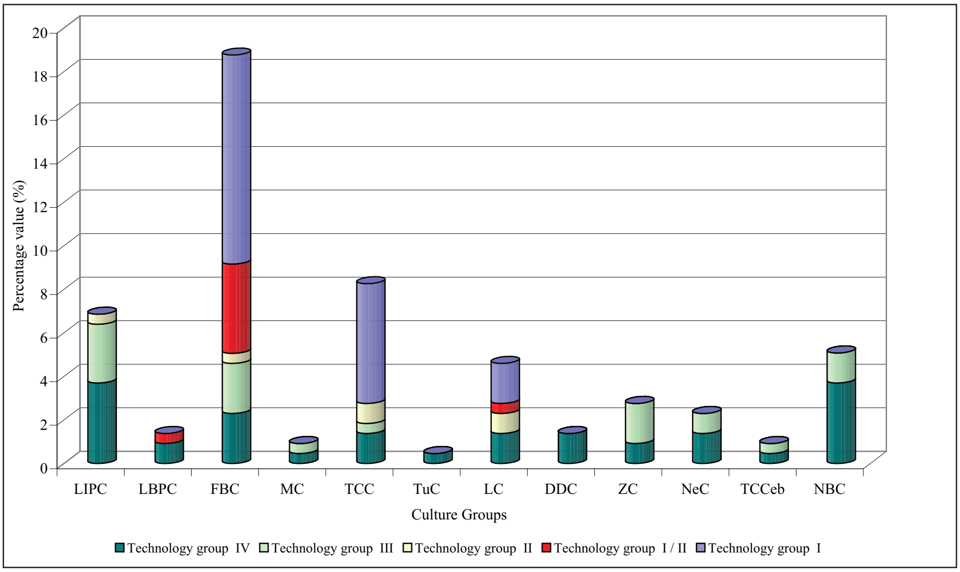


Chart 8. Percentage distribution of post-production residues per technology group

IV.2.1. RESULTS OF STUDIES ON POST-PRODUCTION RESIDUES

The samples representing the post-production residue category or the most numerous group of wood-tar finds (116 samples), come from 48 archaeological sites located in Poland, Belarus and Russia. The comparison with other tar application categories shows that the post-production residues account for 53.2 per cent of all samples. Chart 8 illustrates the percentage distribution of the post-production residue finds on a per culture basis. The category includes fragments of vessels that bear remnants of tars and were designed for wood-tar production or reprocessing, as well as petrified wood-tar lumps. All samples provide essential information on both wood-tar production technology and reprocessing methods.

The samples classified into the wood-tar post-production residue category are associated with two culture circles: *Baltic drainage basin circle* (LIPC – 15 samples: Sr 162, Sr 167, Sr 72, Sr 73, Sr 77, Sr 79, Sr 82, Sr 87, Sr 98, Sr 90, Sr 91, Sr 92, Sr 93, Sr 94 and Sr 97 from 6 archaeological sites; LBPC – 3 samples: Sr 174, Sr 99 and Sr 100 from 2 archaeological sites; FBC – 40 samples: Sr 140, Sr 128, Sr 41, Sr 40, Sr 33, Sr 34, Sr 35, Sr 215, Sr 211, Sr 213, Sr 325-1, Sr 325-2, Sr 325-2, Sr 325-3, Sr 175w, Sr 175z, Sr 193, Sr 42, Sr 43, Sr 55, Sr 56, Sr 28, Sr 30, Sr 31, Sr 263, Sr 264, Sr 328, Sr 321, Sr 464, Sr 466, Sr 468, Sr 177-1, Sr 177-2, Sr 177-3w, Sr 177-3z, Sr 192, Sr 57, Sr 68w, Sr 68z, Sr 67w and

Sr 67z from 20 archaeological sites; MC – 2 samples: Sr 229 and Sr 227 from 2 archaeological sites; TCC – 18 samples: Sr 268, Sr 459, Sr 461, Sr 462, Sr 463, Sr 449, Sr 450, Sr 447, Sr 448, Sr 451, Sr 452, Sr 453, Sr 455, Sr 456, Sr 257, Sr 439w, Sr 439z and Sr 228 from 7 archaeological sites; TuC – 1 sample: Sr 171 from 1 archaeological site; LC – 10 samples: Sr 441, Sr 444-1, Sr 444-2, Sr 71w, Sr 71z, Sr 256w, Sr 256z, Sr 374w, Sr 132w and Sr 132z from 5 archaeological sites) and *Eastern European forest zone culture circle* (DDC – 3 samples: Sr 317, Sr 319, Sr 318 from 1 archaeological site; ZC – 6 samples: Sr 230, Sr 232w, Sr 232z, Sr 233, Sr 234 and Sr 235 from 1 archaeological site; NiC – 5 samples: Sr 520, Sr 320, Sr 356, Sr 236 and Sr 237 from 4 archaeological sites; TCC eastern branch – 2 samples: Sr 331 and Sr 333 from 2 archaeological sites; NBC – 11 samples: 221-1, Sr 221-2, Sr 221-3, Sr 221-4, Sr 221-5, Sr 221-6, Sr 221-7, Sr 332, Sr 334-1, Sr 334-2 and Sr 334-3 from 1 archaeological site). For archaeometric and taxonomic characteristics of all samples discussed below, see Catalogue of Sources. The post-production residue category may be sub-classified into the following several types (technology groups: I, I / II, II, III or IV) based on wood-tar preservation form and production method:

(A) wood tars obtained by the one-vessel method;
(B) wood tars obtained in a two-chamber kiln;
(C) wood tars obtained in a three-chamber kiln.

A. Post-production residues resulting from the one-vessel method constitute a relatively small group of finds that includes both wood-tar lumps and wood-tar deposits on surfaces of ceramic vessels, recorded during archaeological excavations. Ascribed to FBC only, post-production residues in the form of lumps include 7 samples (Sr 41, Sr 40, Sr 33, Sr 34, Sr 42, Sr 43 and Sr 30), all of them representing the middle wood-tar fractions obtained in the range of 120 to 189 °C (Chapter V.1, Tables 5a and 5b). Their complete or partial solubility in organic solvents ascertained by solubility testing (Chapter V.2, Tables 25a and 25c) and the presence of organic radicals with the parameters (g) of approx. 2.0030 and (ΔH) of approx. 0.5 mT derived from EPR spectra (Chapter V.8, Table 78a), allow classification into technology group I. The results of chromatography (Chapter V.3, Table 45a) and spectroscopy (Chapter V.5, Tables 56a and 56c) testing show that birch bark was used to produce tar in samples Sr 41, Sr 40 and Sr 42. FTIR testing (Chapter V.5, Tables 56a and 56c) shows that bark tars are characterized by a higher content of organic acids (1707 cm^{-1} – 1709 cm^{-1}) compared to organic esters.

The reason is that bark has less cellulose than wood, the former having different chemical composition and lower molecular mass [Langer, Keśko 1999: 65]. FTIR testing shows that tars in samples Sr 33, Sr 34, Sr 43 and Sr 30 were produced from the (birch and pine) mixed raw material, with the birch component being quantitatively dominant (Chapter V.5, Tables 56a and 56c). The use of the mixed raw material for these samples is also ascertained by the results of TLC testing (Chapter V.3, Table 45a). The fractures in all of the lumps reveal remnants of the unprocessed raw material with white inclusions. The incompletely processed remnants point to a primitive mode of production in one ceramic vessel, without any separate container to receive wood tar and thereby prevent its mixing with the raw material. The optical and scanning electron microscopic examinations show that, so obtained, tar is strongly contaminated and contains traces of plant cells (Chapter V.4, Photographs 14c, 21b, 21c, 22a, 22b and 23).

Correlative comparison between photographs of wood-tar samples and modern reference samples of bark and wood proves that it was bark instead of wood that was the primary material used for production (Chapter V.4, Photographs 1a and 1b). The microscopic observations provide also evidence for a rapid production process that released large quantities of gases and vapours of volatile substances and led to formation of specific microporous and polymer structures (Chapter V.4, Photographs 14a, 14b, 21a and 21d). The tested tars are archaeologically recorded in the form of black lumps up to approx. 47 mm in length and approx. 30 mm in width. The surface in all of the lumps is rough, with a significant number of cracks and mineral contaminants from direct contact with soil. Furthermore, the surface reveals remnants of the unprocessed bark or wood with white inclusions. The incompletely processed remnants point to a primitive mode of production in one ceramic vessel, without a separate receiver for the end product. Wood tars in samples Sr 33 and Sr 34 are from layers originally adhering to the interior wall and base of the 12 cm wide ceramic vessel used for wood-tar production (sample Sr 35: production vessel) [Kośko, Langer 1986: 592]. A similar history is presumed for the birch tar in sample Sr 41. It is a glassy black lump with clearly visible remnants of unprocessed birch bark and impressions of a vessel base to which it was originally adhering [Szmyt 1992: 77, 82, Fig. 20].

Wood-tar post-production residues deposited on fragments of ceramic vessels are represented by 9 samples ascribed to various cultures (LIPC: Sr 98, Sr 90 and Sr 91; FBC: Sr 35; TCC: Sr 448; NBC: Sr 332). Except for sample Sr 35 (FBC), which exhibits the properties of technology group I with some characteristics typical of technology group II, the samples represent heavy wood-tar fractions of technology groups III (LIPC: Sr 98 and Sr 90; NBC: Sr 332) and IV (LIPC: Sr 91; TCC: Sr 448; NBC: Sr 334-1, Sr 334-2 and Sr 334-3). Although no melting point for wood tar in sample Sr 35 has been detected up to 300 °C (only softening point of 178 °C), complete or partial solubility in organic solvents has been ascertained (Chapter V.1, Table 5a; Chapter V.2, Table 25a). These characteristics enable classification of the wood tar into the group of tars with mixed physico-chemical properties (technology group I / II).

The results of TLC testing have proven that the birch and pine mixed raw material was used for production (as was the case for Sr 33 and Sr 34 likely to have been derived from the same vessel, i.e.). Other samples show high carbonization levels with no solubility in organic solvents and water (Chapter V.2, Tables 23b, 28b and 39) and low solubility in aqueous solutions of acids (HCl) or alkalis (NaOH). However, they give a weak reaction to ammonium thiocyanate (NH_4SCN), which proves low levels of their mineral impurity (Chapter V.2, Tables 23b, 28b and 39). The observations above are further substantiated by the presence of paramagnetic components from soil, with the spectral parameters (g) of 1.8919 to 2.4579 and (ΔH) of 28.23 to 130.87 mT (Chapter V.8, Tables 75, 79a, 85 and 107). Considerably high levels of thermal degradation are reflected in no melting effect detectable up to 300 °C (Chapter V.1, Tables 3, 5a, 9 and 19).

Considerable carbonization to early stages of graphitization may point to either uncontrolled temperature or a leakage effect (e.g. cracks in production vessels while in a hearth) during the production process. Consequently, fire was no longer prevented from penetrating to contact wood tar, causing its partial carbonization. Or, high thermal degradation might have been the effect of repeated heating of wood tar, which caused evaporation of volatile (diagnostic) components. Hence, any identification of the raw material (wood and bark species) used for production is no longer feasible. However, considerable carbonization levels have allowed the FTIR analysis to identify birch as a raw material for two samples, i.e. Sr 90 and Sr 91 (LIPC) (Chapter V.5, Table 54b). The organic nature of the samples has been substantiated by EPR tests proving the presence of carbon radicals with the spectral parameters (g) of approx. 2.0030 and (ΔH) of approx. 0.5 mT (Chapter V.8, Tables 74, 78a, 84 and 106). The considerable signal intensity for carbon radicals proves large concentrations of carbon radicals in the archaeological samples, which concentration results from intense sintering (thermal degradation).

Ascertained by microscopic examination, the presence of microporous structures formed during high temperature-induced intense volatilization confirms the already formulated conclusion that the wood tars were exposed to a naked flame such as in a hearth (Chapter V.4, Photographs 9a, 9b, 10a, 69a and 70b). In consequence, complex polymeric substances were formed, showing high cross-linking levels (formation of a large number of bonds between molecules) (Chapter V.4, Photographs 11a, 11b and 70a). In two samples (LIPC: Sr 90; TCC: Sr 448), spherical objects or spherulites have been identified, formed either from the raw material (wood or bark) melt or through decomposition of vapours and condensation of the resulting macromolecular polymers (Chapter V.4, Photographs 10c, 10d, 44c and 44d). All these observations lead to the conclusion that tars in both samples were produced or reprocessed at relatively high temperatures. As far as production is concerned, the comparison of images obtained for the wood tars with the photograph showing a cellular structure of wood proves that the tars were made from wood. The remnants of the unprocessed raw material, or specific plant structures, prove the organic origin (remnants of bark or wood) for both samples. These findings provide also evidence for a primitive wood-tar production technology, with one production vessel ensuring no separation between the raw material and the end product. The photographs captured with the microscope confirm that the method allowed obtaining the heavy fraction, i.e. tarry distillate containing considerable amounts of the raw material (Chapter V.4, Photographs 9c, 10b, 11c, 15, 44a and 44b). Heavier wood-tar fractions were obtained through slow evaporation of readily volatile tars at high temperature [Langer 1989].

B. Wood-tars obtained in a two-chamber kiln are represented by 96 samples, all collected from the surface of ceramic vessels intended for wood-tar production or reprocessing. The tars are classified into the following technology groups: I (FBC: Sr 140, Sr 128, Sr 175w, Sr 193, Sr 56, Sr 28, Sr 263, Sr 264, Sr 466, Sr 468, Sr 177-1, Sr 177-2, Sr 177-3w, Sr 57, Sr 67w and Sr 67z; TCC: Sr 459, Sr 461, Sr 462, Sr 463, Sr 449, Sr 451, Sr 452, Sr 453, Sr 455, Sr 439w, Sr 439z and Sr 228; LC: Sr 441), I/II (LBPC: Sr 174; FBC: Sr 211, Sr 325-1, Sr 325-2, Sr 325-3, Sr 175z, Sr 55, Sr 328 and Sr 177-3z; LC: Sr 374z), II (LIPC: Sr 79; TCC: Sr 456 and Sr 257; LC: Sr 132w), III (LIPC: Sr 162, Sr 87, Sr 93 and Sr 94; FBC: Sr 213, Sr 464, Sr 192, Sr 68w and Sr 68z; MC: Sr 229; TCC: Sr 450; LC: Sr 444-1, Sr 444-2 and Sr 132z; ZC: Sr 230; Sr 232w, Sr 232z and Sr 235; NC: Sr 520, Sr 236; TCC eastern branch: Sr 333; NBC: Sr 221-6 and Sr 221-7) and IV (LIPC Sr 167, Sr 72, Sr 73, Sr 77, Sr 82, Sr 92 and Sr 97; LBPC: Sr 99 and Sr 100; FBC: Sr 215, Sr 31, Sr 321, Sr 67w and Sr 67z; MC: Sr 227; TCC: Sr 268 and Sr 447; TuC: Sr 171; DDC: Sr 317, Sr 319 and Sr 318; ZC: Sr 233 and Sr 234; NiC: Sr 320, Sr 356 and Sr 237; TCC eastern branch: Sr 331; NBC: Sr 221-1, Sr 221-2, Sr 221-3, Sr 221-4 and Sr 221-5). Moreover, the tars may be split up into three groups according to temperature at which they were obtained, this directly determining the type of the resulting wood-tar fractions. The results of testing show that the light wood-tar fractions (FBC: Sr 468; TCC: Sr 453, Sr 439w and Sr 439z) were obtained at low temperatures (90 – 120 °C) (Chapter V.1, Tables 5c and 8). The decreased softening point (77 – 100 °C) proves the deliberate admixture of plant oils or animal fats to reduce the temperature for intended use of tars (Chapter V.1, Tables 5c and 8).

The above-presented conclusions are substantiated by the fact of complete or partial solubility of tars in organic solvents (Chapter V.2, Tables 25d, 28b and 28c). The results of TLC and FTIR testing prove that the tars were produced from birch wood (FBC: Sr 468; TCC: Sr 453) or birch bark (TCC: Sr 439w and Sr 439z) (Chapter V.3, Tables 45b and 48; Chapter V.5, Tables 56d, 59b and 59c). The organic origin of the discussed tars has been confirmed by the presence of carbon radicals with the parameters (g) of approx. 2.0030 and (ΔH) of approx. 0.5 mT derived from EPR spectra (Chapter V.8, Tables 78b and 84). Signals of the spectral parameters (g) of 2.0054 – 2.2728 and (DH) of 53.73 – 108.77 mT prove the presence of paramagnetic components (mineral substances from accidental contamination of wood tars) (Chapter V.8, Tables 79b and 85). The tested tars come from the interior (TKK: Sr 439w) or exterior (FBC: Sr 468; TCC: Sr 453 and Sr 439z) surfaces of ceramic vessels used in wood-tar production. Samples Sr 439w and Sr 439z are collected from both surfaces of the same vessel. Wood tar collected from the vessel interior forms a thick (4 to 5 mm) and a heavily cracked layer on the wall of the vessel, while tar from the vessel exterior forms a strip which is 1.5 to 2 cm wide and approximately 2 mm thick. The appearance of the strip surface proves that wood tar was allowed to solidify undisturbed on the wall of the vessel. Large amounts of tar deposited on the interior wall indicate that the vessel, whose walls display traces of organic substances, was used in tar production. Tarry traces on the external surface of the vessel should be deemed evidence for the end product of birch bark thermolysis having been poured into another vessel for further processing or other purposes. Tar covers walls of the vessel with rough, matt and slightly cracked layers of variable thickness (2 to 5 mm). Microscopic examinations have revealed a polymeric structure typical of substances formed by thermolysis of wood or bark (Chapter V.4, Photograph 47). At the same time, high purity levels of tar points to a two-chamber kiln having been used with a dedicated receiver for the end product that ensured separation of the raw material and the end product.

The respective softening and a melting points for middle wood-tar fractions (FBC: Sr 140, Sr 128, Sr 175w, Sr 193, Sr 56, Sr 28, Sr 263, Sr 264, Sr 466, Sr 177-1, Sr 177-2, Sr 177-3w and Sr 57; TCC: Sr 459, Sr 461, Sr 462, Sr 463, Sr 449, Sr 451, Sr 452, Sr 455 and Sr 228; LC: Sr 441 and Sr 444-1) are between 85 – 155 °C and 114 – 195 °C, respectively, which points to considerably more intense exposure to high temperature during the production process (Chapter V.1, Tables 5a-5c, 8 and 10). Such exposure resulted also in lower solubility compared with the lightest fractions and in partial solubility in aqueous solutions of acids (HCl) and alkalis (NaOH) (Chapter V.2, Tables 25a-25e, 28a-28c and 30a). Chromatography and spectroscopy (Chapter V.3, Tables 45a, 45b, 48 and 49; Chapter V.5, Tables 56a-56e, 59a-59c and 61a) show that the tars were obtained from birch wood (FBC: Sr 128, Sr 175w, Sr 193, Sr 56, Sr 28, Sr 263, Sr 264, Sr 177-1, Sr 177-2, Sr 177-3w and Sr 57; TCC: Sr 461, Sr 462, Sr 463, Sr 451, Sr 452, Sr 455, Sr 228; LC: Sr 441 and Sr 444-1) or birch bark (FBC: Sr 466; TCC: Sr 459 and Sr 449), except wood tar in sample Sr 140 (FBC) made from the (birch and pine) mixed raw material (Chapter V.3, Table 45a). Measurements of EPR spectra have revealed compositionally meaningful amounts of organic radicals with spectra parameters (g) of 2.0027 – 2.0034 and (ΔH) of 0.45 – – 0.59 mT (Chapter V.8, Tables 78a, 78b, 84 and 88).

Moreover, the EPR tests have ascertained the presence of paramagnetic components (mineral substances from accidental contamination) with spectral parameters (g) of 1.8952 – 2.6535 and (DH) of 50.9 – 187.45 mT (Chapter V.8, Tables 79a, 79b, 85 and 89). Subject to testing have been also tars recorded deposited on the interior (FBC: Sr 140, Sr 128, Sr 175w, Sr 263, Sr 264, Sr 466, Sr 177-1, Sr 177-2 and Sr 177-3w; TCC: Sr 459, Sr 461, Sr 463 and Sr 228; LC: Sr 444-1) and exterior (FBC: Sr 193, Sr 56, Sr 28 and Sr 57; TCC: Sr 462, Sr 449, Sr 451, Sr 452 and Sr 455; LC: Sr 441) surfaces of vessels intended for wood-tar

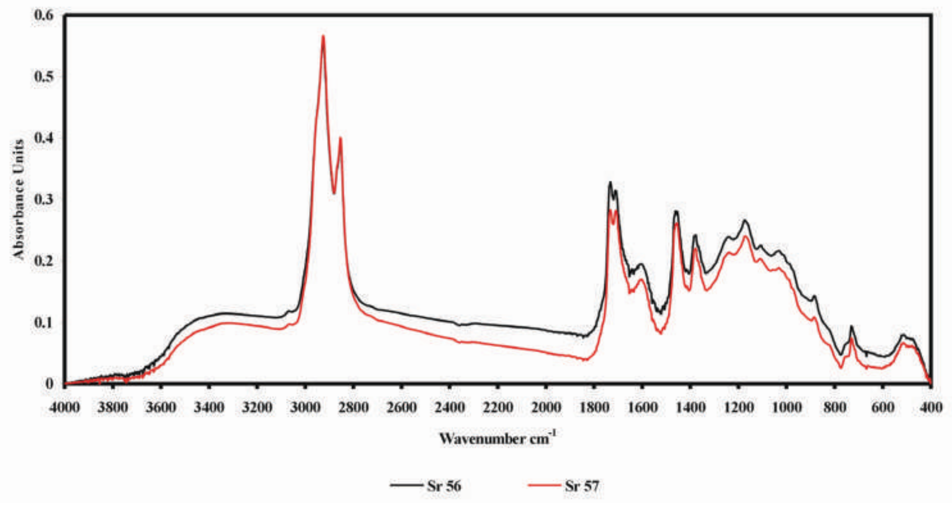


Fig. 20. Infrared spectroscopy correlation for samples Sr 56 and Sr 57

production. Up to 4 mm thick, slightly cracked and containing small amounts of accidental mineral admixture, tar layers adhere closely to pottery substrate. Microscopic images reveal specific heavily porous structures or traces of high temperature-induced volatilization processes (Chapter V.4, Photographs 49a and 49b). As far as tars in samples Sr 177-1, Sr 177-2 and Sr 177-3w (FBC) are concerned, they had not had any prolonged contact with interior walls of the vessels before they underwent a diffusion-reducing rapid thermal degradation process (partial carbonization).

The conclusion thus seems reasonable that they were shortly exposed to superficial high temperature whose source was inside the vessel. Hence, the wood-tar production process must have been uncontrolled to allow tar to ignite inside the production vessel. Made by the tar maker, an attempt to extinguish burning tar with s and is confirmed by significant amounts of mineral contaminants (Sr 177-3w) identified by both the colour-producing reaction to ammonium thiocyanate (NH_4SCN) and FTIR and EPR tests (Chapter V.2, Table 25e; Chapter V.5, Table 56e; Chapter V.8, Table 79b). Compositionally, all three samples (Sr 177-1, Sr 177-2 and Sr 177-3w) contain the same substance (birch tar) that most likely originates from the same production vessel. However, each sample represents a different degree of thermal degradation of the organic substance, caused by ignition of tar. Extinguishing efforts are evidenced by increased amounts of mineral contaminants (s and grains) in sample Sr 177-3w that derives directly from the location of the flame. Interestingly, IR spectra (FTIR) reveal unique compositional similarities (sameness) for samples Sr 56 and Sr 57 (FBC), each collected at a different archaeological site within the same settlement macro-region (Fig. 20). These similarities provide irrefutable evidence for close chemical affinity (sameness) of the tested middle fractions of tar (technology group I) obtained from birch wood and correspond well to the results of the melting point and solubility measurements (Chapter V.1, Tables 5b and 5c; Chapter V.2, Tables 25c and 25e).

Given the production method and the complex composition of wood tar, it is by no means easy, even for modern tar makers, to obtain such high similarity levels for IR spectra (FTIR). On the one hand, these similarities indicate that both tars might have been produced by the same tar maker who might have used even the same tar kiln to obtain and store tar in both cases. On the other, however, they do not rule out the possibility that both tars might have been produced in different locations by different tar makers, but according to the wood-tar production formula strictly adhered to (identical wood-tar production method and subsequent processing method, if any). Similar intensities, positions and widths of EPR lines for organic radical in samples Sr 56 and Sr 57 (Chapter V.8, Tables 78a and 78b) provide evidence for both comparable wood-tar production conditions and similar thermal history of the tested wood-tar layers, confirming the concept of specialisation in production (Langer, Pietrzak 2004a: 603).

The samples identified as heavy wood-tar fractions (LIPC: Sr 162, Sr 167, Sr 72, Sr 73, Sr 77, Sr 79, Sr 82, Sr 87, Sr 92, Sr 93, Sr 94 and Sr 97; LBPC: Sr 174, Sr 99 and Sr 100; FBC: Sr 215, Sr 211, Sr 213, Sr 325-1, Sr 325-2, Sr 325-3, Sr 175z, Sr 55, Sr 31, Sr 328, Sr 321, Sr 464, Sr 177-3z, Sr 192, Sr 68w, Sr 68z, Sr 67w and Sr 67z; MC: Sr 229 and Sr 227; TCC: Sr 268, Sr 450, Sr 447, Sr 456 and Sr 257; TuC: Sr 171; LC: Sr 444-2, Sr 374z, Sr 132w and Sr 132z; DDC: Sr 317, Sr 319 and Sr 318; ZC: Sr 230, Sr 232w, Sr 232z, Sr 233, Sr 234 and Sr 235; NiC: Sr 520, Sr 320, Sr 356, Sr 236 and Sr 237; TCC eastern branch: Sr 331 and Sr 333; NBC: Sr 221-1, Sr 221-2, Sr 221-3, Sr 221-4, Sr 221-5, Sr 221-6 and Sr 221-7) have no melting point up to 300 °C, which suggests either a fault in the production process (e.g. breaks in tar kiln – direct exposure of wood tar to a naked flame) or repeated heating of tar. Partial softening (112 – 280 °C) has only been ascertained for some of these samples (Chapter V.1, Tables 3, 4, 5a-5d, 7-10, 14, 15, 17-19). The above-suggested reasons led to partial or total thermal degradation causing largely reduced solubility or, in some cases, insolubility of tars in organic solvents (Chapter V.2, Tables 23a, 23b, 24, 25b, 25c, 25g, 27, 28a-30b, 34, 35, 37-39). Some of the tars subject to testing remain soluble in aqueous solutions of acids (HCl) and alkalis (NaOH), and, so obtained, the hydrochloric acid solution exhibits small amounts of iron (Fe) compounds probably from accidental contamination with soil, manifesting themselves in a weak reaction to ammonium thiocyanate (NH_4SCN) (Chapter V.2).

These findings are further substantiated by EPR testing revealing the presence of mineral admixture (paramagnetic components) from accidental contamination by post-depositional processes). The presence of contaminants has been ascertained from signals with spectral parameters (g) of 1.8919 – 2.5624 and (DH) of 20.54 – 180.49 mT (Chapter V.8, Tables 75, 77, 79a-79c, 83, 85, 87, 89, 97, 99, 103, 105 and 107), while the presence of organic radical has been expressly indicated by signals with spectral parameters (g) 2.0022 – 2.0041 and (DH) of 0.38 – – 0.92 mT (Chapter V.8, Tables 74, 76, 78a-78c, 82, 84, 86, 88, 96, 98, 102, 104 and 106). Chromatography and spectroscopy testing (Chapter V.3, Tables 43, 44, 45a, 45b, 48 and 49; Chapter V.5, Tables 54a, 55, 56b-56d, 59b and 61b) have proven that most tars subject to physico-chemical analysis were obtained from birch wood (LIPC: Sr 79; LBPC: Sr 174; FBC: Sr 211, Sr 325-1, Sr 325-2, Sr 325-3, Sr 175z, Sr 55 and Sr 177-3z; TCC: Sr 456) or birch bark (FBC: Sr 328; LC: Sr 444-2 and Sr 374z). The exceptions are wood tars collected from the interior (Sr 68w) and exterior (Sr 68z) surfaces of the same vessel, which were made from the birch and pine mixed raw material, as proven by TLC testing (Chapter V.3, Table 45c).

There is also a separate group of tars which, despite their considerable thermal degradation, remain identifiable as birch products (LIPC: Sr 167, Sr 72, Sr 92, Sr 93 and Sr 97; TCC: Sr 450 and Sr 257; LC: Sr 132w) (Chapter V.5, Tables 54a, 54b, 59b, 59c and 61b). Other tars are heavily carbonized (LIPC: Sr 162, Sr 73, Sr 77, Sr 82, Sr 87 and Sr 94; LBPC: Sr 99 and Sr 100; FBC: Sr 215, Sr 213, Sr 31, 321, 464, Sr 192, Sr 67w and Sr 67z; MC: Sr 229, Sr 227; TCC: Sr 268 and Sr 447; TuC: Sr 171; LC: Sr 132z; DDC: Sr 317, Sr 319 and Sr 318; ZC: Sr 230, Sr 232w, Sr 232z, Sr 233, Sr 234 and Sr 235; NC: Sr 520, Sr 320, Sr 356, Sr 236 and Sr 237; TCC eastern branch: Sr 331 and Sr 333; NBC: Sr 221-1, Sr 221-2, Sr 221-3, Sr 221-4, Sr 221-5, Sr 221-6 and Sr 221-7) and thereby containing no diagnostic markers (Chapter V.5, Table 54a, 54b, 55, 56b-56e, 56g, 58, 59b, 60, 61b, 65, 66, 68, 69, 70).

For this reason, identification of their raw materials (wood and/or bark species) is prevented. Seen in IR spectra (FTIR), the presence of aromatic organic acids (~ 1700 cm^{-1}) points to heavy thermal degradation of wood tars (e.g. FBC: Sr 31; TCC: Sr 450; LC: Sr 374z). Furthermore, higher than normal content of saturated (~ 1711 cm^{-1}) and unsaturated (~ 1709 cm^{-1}) organic acids may betoken admixtures of plant oil or animal fats (e.g. LIPC: Sr 79; FBC: Sr 211, Sr 175z and Sr 328; LC: Sr 132w and Sr 132z). In some cases (eg. FBC: Sr 68w and Sr 68z; TCC: Sr 456 and Sr 257; LC: Sr 444-2), increased content of organic acid salts (~ 1600 cm^{-1}) and reduced content of acids (~ 1700 – 1718 cm^{-1}) and acid esters (~ 1733 cm^{-1}) have been detected, which suggests that acids were deliberately neutralised with such substances as calcium carbonate ($CaCO_3$) for better binding between the pottery substrate and wood-tar layers or coats (when applied as binders or colorants). Wood tars subject to testing are also identified on the interior (LIPC: Sr 162, Sr 167, Sr 72, Sr 77, Sr 82, Sr 87, Sr 92, Sr 93 and Sr 94; LBPC: Sr 174, Sr 99 and Sr 100; FBC: Sr 215, Sr 211, Sr 213, Sr 325-1, Sr 325-2, Sr 325-3, Sr 55, Sr 31, Sr 328, Sr 192, Sr 68w and Sr 67w; MC: Sr 229 and Sr 227; TCC: Sr 268, Sr 450, Sr 447 and Sr 257; TuC: Sr 171; LC: Sr 444-2 and Sr 132w; DDC: Sr 317, Sr 319 and Sr 318; ZC:

Sr 230, Sr 232w, Sr 233, Sr 234 and Sr 235; NiC: Sr 520, Sr 320, Sr 356, Sr 236 and Sr 237; TCC eastern branch: Sr 331 and Sr 333; NBC: Sr 221-1, Sr 221-2, Sr 221-3, Sr 221-4, Sr 221-5, Sr 221-6 and Sr 221-7) and exterior (LIPC: Sr 73, Sr 79 and Sr 97; FBC: Sr 175z, Sr 321, Sr 464, Sr 177-3z, Sr 68z and Sr 67z; TCC: Sr 456; LC: Sr 374z and Sr 132z; ZC: Sr 232z) walls of vessels once used in wood and/or bark thermolysis as proven by distribution of organic deposits on their surfaces. Deposits take the form of a relatively thick (approximately 2 to 5 mm) layer of black tar.

A microscopic examination has detected that the layers are strongly sintered to form strongly porous structures resulting from rapid decomposition during wood-tar production or processing at high temperatures (Chapter V.4, Photographs 3a, 3b, 12, 18a, 18b, 57a-58b, 67a-68b). All these observations lead to the conclusion about partial carbonization or, in some cases, early stages of graphitisation. It cannot be ruled out that wood tars were strongly baked deliberately in order to increase the amounts of macromolecular substances and thereby improve their thermal stability, which might have been a desirable functional property (thermally stabilized tars are suitable for use at high temperatures, e.g. as caulking layers in hearths). Wood tars do not exhibit any traces of unprocessed wood or bark, which points to an advanced production method in the two-vessel reactor to separate the product from the reaction chamber (product purified from the raw material).

Sample Sr 174 (LBPC) is associated with what is an interesting example of a production vessel. The material in the sample forms a relatively thick (up to 4 mm) black layer with a glossy and slightly cracked surface. It covers a large part of the vessel interior walls and base (approximately 60%). Both distribution and preservation of the material inside the vessel allow the presumption that the vessel was used in wood-tar production (as an element of the tar kiln comprising a receiver and a cooler) or reprocessing. The material has been identified as organic and belonging to technology group I/II of wood tars. It was generated by thermolysis of birch wood or birch bark. It displays poor melting qualities and low solubility in organic solvents (heavy wood-tar fractions). Coupled with other observations (no traces of intense production of vapours or decomposition process releasing gases, i.e. bubbles or micro bubbles on the surface of, or inside the layer), the these properties indicate that the wood tar was prepared deliberately by slow evaporation of readily volatile wood-tar fractions at high temperature (Chapter V.4, Photographs 13a, 13b).

The resulting increased viscosity and adhesivity might have been the reason for such reprocessing (as evidenced by a specific form of a vessel that was used, i.e. bowl offering a larger surface area for the substance to evaporate faster); therefore, the vessel may be considered a part of the production equipment. High viscosity of wood tar might have been a property determining the subsequent wood-tar uses, including but not limited to repairs of broken vessels (binder). As far as sample Sr 444-2 (LC) is concerned, it is associated with a fragment of a production vessel used to contain the end product or wood tar. Direct exposure of wood tar, this deposited only on the interior surface of the vessel, to a naked flame might have resulted from a leakage problem in the tar kiln, breaks in a clay caulking coat during the production process, or uncontrolled temperature during further processing of the product. Consequently, the wood tar became considerably carbonized and any matter with a melting point below 300 °C was thereby eliminated (Chapter V.1, Table 10).

C. Wood tars obtained in a three-chamber kiln constitute a small group of 4 samples attributed solely to the Lusatian culture (Sr 71w, Sr 71z, Sr 256w and Sr 256z). They represent either middle wood-tar fractions of technology group I (Sr 71w, Sr 71z, Sr 256w), or heavy wood-tar fractions of technology group II (Sr 256z). EPR tests confirmed they are organic, proving the presence of carbon radicals with the spectral parameters (g) of 2.0029 – 2.0035 and (ΔH) of approx. 0.5 mT (Chapter V.8, Table 88). As far as wood tars deposited on the interior (Sr 71) and exterior (Sr 71z) surfaces of the vessel or sample Sr 71 are concerned, they do not display any significant differences in terms of physico-chemical properties [Langer, Pietrzak, Cichocka 2004]. Similar intensities, positions and widths of EPR lines for organic radicals in the exterior and interior layers prove that the tars were produced under identical conditions and share a similar thermal history (Chapter V.8, Table 88). These conclusions are further substantiated by the comparable softening points (90 – 103 °C) and melting points (110 – 140 °C), as well as similar good to very good solubility in most organic solvents, reported for both layers (Chapter V.1, Table 10; Chapter V.2, Table 30a). When added, aqueous solution of hydrochloric acid (HCl) causes elution of insignificant amounts of iron-containing minerals. The presence of iron is confirmed by the colour-producing reaction to ammonium thiocyanate (NH_4SCN). The mineral admixture is further ascertained by the presence of paramagnetic components (iron compounds) with the parameters (g) of 2.0479 – 2.8605 and (ΔH) of 52.92 – 71.78 mT derived from EPR spectra (Chapter V.8, Table 89).

The results of melting point measurements prove that tar from the exterior of the vessel or sample Sr 256 was exposed to higher temperatures (no melting effect up to 300 °C) than the tar from the interior of the same vessel (softening range: 122 – 135 °C, melting range: 144 – 176 °C). High thermal degradation levels for the tar from the exterior of the vessel (Sr 256z) indicate that it did come into direct contact with naked flames (hearth), which might have occurred because of leaks in the reactor or breaks in the clay caulking coat of the reactor occurring during the production process.

In consequence, the organic material became considerably carbonized and any matter with the melting points below 300 °C was eliminated (Chapter V.1, Table 10). These findings are confirmed by the solubility tests: no solubility in organic solvents is reported for the exterior layer (Sr 256z) and good solubility in organic solvents is ascertained for the interior layer (Sr 256w). The results of the EPR testing of wood tars from the interior and exterior layers are comparable, revealing similar spectral parameters for a narrow resonance line for organic radicals (g) of 2.0029 – 2.0031 and (ΔH) of approximately 0.5 mT (Chapter V.8, Table 88). The parameters of EPR lines for organic radicals in both layers indicate that both tars were produced under similar conditions but have different thermal histories, with highly carbonized exterior layer (Sr 256z) being characterised by a weaker signal attributable to organic structures [Langer, Pietrzak, Cichocka 2004].

The TLC results for solutions show similarities between the tested tars and birch tar. This conclusion is also supported by the presence of the fraction with the R_f value of approx. 0.26 (SiO_2, hexane – carbon tetrachloride 3:1), which is alien to the reference pine-tar sample. At the same time, the absence of diagnostic markers, i.e. low polarity substance with R_f of approx. 0.80 and moderate polarity substance of R_f of approx. 0.46, excludes the possibility of the tested tars being pine tars (Chapter V.3, Table 49). The tar from the exterior surface of the second vessel (Sr 256z) has not been subject to TLC because of its very low solubility in organic solvents and considerable thermal degradation. FTIR has revealed signals at 882 cm^{-1} and 730 cm^{-1}, corresponding to markers for birch tar (Chapter V.5, Table 61a). Therefore, the samples in question may be considered containing wood tars or products of thermal decomposition of birch bark or birch wood. This view as further confirmed by GC/MS tests for one of the main fractions in Sr 71w, which have revealed components typically isolable from birch, i.e. lupeol and betulin (retention times of approx. 23 min. 30 sec. and 24 min. 32 sec., respectively) (Chapter V.6, Fig. 24). The tests were using comparative methods and reference samples of birch tar and pine tar (Chapter V.6, Figs. 22 and 23). GC/MS tests for the reference sample of birch tar have detected betulin (retention time of 21 min. 32 sec.) among many other components and have thereby unquestionably proven that Sr 71w was made from birch (Chapter V.6, Fig. 24).

The tests have also isolated glyco-vanillic aldehyde and retene, the latter being usually found in pine tar, which may provide evidence for small-volume admixture of pine tar. Such admixture is also indicated by the results of GC/MS tests for the reference sample of pine tar, which tests have isolated, among others, retene (retention time: 20 min. 37 sec.) or a product of thermal transformation of abietic acid (Chapter V.6, Fig. 23). The admixture might have been accidental and caused by the repeated use of the reactor for processes involving but not limited to pine-tar production. These conclusions correspond to what has been observed using the NMR. The ^{1}H-NMR spectra explicitly point to the content of aromatic compounds with an unsymmetrically substituted benzene ring typical for molecules of glyco-vanillic aldehyde and betulin: position of 7,4 – 8,3 δ, signal multiplets and coupling constants (J_{orto} = 9,07 Hz, J_{meta} = 2,47 Hz and J_{para} = 0,55 Hz) correspond well to the aforesaid structures (Chapter V.7, Fig. 26). The ^{1}H-NMR results for sample Sr 71w are similar to those for the wood-tar reference sample and significantly different from those for the pine tar reference sample (Chapter V.7, Fig. 25).

As far as samples Sr 71w and Sr 71z are concerned, they are from black tar layers up to 1.5 mm thick, adhering to external and internal surfaces of the base of the vessel. The layers have rough surfaces. They are positioned around and partially fill the perforation existing in the base. The edges of the perforation show damage that continues on the base, specifically affecting the interior surface of the base. The damaged surface is coated with wood tar. The manner in which the wood tar or organic substance is distributed on the pottery surface does not rule out the possibility that the vessel might have been a pitch production reactor or an intermediary receiver similar to that discussed by Czopek [1997: 159]. However, the production method involving an intermediary receiver is more advanced and, as such, was developed at a later time. Presumably, the perforation was damaged by attempts of its clearing from solidified pitch, which may prove that the vessel was used multiple times for production purposes.

Contained in samples Sr 256w and Sr 256z, wood tars from the second vessel also form a thin (approx. 1.5 mm) black layer adhering to the interior surface of the base (Sr 256w) and to the exterior surface of the lip (Sr 256z). Surrounding the perforation in the base, the organic material or tar has a rough surface. Given the perforation location close to the outer edge of the base [Langer, Pietrzak, Cichocka 2004: 456, figs. 5b, 5c] and the presumptive base diameter of the vessel, a conclusion seems reasonable that the base might have been with multiple perforations, as it is the case for ceramic vessels from Gródek Nadbużny [Gumiński 1989:Table 14]. In view of the findings above, the pottery fragments discussed may be considered parts of reactors intended for wood-tar (pitch) production. Originally, these intermediary vessels were placed between the reaction chamber and the receiver proper [Langer, Pietrzak, Cichocka 2004: 460, Fig. 9b] and ensured high purity of wood tar.

IV.2.2. RESULTS OF STUDIES ON BINDERS

Among samples subject to physico-chemical analysis, there is a largely diversified category of binders. Binders are recognized in the form of black tar layers on fragments of ceramic vessels or flint inserts, or petrified wood-tar lumps (Catalogue of Sources). In total, the group comprises 32 wood-tar samples ascribed to various cultures from 21 archaeological sites in Pol and or Ukraine. Accounting for 14.7 per cent of all source materials, the category is relatively scanty as shown in Chart 9.

Discussed below, the binders represent the following two culture circles only: *Baltic drainage basin circle* (FBC – 19 samples: Sr 9, Sr 66, Sr 137, Sr 327,

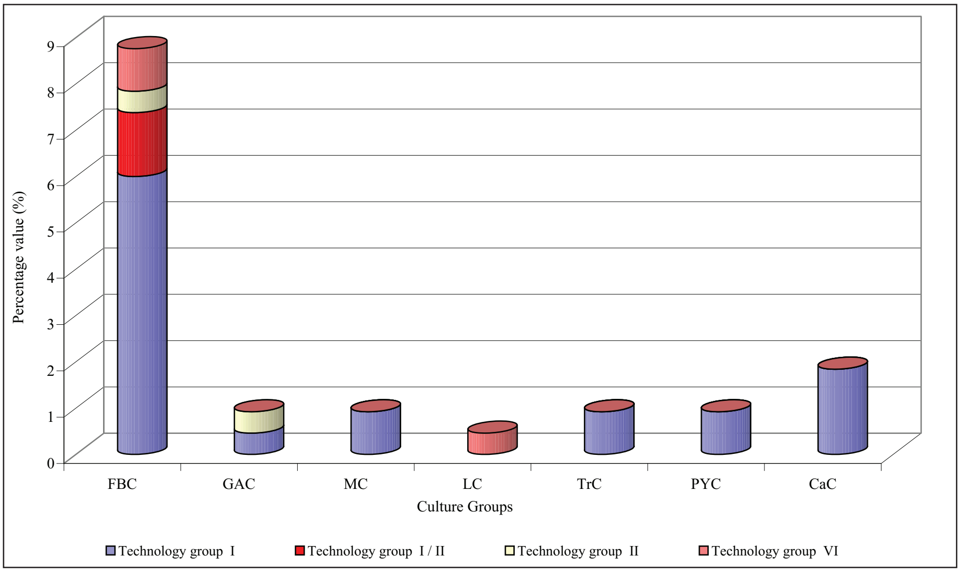


Chart 9. Percentage distribution of binder per technology group

Sr 252, Sr 198w, Sr 198z, Sr 32-1, Sr 32-2, Sr 329w, Sr 329z, Sr 46, Sr 469-2, Sr 37, Sr 36, Sr 58w, Sr 58z, Sr 59 and Sr 243 from 13 archaeological sites; GAC – 2 samples: Sr 517 and Sr 141 from 1 archaeological site; MC – 2 samples: Sr 166 and Sr 326 from 2 archaeological sites; LC – 1 sample: Sr 131 from 1 archaeological site) and *Eastern European forest zone culture circle* (TrC – 2 samples: Sr 47 and Sr 184 from 2 archaeological sites; PYC – 2 samples: Sr 38 and Sr 39 from 1 archaeological site; CaC – 4 samples: Sr 51, Sr 52, Sr 53 and Sr 54 from 2 archaeological sites). For archaeometric and taxonomic characteristics of all samples discussed below, see Catalogue of Sources.

Based on their applications in the past, the binders may be sub-classified into the following several types of wood-tars (technology groups: I, I / II i II) and composites (technology group VI):

(A) binders to repair ceramic vessels;

(B) binders to mount flint inserts;

(C) binders to attach birch bark to exterior surfaces of ceramic vessels;

(D) binders to fill stamped or incised ornaments (inlays) on exterior surfaces of ceramic vessels;

(E) binders for medical or magic purposes.

A. Binders used to repair ceramic vessels are the most abundant group of binders, identified in 16 archaeological samples (FBC: Sr 66, Sr 198w, Sr 198z, Sr 32-1, Sr 32-2, Sr 329w, Sr 329z, Sr 46, Sr 469-2, Sr 37, Sr 36, Sr 58w and Sr 58z; LC: Sr 131; TrC: Sr 47 and Sr 184). Sample Sr 66 (FBC) consists of birch bark tar (Chapter V.3, Table 45a; Chapter V.5, Table 56a) of technology group, which was used to replace a chipped fragment of the exterior surface (peripheral edge) of the vessel base. The same colour and structure of the fabric in both the affected area and the intact surface of the vessel prove that the irregularity occurred during the production process. The vessel was then flawed from the very beginning and, as such, repaired (perhaps under 'warranty') with tar. So repaired, the vessel was not used in high temperatures: repaired surface was not exposed to temperatures in excess of 150 °C (Chapter V.1, Table 5a), so it had no contact with naked flames [Langer, Pietrzak 2000: 414].

Similar applications are ascertained also for birch wood tar (Chapter V.3, Table 45b; Chapter V.5, Table 56c) in samples Sr 198w and Sr 198z (FBC) collected from interior and exterior surfaces, respectively, of the same repaired vessel. Both samples exhibit characteristics typical of wood tars representing technology group I, with certain properties of technology group II (no melting point up to 300 °C – Chapter V.1, Table 5b). Also, both samples show that the binder underwent solidification by melting followed by cooling to below the softening point (i.e. below 130 – 140 °C – Chapter V.1, Table 5b). Subsequently, the seam was subject to thermal consolidation at high temperatures (in excess of 300 °C). The consolidation led to a cross-linked structure (formation of a large number of bonds between molecules) and increased cohesion levels and thereby improved mechanical damage resistance of the seam in both samples.

Collected from the exterior surface of the ceramic vessel and representing technology group VI, sample Sr 131 (LC) shows even stronger cross-linking. Caused by heavy thermal degradation, cross-link density (Chapter V.1, Table 10) is high enough to prevent complete solubility of the binder in organic solvents (solvent molecules could not penetrate into binder molecules – Chapter V.2, Table 30b). The compact and strongly cross-linked structure of the binder caused crumbliness and perishability of the seam. Imperfections in technological methods (excessive hardening – excessive cross-link density) caused fragments bound with the binder to fall apart. Moreover, sample Sr 131 has proven to be a composite having considerable amounts of minerals added deliberately for composition modification purposes. An organic-mineral hybrid nature of technology group VI has been also ascertained for binders in samples Sr 469-2 and Sr 37 (FBC), both collected from exterior surfaces of ceramic vessels: wall (Sr 469-2) and base (Sr 37). All specimens referred to herein were originally used to repair (glue together) fragments of cracked ceramic vessels. Good wettability of the pottery surfaces and good absorption of minerals included in the composite caused high mechanical damage resistance of binder layers (Chapter V.4, Photograph 29).

As far as birch-bark binder in sample Sr 469-2 is concerned (Chapter V.3, Table 45b; Chapter V.5, Table 56e), it shows good solubility in organic solvents and melting point not exceeding 121 °C, which proves that the binder was not baked at temperatures exceeding its production temperature (Chapter V.4, Photograph

28). Thus, the binder was not subject to any additional thermal modification and, as such, was used away from any high temperature source. But the examination of a contact area between the layer of the mixed wood-tar (birch and pine tar – Chapter V.3, Table 45b) binder (Sr 37) and the wall of the affected vessel allows the conclusion that binder was liquid when applied. The binder was applied onto the cracked area at the seam between the body and the base of the vessel and subsequently thermally hardened [Kośko, Langer 1986: 593]. The hardening process is ascertained by significantly reduced solubility of the binder in organic solvents and no melting effect up to 300 °C (Chapter V.1, Table 5c). As soon as the repair was completed, the vessel was suitable for cooking, boiling, or processing of various products at high temperatures, including those in excess of 300 °C.

Other samples classified into technology group I of binders intended for repairing ceramic vessels, i.e. Sr 32-1, Sr 32-2, Sr 329w, Sr 329z and Sr 46 (FBC), as well as Sr 47 and Sr 184 (TrC), represent typical wood tars never exposed to naked flames as proven by their melting points not exceeding 142 °C (Chapter V.1, Tables 5b and 11). Binders in samples Sr 32-1, Sr 32-2, Sr 329w, Sr 329z and Sr 46 (FBC) were obtained from birch wood (Chapter V.3, Table 45b; Chapter V.5, Table 56d), while those in samples Sr 47 and Sr 184 (TrC) were made from the birch and pine mixed raw material (Chapter V.3, Table 50). Representing technology group I, samples Sr 32-1 and Sr 32-2 were collected from two cracked yet tightly refitted lip fragments of the vessel. To glue both fragments together, a thin layer of the binder was applied covering exterior surfaces of both fragments and each side of the vertical fracture. Visible on SEM photographs (Chapter V.4, Photographs 24a and 24b), microporous structures result from rapid volatilization induced by high temperatures during the wood-tar production process.

The wood-tar application for the purpose of repairing damaged vessels has been also ascertained in samples Sr 329w and Sr 329z (both collected from exterior and interior surfaces of the same vessel), Sr 47 and Sr 184 (exterior surface) and Sr 46 (fracture and exterior surface of the lip). The samples represent wood tars of technology group I. They preserve impressions (negative forms) of pottery fragments, caused by pressing broken pottery pieces together for fitting them back into position. Sample Sr 46 shows specific distribution of the binder on the fracture and exterior surface of the vessel lip suggesting the attempt of gluing back the chipped-off piece together with the rim. Given low melting points for samples Sr 47 and Sr 184 (Chapter V.1, Table 11), one should reckon with the possibility that both binders might have been deliberately modified by adding fatty substances of plant or animal origin. It should be also noted that the surface of sample Sr 47 exhibits traces of unprocessed bark, which point to a one-vessel reactor having been used for wood-tar production purposes (Chapter V.4, Photographs 51a and 51b). A somewhat more advanced wood-tar production method with a separate receiver is ascertained for sample Sr 184 which shows no traces of any raw material (Chapter V.4, Photographs 52a and 52b).

As far as sample Sr 36 is concerned, the examination of the contact area between a 2 mm thick layer of the wood-tar binder and the vessel surface proves that binder was intentionally applied onto the fragment of the broken vessel. The layer does not cover the entire available surface of the pottery fragment, which proves a rapid wood-tar petrification process. The binder represents a middle wood-tar fraction obtained from mixed birch and pine bark (Chapter V.3, Table 45c), technology group I, as proven by its melting point below 140 °C (Chapter V.1, Table 5c) and complete or partial solubility in organic solvents (Chapter V.2, Table 25f). No trace of any raw material in the sample points to high purity of wood tar, achieved through the use a separate receiver [Kośko, Langer 1986: 593].

Binders in samples Sr 58w and Sr 58z (collected from interior and exterior surfaces of the same vessel) were used to repair (glue) a broken base of a ceramic vessel. Their low melting points (Chapter V.1, Tables 5c and 5d) show that, once repaired with the wood-tar binder, the vessel was used at low temperatures only (approx. 100 °C), therefore never for cooking or boiling purposes. Similar surface texture combined with a typically irregular picture in the fracture of the wood-tar layers (both from the interior and the exterior) proves the potter's efforts purposeful. At the same time, it is noticeable that the wood-tar seam subsequently broke down together with the entire vessel. These observations rule out the possibility that the pottery fragments might have been accidentally dirtied with wood tar after the vessel had broken down [Langer, Pietrzak 2000: 414]. The microscopic examinations (Chapter V.4, Photographs 35a and 35b) revealing remnants of plant tissues indicate that the one-vessel method was used for production of both binders, with no separation between the raw material and the end product.

B. Binders used to mount flint inserts are represented by sample Sr 166, ascribed to the MC community. The binder in the sample belongs to wood-tar technology group I and was used to attach a flint arrowhead to a wooden shaft. The binder belongs to middle fractions obtained from birch wood (Chapter V.3, Table 47; Chapter V.5, Table 58) enriched with fatty substances of animal or plant origin for lower softening point (Chapter V.1, Table 7). Certainly, the production method should be considered advanced, involving two-vessel reactors, as birch tar shows relatively high purity levels with no traces of raw material contamination detectable by microscopy.

C. Binders used to attach birch bark to the ceramic vessels have been identified only on pottery fragments ascribed to the FBC, i.e. Sr 9 and Sr 137 and the GAC, i.e. Sr 517 and Sr 141. They have been classified into technology groups I (Sr 137 and Sr 517) or II (Sr 9 and Sr 141). The binders in samples Sr 9 and Sr 141 were exposed to temperatures higher than those in samples Sr 137 and Sr 517 (Chapter V.1, Tables 5a and 6), which may prove deliberate thermal hardening of the former. This conclusion is further confirmed by their insolubility in organic solvents (Chapter V.2, Tables 25a and 26) and the presence of high temperature-induced microporous structures (Chapter V.4, Photographs 40a and 40b). All binders discussed are middle or heavy birch-tar fractions obtained by dry distillation of birch wood (Sr 137) or birch tar (Sr 9, Sr 517 and Sr 141) as proven by comparative tests using modern wood-tar reference samples (Chapter V.3, Tables 45a and 46; Chapter V.5, Tables 56a and 57). In all cases, the binders were applied solely on exterior surfaces of ceramic vessels, in evenly distributed layers 0.5 to 3 mm thick running vertically down from the vessel rim [Langer, Rola 1997: 35-38]. Such a specific application method proves that, originally thick in consistency, birch tar was deliberately used as a binding agent to add aesthetic value (attach bark cut ornaments) to pottery pieces. Noticeable traces of deep cavities in the binder surface confirm the possibility of birch tar having been used to affix bark cut ornaments which subsequently fell off together with some portion of the organic substrate (Chapter V.4, Photograph 41). Traces have also been ascertained which point to birch tar having been applied onto the pottery surface with a brush, which confirms the conclusion drawn above that birch bark was used deliberately (Chapter V.4, Photographs 40a and 40b). No remnants of the raw material (bark or wood) detectable by microscopy (Chapter V.4, Photographs 40a and 40b) suggest an advanced wood-tar production method with two-vessel reactors (with a separate receiver).

D. Binders used to fill ornaments (inlays) stamped or incised on exterior surfaces of ceramic vessels are unique as far as wood-tar finds are concerned and only represented by two samples (Sr 252 and Sr 59) ascribed to the FBC phase III B – III C / III C and V A, respectively. Both samples are very interesting because they illustrate applications of wood tar for decorative purposes. However, wood tar is not applied as a typical colorant to create a homogenous layer of colour (Chapter 6.2.4). Instead, it is used as a black inlay material to fill decorative vertical bands (Sr 252) or oval (Sr 59) depressions. Traces of pressing and kneading of the still plastic binders prove the potters having acted intentionally while covering the vessel surfaces with liquid wood-tar layers. The vessel, from which sample Sr 59 has been collected, was not heated to temperatures exceeding 100 °C, which proves that the vessel was used away from any strong heat source (Chapter V.1, Table 5d). In this case, a faulty binder preparation process (insufficient hardening) may be suspected to have largely reduced cohesion thereby decreasing mechanical damage resistance of the seam due to insufficient cross-link density. The binder in sample Sr 252 underwent somewhat different modifications. Its physico-chemical properties indicate thermal stabilisation on the surface of the vessel (Chapter V.1, Table 5b; Chapter V.2, Table 25c).

The properties are beneficial in terms of production technology and applications (safe use at higher temperatures) [Langer, Pietrzak 2004: 105]. Microscopic examination has revealed the presence of microporous structures (Chapter V.4, Photographs 36a and 36b) resulting from high temperature exposure (release of vapours and gases of more readily volatile substances during the production process). Classified into technology group I with some elements typical of technology group II, the binder in sample Sr 252 was produced from birch wood, while, classified into technology group I, the binder in sample Sr 59 was made from birch bark. In both cases, the wood-tar makers used the double-pot method with the raw material having been separated from the end product as proven by high purity of the latter exhibiting no traces of any unprocessed raw material (Chapter V.4, Photographs 36a and 36b).

E. Binders used for medical or magic purposes are very rare among the excavatable wood-tar remnants, representing exclusively technology group I: Sr 327, Sr 243 (FBC); Sr 326 (MC); Sr 38, Sr 39 (PYC); Sr 51, Sr 52, Sr 53, Sr 54 (CaC). A noteworthy fact is that all these binders occur in burial contexts. A very interesting example of a poultice made from birch tar mixed with medicinal herbs (Sr 326) comes from a richly equipped grave of an approximately 30-year-old female, ascribed to the late phase of MC [Baczyńska 2004]. The poultice was most likely applied deliberately for medical purposes onto a wound located somewhere near the collarbone of the deceased. The conclusion about the medical use is all the more reasonable given strong antiseptic properties of birch tar and pharmacological action of *Lithospermum officinale L.*, which include, but are not limited to speeding up a wound healing process [Baczyńska 2004; Baczyńska, Lityńska-Zając 2005]. Made from wood tar and fruits of *Lithospermum officinale L.*, the poultice was applied warm directly onto the body, presumably onto the wound, as proven by the collarbone impression on the interior surface of the poultice. On the exterior surface of the poultry, there is a large number of short crystallized fibres which may point to the poultice having been adhering to some kind of textile that could conceivably be linen (Chapter V.4, Photographs 42c and 42d). The poultice mixture formed a 0.15 mm thick oval shape that subsequently suffered chips in the edges.

The observations above prove that the poultice was originally round, with its diameter of up to 5 cm [Baczyńska 2004; Baczyńska, Lityńska-Zając 2005]. The medical use has been also ascertained for the substance in sample Sr 327 collected from the grave ascribed to FBC. The substance has proven to contain no herbal admixture, but its preserved shape (long and curled wood-tar strip or plaster) allows seeing is as medical dressing. Moreover, the plaster might have originally contained some plant additives such as herbs. The layers in both samples reveal the makers' unique attention to high purity of tar, which seems reasonable given its unique use. The absence of microscopy-detectable remnants of raw materials (Chapter V.4, Photographs 16a-16c, 42a and 42b) proves that birch tars (Chapter V.3, Tables 45a and 47; Chapter V.5, Tables 56a and Sr 58) intended for medical purposes were obtained by dry distillation in two-vessel tar kiln. The temperature used for the production process was typical of middle wood-tar fractions (Chapter V.1, Tables 5a and 7) and ensured a high degree of poultice plasticity desirable for dressings. In both cases discussed, we are most likely dealing with finds associated with medical practices whose effectiveness was enhanced by magic remedies.

Classified into technology group I, the substance in sample Sr 243 (FBC) is a lump with clearly visible impressions of wood fragments on the surface. The cross-sectional analysis of the lump reveals that the lump was used as a wood-tar binder to consolidate and caulk the seam between two structural timber elements of the casket or coffin containing a corpse [Duday, Kowalewska-Marszałek 2003: 96]. In this case, the double role of the binder is ascertained with having been used for utilitarian (sort of glue) purposes and magic (to protect remains of the deceased and deter evil spirits). Chromatography (Chapter V.3, Table 45c), spectroscopy (Chapter V.5, Table 56g) and remnants of unprocessed birch wood visible even with the necked eye (Catalogue of Sources) prove that the binder represents middle wood-tar fractions obtained in one vessel.

Insights into wood-tar applications for broadly understood magic purposes are provided by samples collected for barrow burials attributed to FBC (Sr 38 and Sr 39) and CaC (Sr 51, Sr 52, Sr 53 and Sr 54). As far as samples from the FBC contexts are concerned, the binders form plastic layers covering heads of the deceased, applied most probably during a funeral rite of positioning scalps back onto the heads [Klejn 1961; Kośko, Langer 1986]. Chromatography (Chapter V.3, Table 51) and spectroscopy (Chapter V.5, Table 64) have revealed that both FBC samples (Sr 38 i Sr 39) represent light and middle wood-tar fractions, enriched with plant or animal fats to decrease melting and softening points (Chapter V.1, Table 12) and obtained from a birch and pine mixed raw material. Particularly noteworthy is the unique correspondence between chemical compositions of both samples, each collected from a different grave. Detected by FTIR testing, unusual spectral similarity between the samples (Fig. 21) points to either strict adherence to the production formula (ritual production practices) or the same production batch in both samples. It cannot be ruled out that ancient peoples were producing a special type of wood-tar, using raw materials in precise proportions. Such wood-tar was then used exclusively for the most important practices or rituals not infrequently separated by considerable time gaps [Kośko, Langer 1986: 598].

In both samples, microscopy has revealed microporous structures which evidence rapid release of vapours and gases of more readily volatile substances during the wood-tar production process (Chapter V.4, Photographs 53a and 53b). Moreover, remnants of the unprocessed raw material have been found, which prove that the primitive wood-tar production method with one ceramic vessel and direct contact between the starting material and the end product was used (Chapter V.4, Photograph 54).

Representing technology group I, binders in samples collected from tumuli graves of early CaC (Sr 51, Sr 52, Sr 53 and Sr 54) were generated by pyrolysis of birch and pine mixed in precise proportion of 2:1 (Chapter V.3, Table 52). As with the FBC samples, CaC wood-tar remnants are closely connected with burial contexts, as all of them have been revealed in the head area of the deceased. Thus, wood tars might have been applied during funeral rites to position the scalp back

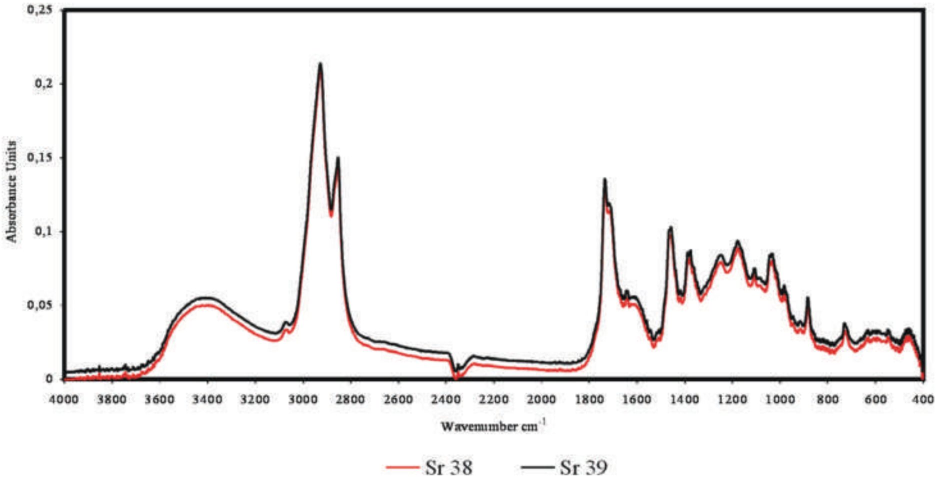


Fig. 21. Infrared spectroscopy correlation for Sr 38 and Sr 39

onto the head of the deceased. At the same time, we cannot rule out the possibility that wood tar was used for a death mask covering the face of the deceased. All the samples represent middle wood-tar fractions. Binders in samples Sr 51 and Sr 54 were obtained in the same way as those in FBC samples, i.e. using the method resembling a fat rendering process in one vessel. Other binders do not exhibit any traces of raw materials in the form of unprocessed birch bark or birch wood. These observations point to the more advanced method of their production with a two-vessel reactor to separate and purify the product from the raw material remnants (Sr 52 and Sr 53). Microscopy has also revealed structures evidencing a rapid generation process and polymerization of the binders (Chapter V.4, Photographs 55a and 55b).

IV.2.3. RESULTS ON VESSEL CAULKING STUDIES

Accounting for 15.1 per cent of all source materials, 33 samples from 17 archaeological sites are classified into the category of caulking layers applied to walls of ceramic vessels. Chart 10 shows the percentage distribution of the caulk samples by culture.

Wood tars subject to physico-chemical analysis come from two culture circles: *Baltic drainage basin circle* (LIPC – 8 samples: Sr 74, Sr 80, Sr 81, Sr 83, Sr 88-2,

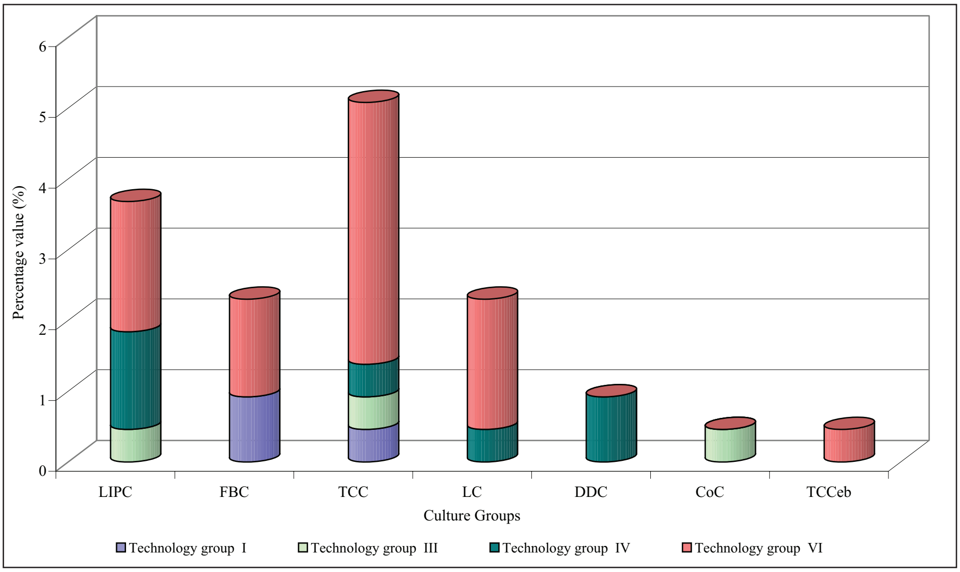


Chart 10. Percentage distribution of caulking layers applied to ceramic vessels, per technology group

Sr 89, Sr 95 and Sr 96 from 3 archaeological sites; FBC – 5 samples: Sr 465, Sr 467, Sr 253, Sr 254 and Sr 3w from 3 archaeological sites; TCC – 11 samples: Sr 271, Sr 272-1, Sr 272-2, Sr 460, Sr 454, Sr 457, Sr 220, Sr 223, Sr 224, Sr 258 and Sr 225 from 6 archaeological sites; LC – 5 samples: Sr 267, Sr 270, Sr 374w, Sr 129w and Sr 133w from 3 archaeological sites) and *Eastern European forest zone culture circle* (DDC – 2 samples: Sr 315w and Sr 315z from 1 archaeological site; CoC – 1 sample: Sr 231 from 1 archaeological site; TTC eastern branch – 1 samples: Sr 330 from 1 archaeological site). In the past, these hydrophobic wood-tar substances were used to caulk a porous microstructure of interior and exterior surfaces of ceramic vessels designed for boiling, drinking and storing liquids. For archaeometric and taxonomic characteristics of all the samples discussed below, see Catalogue of Sources.

The category of ceramic vessel caulks includes both wood-tars (technology groups: I, I / II i II) and composites (technology group VI). A primary criterion to classify the samples into the following two sub-groups is temperature (high or low) at which ceramic vessels with caulking layers were used:

(A) vessels with caulking layers, used at low temperatures;

(B) vessels with caulking layers, thermally stabilized.

A. 4 samples are classified into the group of vessels with caulking layers, used at low temperatures (FBC: Sr 465, Sr 253 and Sr 3w; TCC: Sr 457). Applied only onto interior surfaces of ceramic vessels, the caulks in samples Sr 465 and Sr 3w

(FBC) and Sr 457 (TCC) are wood-tars of technology group I. Present on the exterior surface of the vessel fragment, the caulk in Sr 253 (FBC) represents, on account of its properties, composites of technology group VI.

The results of chromatography and spectroscopy demonstrate that the caulks of technology group I referred to above are the lightest fractions of typical wood tars obtained by dry distillation of birch wood (Sr 465 and Sr 457 – Chapter V.3, Tables 45b and 48; Chapter V.5, Tables 56d and 59b) or birch and pine mixed raw material (Sr 3w – Chapter V.3, Table 45c). Revealed by EPR, intense lines produced by carbon radicals prove that the caulks are organic (Chapter V.8, Tables 78b, 78c and 84). They were deliberately applied to pottery surfaces in relatively thin and evenly distributed layers of hard caulking putty which has its softening point between 85 and 105 °C and a melting point between 105 and 120 °C (Chapter V.1, Tables 5b, 5c, and 8). Indicated by FTIR, excessive amounts of acids and esters in the samples provide evidence for a deliberate admixture of animal fat or plant oil to decrease a wood-tar melting point (Chapter V.1, Tables 5b, 5c and 8). Low melting points of the caulks indicate that the vessels with caulking layers were used far away from strong heat sources such as hearths. The ceramic vessels were unsuitable for cooking, boiling, or raw material processing at high temperatures. Indicating complete or partial solubility of all three caulks in organic solvents, the results of the solubility test (Chapter V.1, Tables 25d, 25f and 28b) correspond with the observations presented above. Moreover, the caulks give a weak colour-producing reaction to ammonium thiocyanate (NH_4SCN), which proves that they contain small amounts of iron (Fe) compounds from contamination by post-depositional processes. Microscopic examinations have also confirmed that volatile substances were not subject to rapid release but gradual evaporation during the application and hardening of caulking layers [Langer, Kośko 1999: 71].

The composite of technology group VI (FBC: Sr 253) constitutes a separate category. It exhibits complete or partial solubility in organic solvents (Chapter V.2, Table 25e). Furthermore, its softening point (93 – 112 °C) and melting point (121 – 142 °C – Chapter V.1, Table 5c) indicate the presence of middle wood-tar fractions with smaller amounts of macro-molecular substances, obtained by dry distillation of birch wood as demonstrated by the results of chromatography and spectroscopy (Chapter V.3, Table 45c; Chapter V.5, Table 56e). Also, the preparation method for the caulk in sample Sr 253 (no thermal stabilisation) points to it having been used at low temperatures away from any strong heat source. These observations lead to the conclusion that the caulk was used at lower temperatures, i.e. cold (the vessel might have served for preparing meals that did not require any cooking or boiling, or for storing or transporting products, including liquids). A colour-producing reaction to ammonium thiocyanate (NH_4SCN), dominance of inorganic constituents revealed both by FTIR and EPR (in the form of paramagnetic components) point to large amounts of minerals having been deliberately added (Chapter V.2, Table 25e; Chapter V.5, Table 56e; Chapter V.8, Table 79b).

At the same time, the tested caulk displays a considerable amount of carbon radicals that prove its organic origin (Chapter V.8, Table 78b). It appears evident that the maker intended to modify original properties of the wood tar, thereby obtaining a mix of organic matter and minerals, characterized by improved mechanical damage resistance (e.g. resistance to abrasion).

B. Vessels with caulking layers applied both to interior surfaces (LIPC: Sr 74, Sr 80, Sr 81, Sr 83, Sr 88-2, Sr 89, Sr 95 and Sr 96; FBC: Sr 467 and Sr 254; TCC: Sr 271, Sr 272-1, Sr 272-2, Sr 220, Sr 224, Sr 258 and Sr 225; LC: Sr 267, Sr 270, Sr 374w, Sr 129w and Sr 133w; DDC: Sr 315w; CoC: Sr 231; TCC eastern branch: Sr 330) and external surfaces (FBC: Sr 253, TCC: Sr 460, Sr 454 and Sr 223; DDC: Sr 315z) and thermally stabilized are represented by 30 samples. Showing a high degree of thermal degradation, heavy wood-tar fractions with properties attributable to technology groups III (LIPC: Sr 89; TCC: Sr 460; CoC: Sr 231) and IV (LIPC: Sr 74, Sr 80 and Sr 81; TCC: Sr 271; KL: Sr 267; DDC: Sr 315w and Sr 315z) were applied purposefully to the vessel surfaces, in evenly distributed black layers (Chapter V.4, Photograph 56b) up to 2 mm in thickness. The bonding between the organic layer and walls of the vessels proves that wood tar was applied in a liquid state. This finding is further confirmed by traces of a brush-like tool used for application of still runny wood tar (Chapter V.4, Photograph 56a).

The samples should be considered the results of intentional activities of the sealer intending to thermally stabilize wood tar on both interior and exterior surfaces of ceramic vessels. Microscopic examinations have revealed microporous structures that prove high temperatures having been used for deliberate thermal modification accompanied by intensive volatilization (Chapter V.4, Photographs 60a and 60b). Direct contact with naked flames is also evidenced by strong sintering and significant cracking of the organic layers (Chapter V.4, Photographs 4a and 4b). The resulting considerable carbonization of the organic substances and elimination of diagnostic markers prevent any identification of raw materials for these caulks (Chapter V.5, Tables 54a, 54b, 59a, 61a, 65 and 67). The only exception is sample Sr 460 (TCC) which, although largely affected by thermal degradation, contains detectable (FTIR testing) chemical components specific to birch raw material (Chapter V.5, Table 59a). Once applied to vessels, wood tars were exposed to high temperatures exceeding 400 °C. Wood tars in eight samples, i.e. Sr 74, Sr 80 and Sr 89 (LIPC); Sr 460 (TCC); Sr 267 (LC); Sr 315w and Sr 315z (DDC) and Sr 231 (CoC), show slight softening effects at temperatures between 145 and 265 °C (Chapter V.1, Tables 3, 8, 10, 14 and 16).

The deliberate thermal modification of the organic layers rendered them more tolerant to high temperatures, thereby allowing the safe use of the vessels at temperatures below 300 °C with no risk of damage to caulking layers. Obtained through such modification, the new properties made the ceramic vessels suitable for such uses as storing or processing liquid products. These observations are substantiated by total insolubility in organic solvents and water, which insolubility is typical of materials strongly affected by thermal degradation. Some wood tars show just partial solubility in aqueous solutions of hydrochloric acid and sodium hydroxide (NaOH) and weak colour-producing reaction to ammonium thiocyanate (NH_4SCN), which proves the presence of a small accidental addition of minerals from soil (Chapter V.2, Tables 23a, 23b, 28a, 30a, 34 and 36). All the samples referred to above represent organic substances as evidenced by the presence of organic radicals (spectral parameters (g) of approx. 2.0024 – 2.0040 and (ΔH) of approx. 0.42 – 0.64 mT) revealed by EPR (Chapter V.8, Tables 74, 84, 88, 96 and 100). Traces of plant structures (remnants of raw material: wood or bark), which prove use of the primitive wood-tar production method whereby the raw material and the product were mixed, have been found in sample Sr 81 (LIPC) (Chapter V.4, Photographs 5a and 5b). Other samples show no remnants of raw material (unprocessed wood or bark), which points to high purity of tars obtained by the advanced two-vessel production method with a reaction chamber and a receiver (Chapter V.4, Photographs 4a, 4b, 60a and 60b).

Samples classified into technology group VI of hybrid organic-mineral composites, are clear standouts (LIPC: Sr 83, Sr 88-2, Sr 95 and Sr 96; FBC: Sr 467 and Sr 254; TCC: Sr 272-1, Sr 272-2, Sr 454, Sr 220, Sr 223, Sr 224, Sr 258 and Sr 225; LC: Sr 270, Sr 374w, Sr 129w and Sr 133w; TCC eastern branch: Sr 330). Small thickness (approximately 1 to 2 mm) and even distribution of composite layers on the interior (LIPC: Sr 83, Sr 88-2, Sr 95 and Sr 96; FBC: Sr 467 and Sr 254; TCC: Sr 272-1, Sr 272-2, Sr 220, Sr 224, Sr 258 and Sr 225; LC: Sr 270, Sr 374w, Sr 129w and Sr 133w; TCC eastern branch: Sr 330) and exterior surfaces (TCC: Sr 454 and Sr 223) of vessels indicate that the tested composites served to form caulking and insulating layers.

So modified, the vessels obtained properties that were particularly important for storing or processing liquid products and keeping heat in for a longer time (improvement of thermal conductivity in vessel walls). Moreover, the tested composites were prepared in a specific way (mixed organic-mineral material) which indicates a high degree of technological advance among producers A structural role in the composites was played by a mineral constituent (s and grains), while wood tar was an organic binder to bind structural components and protect them against external factors. Also in the case of the composites, EPR testing has ascertained the presence of carbonized organic components producing specific lines with spectral parameters (g) of approx. 2.0027 – 2.0048 and (DH) of approx. 0.46 – 1.97 mT (Chapter V.8, Tables 74, 78b, 84, 88 and 104) overlapping broad signals that correspond to paramagnetic (mineral) components with parameters (g) of approx. 1.8150 – 2.4892 and (DH) of approx. 27.06 – 130.7 mT (Chapter V.8, Tables 75, 79b, 85, 89, and 105). In addition, all composites were subjected to intentional thermal stabilisation as proved by their poor to non-existent solubility in organic solvents (Chapter V.2, Tables 23a, 23b, 25d, 25f, 28a, 28b, 28c, 30a, 30b and 38) and no melting point up to 300 °C (Chapter V.1, Tables 3, 5c, 8, 10 and 18), which at the same enables the conclusion about the raw material (wood or bark) used in their production process. High temperatures increased the amounts of macromolecular components, thereby improving thermal stability of wood-tar layers.

These observations are substantiated by microscopic examinations that have revealed the presence of polymeric structures specific to organic substances significantly affected by carbonization (Chapter V.4, Photographs 8b, 65a and 65b). Noticeable is also strong bonding between the composite layers and pottery substrate. Described above, modifications in the composites of technology group VI resulted in caulking layers with very high mechanical and temperature damage resistance levels. Performed with a scanning electron microscope (SEM), the examinations point to intentional adding of minerals or important components of the composite. The examinations have ascertained even distribution of the mineral admixture on the surface of the vessel (Chapter V.4, Photographs 26, 45a, 46, 50 and 66) and a hybrid (organic-mineral) nature of the tested composite (Chapter V.4, Photographs 6a, 6b, 8a, 25 and 45b).

IV.2.4. RESULTS OF STUDIES ON COLORANTS

Among tar samples subjected to physico-chemical analysis, there are 37 samples originating from 26 archaeological sites and accounting for 17 per cent of all source materials, which are specifically outstanding in terms of their application purposes. Chart 11 shows the percentage distribution of the colorant category samples by culture. All sampled tars (colorants) were applied by ancient producers in thin layers to surfaces of ceramic vessels to add aesthetic value to those pottery products.

The colorant samples derive from three culture circles: *Baltic drainage basin circle* (LIPC – 1 sample: Sr 88-1 from 1 archaeological site; FBC – 20 samples: Sr 16, Sr 212, Sr 214, Sr 1, Sr 469-1, Sr 189, Sr 249, Sr 3z, Sr 12, Sr 5, Sr 284, Sr 324, Sr 8, Sr 219, Sr 13, Sr 23, Sr 24, Sr 14, Sr 25 and Sr 26 from 14 archaeological site; GAC – 2 samples: Sr 18 and Sr 19 from 2 archaeological sites; TCC – 1 sample: Sr 440 from 1 archaeological site; TuC – 1 sample: Sr 172 from 1 archaeological site; LC – 4 samples: Sr 443, Sr 129z, Sr 130 and Sr 133z from 2 archaeological sites), *Eastern European forest zone culture circle* (NC – 5 samples: Sr 255-1, Sr 255-2, Sr 188, Sr 355 and Sr 238 from 4 archaeological sites) and *Carpathian Basin culture circle* (LIPC – 2 samples: Sr 10 and Sr 438 from 2 archaeological sites; BüC – 1 sample: Sr 151 from 1 archaeological site). For

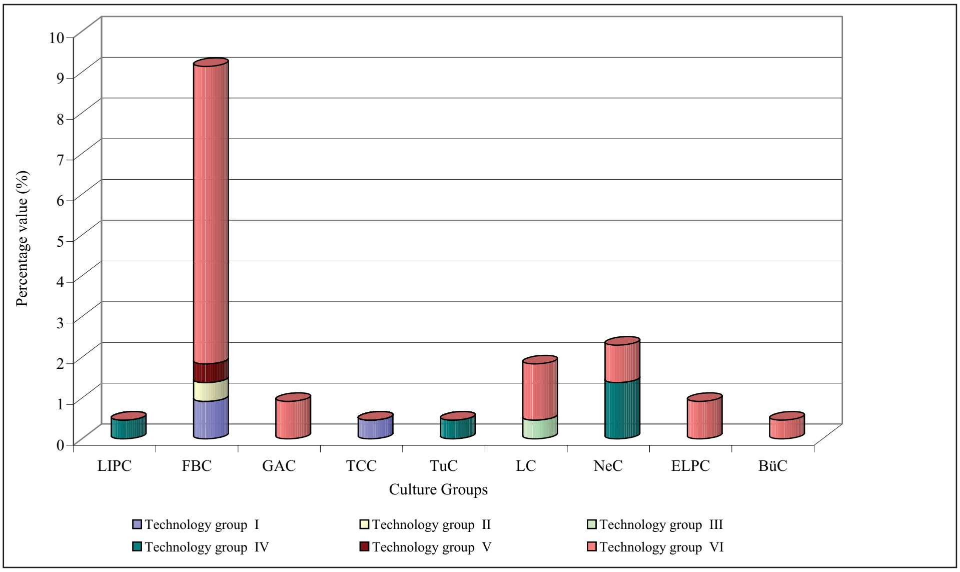


Chart 11. Percentage distribution of colorants per technology group

archaeometric and taxonomic characteristics of all samples discussed below, see Catalogue of Sources.

The category of colorants comprises wood tars (technology groups I to IV), bitumens (technology group V) and composites (technology group VI). A primary classification criterion for the category has been a thermal treatment method used by potters for pottery surfaces with applied layers of organic colorants. All the organic colorant samples referred to above are thus divided as follows:

(A) vessels with colorant coats, used at low temperatures,

(B) vessels with colorant coats, thermally stabilised.

A. Vessels with colorant coats, used at low temperatures constitute a group of 7 samples. The colorants are wood tars of technology group I (FBC: Sr 469-1 and Sr 5; TCC: Sr 440) and composites of technology group VI (Sr 214, Sr 3z, Sr 12 and Sr 24). Representing light and middle wood-tar fractions, the colorants had no prolonged contact with any high-temperature source, as proved by their softening point (82 – 156 °C) and melting point (106 – 195 °C – Chapter V.1, Tables 5a, 5c and 8). Our observations are substantiated by the fact of their complete or partial solubility in organic solvents (Chapter V.2, Tables 25b, 25e, 25f, 25g and 28c). Vessels, which display surfaces with coats of organic colorants showing low resistance to high temperatures, were unsuitable for cooking, boiling, or thermal processing of other products in hearths. The results of chromatography (Chapter V.3, Tables 45b, 45c and 48) and spectroscopy (Chapter V.5, Tables 56b, 56e, 56f and 59c) clearly indicate that all tars described above were obtained by dry distillation of birch wood (FBC: Sr 214, Sr 12 and Sr 5) or birch bark (FBC: Sr 469-1; TCC: Sr 440).

The only exceptions are samples Sr 3z and Sr 24 (FBC), which contain tars made from a mixed birch and pine raw material (Chapter V.3, Table 45c). Microscopic examinations reveal high purity of all tested colorants, with no remnants of unprocessed raw material manifesting themselves in the form of structures typical of wood or bark (Chapter V.4, Photographs 27a and 27b). Wood tars classified into technology group I as well as organic-mineral composites classified into technology group VI, contain carbon radicals with parameters (g) of approx. 2.0023 – 2.0034 and (ΔH) of approx. 0.46 – 0.61 mT, which unquestionably proves their organic origin (Chapter V.8, Tables 78a-78c and 84). Confirming the presence of iron compounds, a reaction (intense red coloration) to ammonium thiocyanate (NH_4SCN) indicates considerable amounts of minerals having been added to the composites (Chapter V.2, Tables 25b, 25f and 25g).

Samples Sr 469-1, Sr 3z, Sr 12, Sr 5 and Sr 24 (FBC) as well as sample Sr 440 (TCC) show tars in the form of homogeneous thin black coats covering entire surfaces of the vessels. The samples evidence the use of wood tars for decorating exterior surfaces (painted colouring coats) and improving functional properties (improved water-tightness and thermal conductivity) of ceramic vessels. The fact that the potters were acting intentionally while generating black organic coats for aesthetic purposes on vessel walls raises no doubts most of all because the coats are evenly distributed (Chapter V.4, Photograph 27a). The aesthetic interpretation is further substantiated by relatively small yet quite equal thickness of up to 1 mm in organic coats (in most cases: below 1 mm), the use of mineral primers (FBC: Sr 214, Sr 3z, Sr 12 and Sr 24) to modify (smooth) the pottery surfaces and visible traces of a brush-like tool (Chapter V.4, Photograph 31). Microscopic examinations indicate that the colorants were applied purposefully in the form of liquid paint onto thin coats of mineral and usually red (iron compounds) primer, and, as such, cannot be considered accidental wood-tar deposits generated by burning wood in a hearth. The cross-sectional analysis of the coats displays their specific regularity that results from applying (with a brush?) one liquid or semi-liquid coat of a wood-tar colorant over another that is already solidified on the primer (Chapter V.4, Photography 30). Moreover, sample Sr 3z (FBC) shows high concentrations of iron (Fe) particles in the colorant layer (exceeding those in pottery substrate), which are comparable with blood cells in terms of size. Most interesting of all is, however, the chemical composition of the colorant: opposite to what might naturally be expected from such large concentrations of iron (Fe), the colorant exhibits all and any characteristics of organic material. Moreover, concentrations of sulphur (S) particles have been identified, whose sizes are comparable with those of erythrocytes. Sulphur constitutes an important component of proteins and, as such, together with iron, may be considered evidence of blood having been added to prepare the colorant [Langer, Kośko 1992: 64].

A thin (below 1 mm), matt and slightly cracked black tar coat (FBC: Sr 214) forming strong bonding with a on the exterior surface of the thick-walled pottery surface represents a different method of vessel decoration. The colorant was applied to the vessel walls purposefully not to decorate the entire available surface but just to paint diagonal geometric shapes (bands of approximately 5 mm in thickness). It seems that, painted at equal distances from each other, the shapes might have covered a larger part of the vessel (Catalogue of Sources). The organic surface of the tested colorant shows traces of an evenly distributed mineral matter (Chapter V.4, Photograph 17). The matter was added purposefully to modify the colorant properties by increasing its mechanical damage resistance. Sand grains look embedded into the surface, which proves that they were added when the colorant was still semi-liquid. Traces of applying the colorant onto the pottery substrate with a brush-like tool confirm that the colorant was used while in a liquid state. The noticeable presence of micro bubbles points to rapid volatilization occurring during the wood-tar production process.

B. Vessels with colorant coats, thermally stabilised, are represented by 30 samples classified into wood-tar of technology groups II (FBC: Sr 8), III (LC: Sr 130) and IV (LIPC: Sr 88-1; TuC: Sr 172; NiC: Sr 255-1, Sr 255-2 and Sr 188), bitumens of technology group V (FBC: Sr 14) and composites of technology group VI (FBC: Sr 16, Sr 1, Sr 189, Sr 249, Sr 284, Sr 324, Sr 219, Sr 13, Sr 23, Sr 25 and Sr 26; GAC: Sr 18 and Sr 19; LC: Sr 443, Sr 129z and Sr 133z; NiC: Sr 355 and Sr 238; ELPC: Sr 10 and Sr 438; BüC: Sr 151).

Colorants included in this category are thermally stabilized and thereby considerably improved in terms of their thermal resistance levels. Vessels covered with organic colorants, which were modified in such a way, were suitable for use at temperatures exceeding 300 °C, for cooking, boiling, or thermal processing of other products, with no risk of damage to the colorant. These observations are substantiated by total insolubility of the colorants at temperatures up to 300 °C. In most cases (FBC: Sr 16, Sr 212, Sr 189, Sr 249, Sr 284, Sr 324, Sr 8, Sr 219, Sr 13 and Sr 26; GAC: Sr 18 and Sr 19; TuC: Sr 172; LC: Sr 443 and Sr 130; NiC: Sr 255-1, Sr 255-2 and Sr 188; ELPC: Sr 10 and Sr 438; BüC: Sr 151), a weak softening effect has been recorded in the range of 112 to 295 °C (Chapter V.1, Tables 5a, 5c, 5d, 6, 9, 10, 17, 20 and 21). Largely reduced solubility and sometimes even total insolubility in organic solvents and water, accompanied by partial solubility in aqueous solutions of acids and alkali is typical of highly polymerised and thermally degraded substances (Chapter V.2, Tables 23b, 25a, 25b, 25e, 25f, 25g, 26, 29, 30a, 40 and 41).

The method of applying colouring organic coats allows concluding that heavy wood-tar fractions were applied hot and melt and subsequently exposed to high temperatures for stabilization. Such procedure resulted not only in hardening and melting incapability of the colouring coats but also in their considerable compositional impoverishment in consequence of thermal degradation of many chemical compounds, leading to generation of almost pure carbon manifesting itself in less spectacular IR absorption spectra (FTIR). The only exception is the colorant in sample Sr 219 with its softening point of 123 – 174 °C (Chapter V.1, Table 5c) and good solubility in organic solvents (Chapter V.2, Table 25f). These properties enable its classification into heavy wood-tar fractions obtained from birch bark (Chapter V.3, Table 45c; Chapter V.5, Table 56f). Despite thermal modification (stabilisation), FTIR testing shows the chemical composition of the colorants in some samples (FBC: Sr 16, Sr 212, Sr 189, Sr 284, Sr 324, Sr 13, Sr 25 and Sr 26; TuC: Sr 172; ELPC: Sr 10; BüC: Sr 151) continuing to include diagnostic markers pointing to the colorant having been produced from birch (Chapter V.5, Tables 56a, 56b, 56e, 56f, 56g, 60, 71 and 72).

As far as other samples are concerned, which exhibit larger degrees of thermal degradation leading to permanent removal of components with melting points below 300 °C, the identification of the raw material is prevented. Results of EPR spectra of the colorants with spectral parameters of narrow resonance lines typical of carbon radicals, i.e. (g) of approx. 2.0018 – 2.0037 and (ΔH) of approx. 0.45 – 1.59 mT, point to them being organic (Chapter V.8, Tables 74, 78a-78c, 80, 86, 88, 102, 108 and 110). Similar intensities, positions and widths of EPR lines prove comparable wood-tar production conditions and similar thermal history of the colorants. Examinations of surfaces of the colorants have revealed a layered microporous structure generated through high temperature-induced evaporation of volatile substances (Chapter V.4, Photographs 61b, 63a, 63b, 64, 71e and 71f), which further substantiates the observations presented above. The colorants in samples Sr 172 (TuC) and Sr 443 (LC) were produced by the one-vessel production method causing the intermingling of the remains of the raw material (wood and bark) with the product (wood tar), as evidenced by the presence of plant structures (Chapter V.4, Photographs 43b and 48d). Other colorants were obtained by the two-vessel method, using a kiln with a separate reaction chamber and a product receiver (Chapter V.4, Photographs 61b, 63a, 63b, 64, 71e and 71f). Yet a separate issue is the colorant in sample Sr 14 (FBC). Its geogenic origin is unique for the discussed organic colorants and its characteristics correspond to those of bitumen (Chapter V.5, Table 56g) with properties typical of such natural substances as asphalt or oil [Langer, Kośko 1999: 72]. It seems that it was a black wood-tar-like colour of the substance in sample Sr 14 that determined its use as a colorant on the vessel surface.

The way in which the black coats of colorants were applied to cover the entire surface of the vessels (LIPC: Sr 88-1; FBC: Sr 16, Sr 212, Sr 1, Sr 189, Sr 249, Sr 284, Sr 324, Sr 8, Sr 219, Sr 13, Sr 23, Sr 14, Sr 25 and Sr 26; GAC: Sr 18 and Sr 19; TuC: Sr 172; LC: Sr 443, Sr 129z, Sr 130 and Sr 133z; NiC: Sr 255-1, Sr 255-2, Sr 188, Sr 355 and Sr 238) shows that, once the vessels were dry, they were painted with the liquid organic colorant and subsequently intentionally subjected to thermal stabilisation. Coats of colorants were exposed to high temperatures exceeding 300 °C not until they were was applied to the surfaces of the vessels. The organic colorants were applied in thin (bellow 1 mm) and regularly distributed coats (Chapter V.4, Photographs 39b, 43a, 48a-48c, 61a and 62). Moreover, the vessel surfaces display thin coats (approx. 0.1 mmm thick) of a mineral primer, onto which the organic colorants were applied with a brush-like tool (Chapter V.4, Photographs 33, 34a and 39a), which substantiates the hypothesis about the intentional use of tars to add aesthetic value (colorants) to the vessels.

Ascertained already at the microscopic examination stage, the use of the mineral primer containing iron compounds (red colour) is particularly clear in samples Sr 88-1 (LIPC), Sr 212, Sr 284 and Sr 23 (FBC) (Catalogue of Sources). The samples also include those (technology group VI) evidencing the intentional use of mineral fillers, which permitted to obtained organic-mineral composites and increased allowable temperature for the intended use of the vessels above 300 °C. The purposeful admixture of considerable amounts of mineral matter is indicated by the mineral matter being both evenly distributed and embedded into the organic matter and confirmed by microscopic examinations (Chapter V.4, Photographs 7a, 7b, 20a, 20b, 32 and 34b). The admixture allowed smoothing the pottery surface, reducing abrasibility and increasing mechanical damage resistance of coats of organic colorants. The unique method used to prepare composite colorants proves a high degree of technological advance among makers who intended to achieve the substance highly resistant to mechanical and thermal damage.

The microscopic examinations of the surface in sample Sr 1 show that, once it was dry, the vessel surface was painted with the colorant mixed with the base material (substrate or clay) to form thin suspension (paint) during painting. Compositionally, the colorant in sample Sr 1, alike the colorant in sample Sr 3z, contains concentrations of iron particles, whose sizes are comparable to those of blood cells (red cells or erythrocytes). The correlation between the iron distribution pattern and blood cell sizes may provide the evidence for blood having been used as a source for iron (Chapter V.4, Photographs 19). It is likely that blood was used because the colorant makers were aware of its colouring properties, particularly after the colorant makers had revealed that the colour could be fixed during firing.

It should be highlighted that, as the organic matter underwent total degradation while exposed to high temperatures, the statistical correlations remain the only pieces of evidence for the use of blood admixtures for colouring purposes in samples Sr 1 and Sr 3z. The colorant in sample Sr 8 is very high in organic acid salt content (1617 cm^{-1}) and, at the same time, low in ester (1730 cm^{-1}) and carboxylic (1700 cm^{-1}) content, which may be the result of purposeful efforts of the colorant makers to neutralize acids during the colorant preparation process. To neutralize organic acids in the colorant and thereby improve bonding between wood tar and pottery substrate, either calcium hydroxide ($Ca(OH)_2$) or calcium carbonate ($CaCO_3$) was used [Langer, Rośko 1999: 71].

Classified into technology group VI and contained in samples Sr 10, Sr 438 (ELPC) and Sr 151 (BüC), the composites represent a different mode of painting surfaces with organic colorants. In all of the three samples, black organic components were applied in relatively thin (below 1 mm) matt, evenly distributed and now slightly cracked coats filling geometric incised decorative motifs (Catalogue of Sources). Sample Sr 438 (ELPC) shows the colorant coat on the exterior wall of a square rim footed bowl, whose both shape and decoration echoes the tradition of the Eastern Linear Pottery culture circle (Tiszadob-Kapušany group) [Kirkowski 1994: 64, 90, Fig. 17: 1; Grygiel 2001: 302, Fig. 4]. Poor preservation of the colorant combined with the fact that the bowl is only partially reconstructable allows nothing but the presumption that the painted ornament used to cover the entire surface of the bowl. The exterior surface of the bowl displays traces of a coat of red (iron oxides) mineral primer of 0.1 to 0.3 mm in thickness, over which a thin (0.1 mm in thickness) coat of a black colorant was applied.

The microscopic examinations have proved that the mineral primer was used for a smoother surface and better binding between the organic material and the pottery surface. The same method was used to apply coats of organic colorants in samples Sr 10 (ELPC) and Sr 151 (BüC). Microscopy has revealed considerable amounts of mineral inclusions (s and grains) whose even distribution indicates that they were deliberately added to modify properties of the organic colorants (Chapter V.4, Photographs 71b and 72). Likewise in the case of organic colorants of FBC, here, the mineral additives improved the adhesion and durability levels and considerably increased abrasion resistance of the colorants [Langer, Kośko 1999: 70]. The deliberate admixture of mineral additives led to the generation of organic-mineral composites with tars playing the role of an organic binder and mineral inclusions serving as fillers. The modifications resulted in formation of the composites that were externally homogenous but with borders between components visible through the macrographic examination (Chapter V.4, Photographs 71a and 71d).

The advanced production method for the tested colorants, with a tar kiln having two chambers and a receiver, is clear from high purity of the colorants with no remnants of unprocessed wood or bark, ascertained using SEM (Chapter V.4, Photograph 71c). The conclusion about exposure to high temperatures is confirmed through relevant analyses (Chapter V.1, Tables 20 and 21; Chapter V.2, Tables 40 and 41) whose results show that tars have highly porous, heavily cracked and foamed structure (Chapter V.4, Photographs 71c, 71e, and 71f). Thermal degradation of the colorant coats might have been intentionally induced to improve their thermal resistance. In consequence, the vessels with painted decoration were suitable for use at high temperatures, which might have been their major functional property.

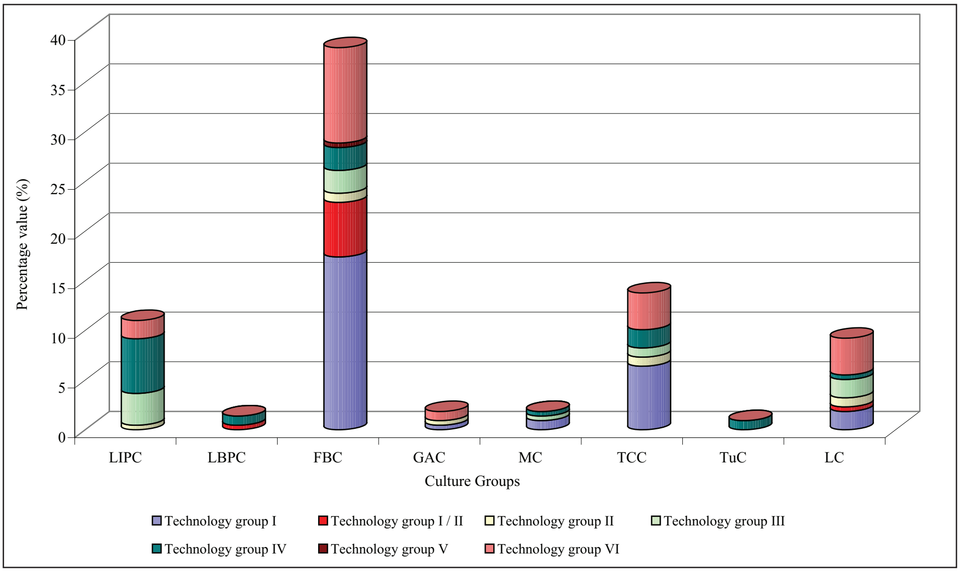


Chart 12. Percentages of technological groups of examined substances in particular cultural units of the *Cycle of cultural systems of the Baltic drainage basin*

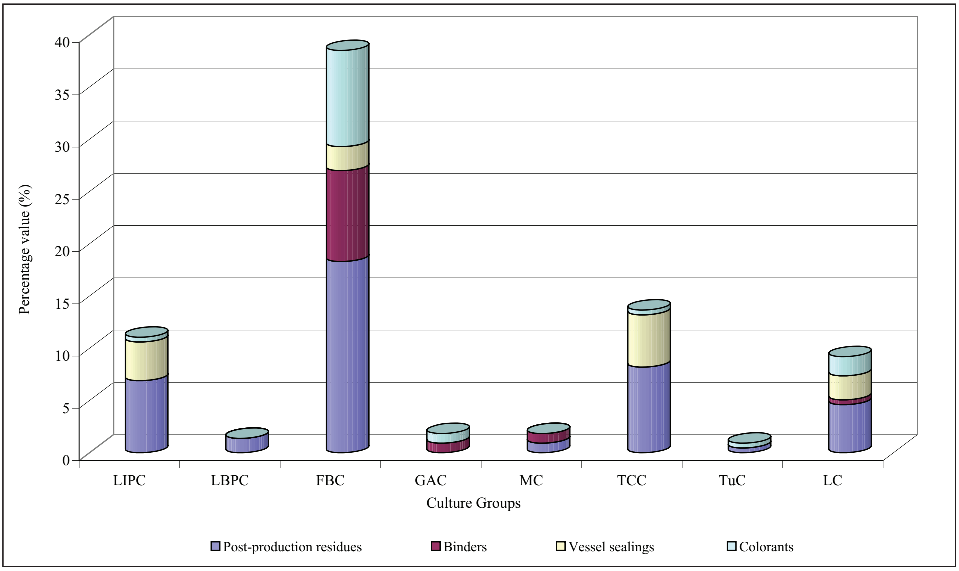
IV.3. VARIETY OF WOOD-TAR PRODUCTION TECHNOLOGY AND APPLICATION IN PARTICULAR CYCLES OF CULTURAL SYSTEMS

The results of the examination of the entire set of source materials (218 samples) coming from both the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*) and comparative territories (*Cycle of cultural systems of Eastern Europe's steppes and forest steppes, Cycle of cultural systems of Eastern Europe's forest zone, Cycle of cultural systems of the Carpathian Basin*) show the considerable variety of production technology and application of wood tar.

Cycle of cultural systems of the Baltic drainage basin

The large variety of wood-tar production technologies is best illustrated by pitch substances coming from the diagnostic territory (*Cycle of cultural systems of the Baltic drainage basin*), which makes them the most informative. The territory is represented by 171 samples, accounting for 78.4 per cent of all materials examined (Chart 12).

A vast majority of the set, or 27 per cent, consists of typical wood-tar substances belonging to technological group I – 59 samples. Most preparations are linked to FBC (38 samples – 17.4%) and TCC materials (14 samples – 6.4%)



C h a r t 13. The percentages of wood-tar and pitch applications in particular cultural units of the *Cycle of cultural systems of the Baltic drainage basin*

with a relatively small share of the LC (4 samples – 1.8%), MiC (2 samples 0.9%) and GAC (1 sample – below 0.5%). The second largest group of preparations comprises composite materials (43 samples – 19.7%) assigned to Technological Group VI. As with Group I wood-tar substances, a clear domination of materials associated with the FBC (21 samples – 9.6%), TCC (8 samples – 3.7%) and the LC (8 samples – 3.7%) is observed, with the number of samples linked to LIPC (4 samples –1.8%) and GAC (2 samples – 0.9%) being much lower. The next, Technological Group IV, comprises 27 samples which account for 12.4 per cent of all available pitch substances. In this case, what draws attention is a higher share of LIPC materials (12 samples – 5.5%) with respect to the other substances in this group: FBC (5 samples – 2.3%), TCC (4 samples – 1.8%),), LBPC (2 samples – 0.9%), TC (2 samples – 0.9%), MiC (1 sample – below 0.5%). and LC (1 sample – below 0.5%). Not much less numerous, Group III wood-tar substances count 19 samples, accounting for 8.7 per cent of all preparations examined. A preponderance of LIPC (7 samples – 3.2%) and FBC (5 samples 2.3%) materials is noticeable relatively to the LC (4 samples – 1.8%), TCC (2 samples – 0.9%) and MiC (1 sample – below 0.5%). Technological Group I/II is represented by 14 samples accounting for 6.4 per cent of all source materials examined. The preparations of this group are associated with three cultural units only: FBC (12 samples 5.5%), LBPC and LC (1 sample – below 0.5% each). Technological Group II comprises only 8 samples, accounting for 3.7 per cent of all pitch substances examined.

A similar number of samples was recorded in the inventories of the FBC, TCC and LC (2 samples – 0.9% each), compared to very low numbers of the LIPC and GAC (1 sample – below 0.5% each). Finally, Technological Group V consists of a single (below 0.5%) sample of a bituminous substance associated with the FBC.

The tests showed that pitch substances were applied in a complex and diverse manner, which is shown in Chart 13. The most numerous form of wood-tar application is post-production residues, accounting for 40.8 per cent (89 samples) of all source materials. The preparations included in this category of wood-tar applications are strongly dominated by those identified with the FBC (40 samples – 18.3%), TCC (18 samples – 8.2%) and LIPC (15 samples – 6.9%) while the share of preparations linked to the LC is smaller (10 samples – 4.6%) and the presence of LBPC- (3 samples – 1.4%), MiC- (2 samples – 0.9%) and TC- (1 sample –below 0.5%) -associated samples is very small indeed.

Two categories of pitch-substance applications – vessel sealings and colorants – include an identical number of preparations, namely 29 and account for 13.3 per cent of all source materials each. The greatest number of vessel sealings were recorded in the case of the TCC (11 samples – 5%) and LIPC (8 samples –3.7%), with the share of FBC (5 samples – 2.3%) and LC (5 samples – 2.3%) materials being smaller. In turn, as colorants the following numbers of samples were classified: FBC (20 – 9.2%), LC (4 – 1.8%), GAC (2 – 0.9%) and LIPC, TCC and TC (1 – 0.5% each). By far, the least number of samples were classified as binders. This category holds 24 samples accounting for 11 per cent of all pitch substances examined. Among the organic substances in this category, FBC materials dominate (19 samples – 8.7%), with the share of GAC (2 samples – 0.9%), MiC (2 samples – 0.9%) and LC (1 sample – below 0.5%) preparations being much smaller.

After analyzing 171 samples coming from the *Cycle of cultural systems of the Baltic drainage basin*, a complex picture of technologies used to produce pitch substances emerged, which is illustrated in Chart 12. A vast majority of samples fits into three most numerous Technological Groups I, VI and 4. Significantly fewer preparations were assigned to Technological Groups III, I/II and II, while a negligible number of bituminous substances were classified as Technological Group V. A considerable share of preparations in Groups I, I/II and II were found to have been obtained from birch wood or bark. It was also found that a small group of samples (FBC) had been made from a mixed, birch-pine raw material. The most numerous technological groups comprise above all post-production residues and binders and only few vessel sealings and colorants. In turn, less numerous technological groups hold also post-production residues and binders, with a lower share of vessel sealings and colorants. An incidental find, an FBC sample (Sr 14) was included in Technological Group V of bituminous substances. The major products obtained in the process of production of wood-tar substances were light and medium wood-tar fractions. They were used, therefore, mainly as binders and less often as vessel sealings and colorants. A relatively high incidence of composite materials of Technological Group VI testifies to the importance of such substances which were used as colorants, vessel sealings and binders. Modified in this way, the substances are much more resistant to mechanical damage or high temperatures. Heat setting must have been applied to the vessel sealings, colorants and binders of Technological Groups I/II, II, III and 4. The treatment, no doubt, allowed them to be used later in high temperatures, for instance in a hearth, without a danger of damaging the layers of pitch substances.

Post-production residues, in turn, from Technological Groups I/II–IV could have also been purposefully annealed in high temperatures to make the substances more heat resistant before they were applied to archaeological artefacts. In some cases, we encounter clear traces of the production process going wrong, which is seen in advanced thermal degradation brought about by a direct contact with fire. A possible explanation is that a clay insulation cover or a production container cracked while over the hearth. This, in turn, justifies a conclusion that the pitch substances were exposed to high temperatures in an uncontrolled manner and for a long time. In extreme cases, this led to the strong charring of organic substances. The examined preparations were produced using all available methods, beginning with the single-vessel method (LIPC, FBC, TCC), through the double-vessel process (LIPC, LBPC, FBC, GAC, MiC,TCC, TC, LC) to the most advanced technology of producing wood tar in a three-chamber set (LC). This variety may testify to a wide spectrum of pitch substances being produced designated perhaps for various uses, requiring wood tar of specific purity and physico-chemical properties. It is also possible that in order to obtain quickly a necessary product, the least complex production methods were used, for instance, in a single vessel.

Cycle of cultural systems of Eastern Europe's steppes and forest steppes

In the case of wood-tar materials coming from the comparative territory of the *Cycle of cultural systems of Eastern Europe's steppes and forest steppes* exceptional technological homogeneity was ascertained, which is shown in Chart 14. All examined preparations (8 samples – 3.7 per cent of the total number of source materials) are included in Technological Group I.

The most numerous substances are those associated with the activities of the CC (4 samples – 1.8%). The other preparations are included in the inventories of the TrC and PYC (2 samples – 0.9% each). All the samples fall into the application category of binders, which is shown in Chart 15. The greatest amount of wood-tar materials is linked to the CC (4 samples – 1.8%), whereas TrC and PYC preparations are represented by two samples each (0.9%).

The examinations show that materials representing the *Cycle of cultural systems of Eastern Europe's steppes and forest steppes* are all included in Technological Group I comprising typical wood-tar substances obtained from a mixed, birch-pine raw material. The samples were enriched by adding vegetable or animal fats to lower their softening and melting points. The enrichment, however, precludes

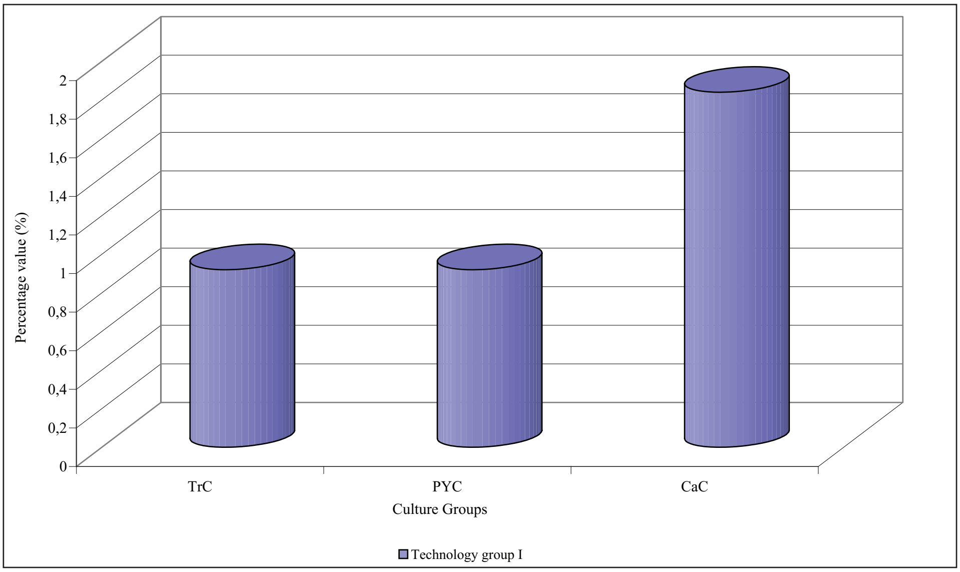


Chart 14. The percentages of technological groups of examined substances in particular cultural units of the *Cycle of cultural systems of Eastern Europe's steppes and forest steppes*

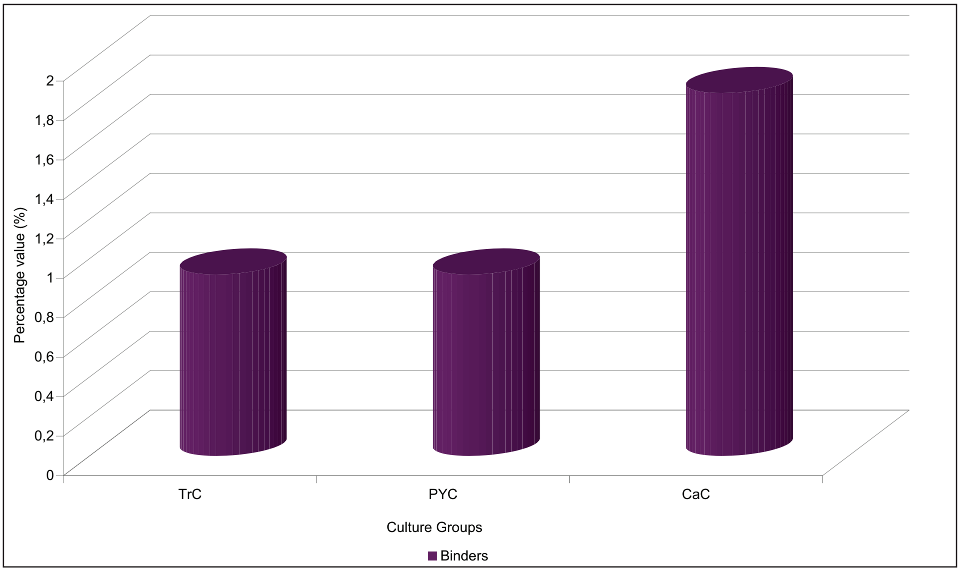


Chart 15. The percentages of applications of examined substances in particular cultural units of the *Cycle of cultural systems of Eastern Europe's steppes and forest steppes*

their use in higher temperatures. All the wood-tar materials were used as binders and their majority (except for TrC preparations) is linked to grave finds and associated with funerary rituals [Klejn 1961; Kośko, Langer 1986]. A very interesting fact concerns PYC samples – they are identical in their chemical compositions in spite of the fact that they were found in different graves. This may indicate that either ritual technological recipes were followed closely or the samples were made in the same production run. It is noteworthy to observe that the samples from this cycle of cultural systems were not found to have been applied in any other way.

Cycle of cultural systems of Eastern Europe's forest zone

Tar substances coming from the comparative territory of the *Cycle of cultural systems of Eastern Europe's forest zone* have an uncomplicated technological structure since they all belong only to three technological groups (III, IV and VI). In total, they comprise 36 samples corresponding to 16.5 per cent of all source materials examined (Chart 16). Group IV is the largest with 22 samples or 10.1 per cent of all samples analyzed. In it, a domination of NBC (8 samples – 3.7%) and NiC (6 samples – 2.7%) materials is noticeable with a smaller share of the DDC (5 samples –2.3%) and a minor presence of the ZC (2 samples – 0.9%) and the eastern version of the TCC (1 sample – below 0.5%). The second largest group is Technological Group III, comprising 11 samples or 5 per cent of all pitch substances. The distribution of the samples across individual cultural units is as follows: ZC (4 samples – 1.8%), NBC (3 samples – 1.4%), NiC (2 samples – 0.9%) CoC (1 sample – below 0.5%), eastern version of the TCC (1 sample – below 0.5%). Technological Group VI, comprising composite substances, is the smallest: it holds only three samples identified with the activities of the NiC (2 samples – 0.9%) and the eastern version of the TCC (1 sample – below 0.5%).

As far as the application of pitch substances associated with this cycle of cultural systems is concerned, the largest group of materials is formed by post-production residues (Chart 17). There are 27 such samples accounting for 12.3 per cent of all source materials. Among them, NBC materials clearly dominate (11 samples – 5%); ZC organic substances are less frequent (6 samples – 2.7%) as are those of NiC (5 samples – 2.3%) while the samples of the DDC (3 samples – 1.4%) and the eastern version of TCC (2 samples – 0.9%) account for the smallest share. In turn, the category of colorants comprises 5 preparations accounting for 2.3 per cent of all materials examined. All the colorants are associated solely with the NiC. Even less numerous category of pitch substance applications, vessel sealings are represented by 4 samples, corresponding to 1.8 per cent of all source materials examined.

Analyses showed that the materials coming from the *Cycle of cultural systems of Eastern Europe's forest zone* had been produced using the technologies of groups IV and III with a small share of composite substances, belonging to Technological Group VI (Chart 16). This shows that producers used as a rule the heat setting of

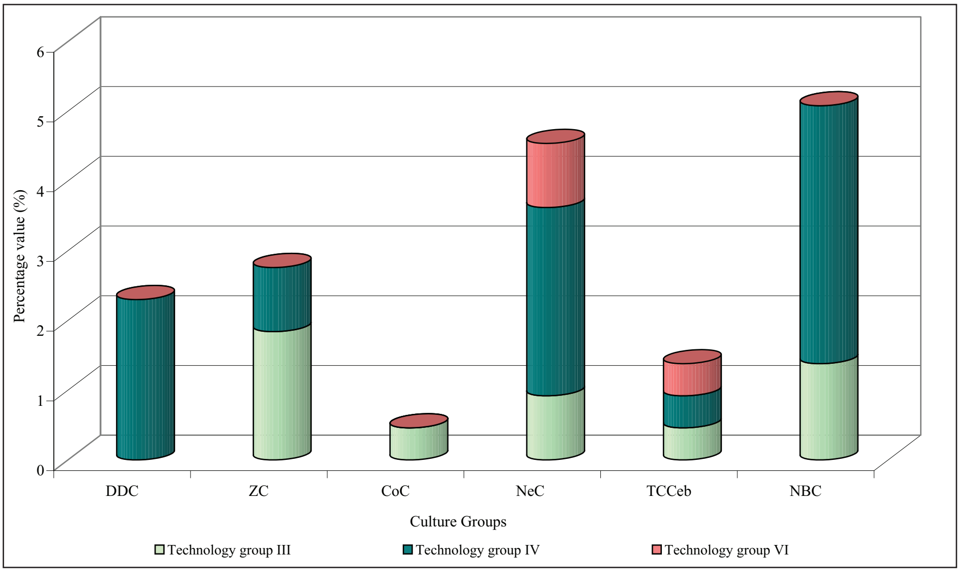


Chart 16. The percentages of technological groups of examined substances in particular cultural units of the *Cycle of cultural systems of Eastern Europe's forest zone*

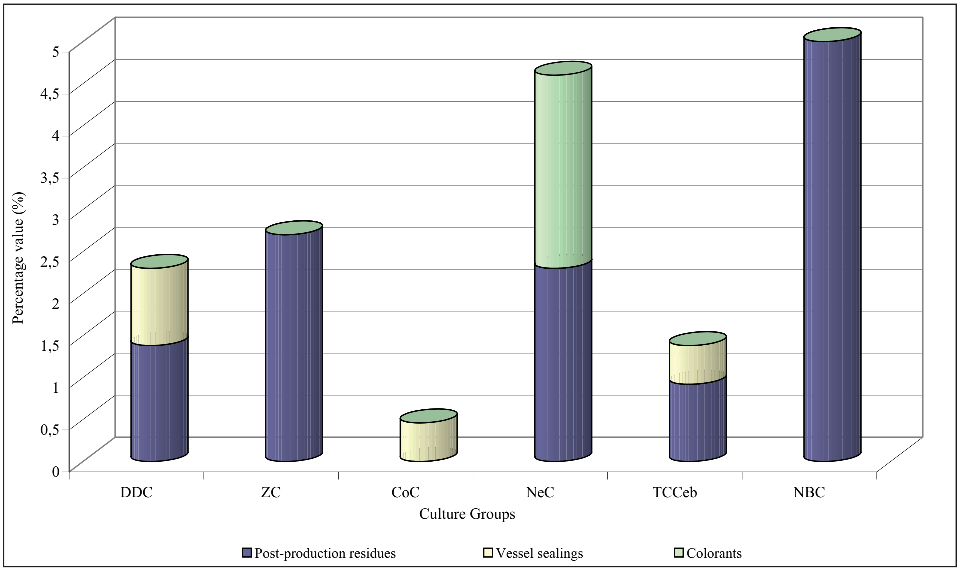


Chart 17. The percentages of applications of examined substances in particular cultural units of the *Cycle of cultural systems of Eastern Europe's forest zone*

layers of pitch substances on vessel surfaces. This is particularly important in the case of colorants and vessel sealings where resistance to high temperatures was a desired feature, allowing people to use ceramic vessels in hearths. It cannot be exclude either that some samples in the most numerous category of applications – post-production residues – could have been purposefully exposed to high temperatures. In effect, infusible, hardly soluble materials were obtained. The other post-production residues suffered strong thermal degradation because of mistakes made by their producers. In the first place, they did not control the temperature of pitch substance production process and, secondly, there were mechanical defects in the production set. For instance, a crack in the clay sealing cover or the vessel itself, allowing flames inside the vessel. A striking technological difference distinguishes this set of samples from the materials of the *Cycle of cultural systems of the Baltic drainage basin* and *Cycle of cultural systems of Eastern Europe's steppes and forest steppes*, seen in the total absence of typical wood-tar substances of Technological Groups I, I/II and II (Chart 16).

For the sake of comparison, substances assigned to the Technological Groups named above in the *Cycle of cultural systems of the Baltic drainage basin* are represented by 81 samples altogether (over 37% of all materials examined) while the number of samples coming from the *Cycle of cultural systems of Eastern Europe's steppe and forest-steppe* is 8 (3.7% of all materials examined). This points to the lack of typical wood-tar substances in the inventories of the *Cycle of cultural systems of Eastern Europe's forest zone*, which may result from a different technology of treating pitch substances. Moreover, the category of binders is absent altogether suggesting that the communities of this cycle of cultural systems were ignorant of the binding properties of the examined substances. The above mentioned absence may also follow from the technology of producing and treating organic substances, which prevented the use of pitch substances as binders (too weak binding properties). Among the wood-tar substances assigned to the category of binders in the inventories of the *Cycle of cultural systems of the Baltic drainage basin* there are 24 samples (11% of all source materials examined) while in the inventories of the *Cycle of cultural systems of Eastern Europe's steppe and forest-steppe* there are 8 samples (3.7% of all source materials studied).

Furthermore, it cannot be ignored that the exploration of pitch substances coming from this zone is not satisfactory when compared to that of the materials from the diagnostic territory. To produce most of the materials under discussion, a two-chamber production set was used fitted with a separate vessel to collect the product. In this way, pitch substances could be separated from raw material remains. In the case of a single sample – NBC (Sr 332) – a single vessel was used and a very contaminated substance was obtained containing unprocessed raw-material remains. It can be presumed that a single-vessel production process could be used for emergency purposes when a necessary substance was needed quickly (beyond planned production). It cannot be ruled out that both methods were employed but the sub-

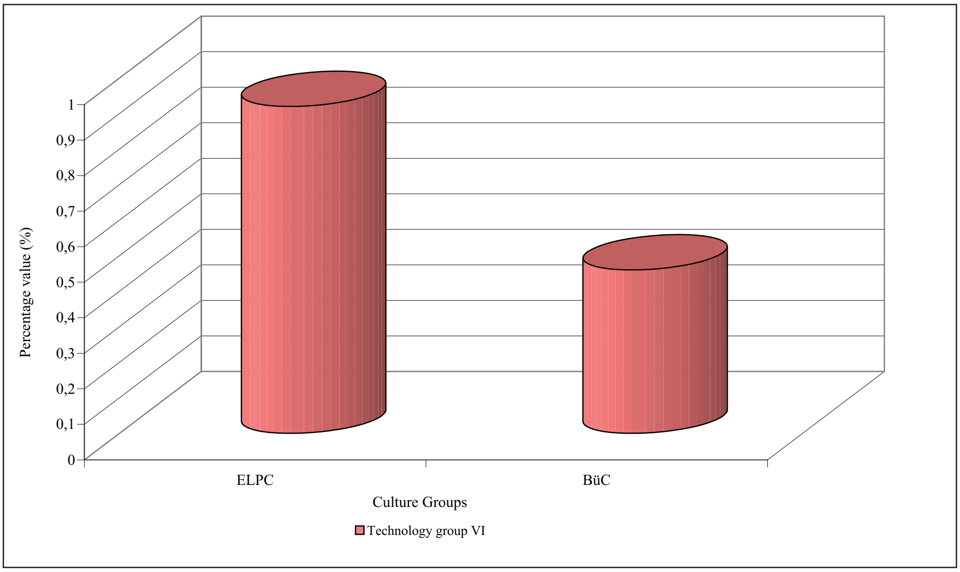


Chart 18. The percentages of technological groups of examined substances in particular cultural units of the *Cycle of cultural systems of the Carpathian Basin*

stances obtained were used for different purposes. Pitch substances produced in a single vessel could have been used for common purposes while high-purity materials, obtained using the two-vessel process, for special ones?

Cycle of cultural systems of the Carpathian Basin

The smallest set of substances examined physico-chemically includes three samples coming from the comparative territory of the *Cycle of cultural systems of the Carpathian Basin* which account for 1.4 per cent of the whole set of source materials (Chart 18). The samples have similar physico-chemical properties and were therefore included in the same Technological Group VI (composite materials of an organic-mineral nature).

Equally uniform, the structure of the applications of the preparations coming from this cycle of cultural systems, is represented solely by the category of colorants: ELPC (2 samples – 0,9%) and BüC (1 sample – below 0.5%), which is shown in Chart 19.

Analyses showed that the materials coming from the *Cycle of cultural systems of the Carpathian Basin* represent only the category of colorants, using composite technology and assigned to Technological Group VI. The use of hybrid, organic-mineral materials helped increase abrasion and heat resistance. It must be observed that a failure to explore other pitch substance applications in this cycle of cultural systems significantly limits our ability to draw any far-reaching conclusions.

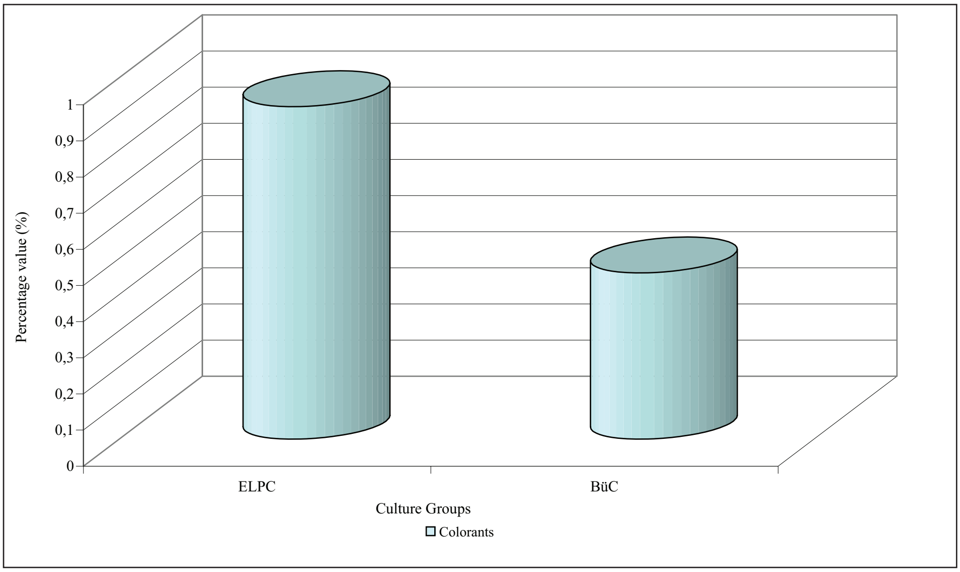


Chart 19. The percentages of applications of examined substances in particular cultural units of the *Cycle of cultural systems of the Carpathian Basin*

In conclusion, it can be said that the comparative analysis of all the cycles of cultural systems shows that the same technological groups hold substances classified as post-production residues, binders, vessel sealings and colorants. This proves that their producers acted with clear intentions and that the organic materials used had some universal characteristics. The materials employed were diverse varieties of wood-tar substances, the properties of which were modified to suit particular applications.

V. CATALOGUE OF PHYSICO–CHEMICAL RESEARCH RESULTS

V.1. TEMPERATURE OF MELTING POINT MEASUREMENT

For the above initial aim 218 samples of wood tar substance and composition were used (would tar derivatives] from 80 archaeological sites (Neolithic – Bronze Age) located in the interfluvial region of the Dnieper and Łaba rivers, which qualified for laboratory analysis on the basis of macroscopic verification.

The results of all the archaeological preparations subject to physico-chemical analysis and various samples of wood tar obtained in modern times in laboratory conditions, were placed below in tables or in the form of microscopic Photos, or spectroscopic images. The sequence of the results of laboratory analysis was established according to that of research methods discussed in Chapter IV. In the context of each chapter section that contains laboratory research results, a graduation of samples has been completed according to chronology and culture in respect to particular cycles of cultural systems and corresponding taxonomic units (archaeological culture and cultural circle).

The archaeological preparations subject to analysis were categorised into three centres of culture of the development of wood tar production:

Cycle of cultural systems of the Baltic drainage basin:

Linear Pottery culture (LIPC), Late Linear Pottery culture (LLPC), Funnel Beaker culture (FBC), Globular Amphora culture (GAC), Mierzanowice culture (MC), Trzciniec Cultural circle (TCC), Tumulus culture (TuC), Lusatian culture (LC)

Cycle of the cultural systems of the steppe and forest steppe:
Tripolye culture (TrC), Pre-Yamnaya culture (PYC), Catacomb culture (CaC)

Cycle of cultural systems of the forest zone in Eastern Europe:
Dnieper-Donets culture (DDC), Zedmar culture (ZC), Comb culture (CoC), Neman culture (NeC), Trzciniec Cultural circle eastern branch (TCCeb), North Belarus culture (NBC)

Cycle of the cultural systems of the Carpathian basin:

Eastern Linear Pottery culture (ELPC), Bükk culture (BüC) delineating their difference both in the cultural sphere as well as material (also production and use of wood tars).

The means of recording in respect to the macroscopic and microscopic identification of form and function, technological classification, as well as the cultural-chronological context of all the archaeological preparations subject to analysis has been presented in the so-called catalogue of finds.

The archaeological preparations subject to physico-chemical analysis were obtained in the context of collaboration with Polish (IP UAM in Poznań; ZA UŁ in Łódź; IA UW in Wrocław; IA UMK in Toruń; KA UMCS in Lublin; IAiE PAN in Warsaw; IAiE PAN, Kraków; IAiE PAN, Poznań; MA in Poznań; MAiE in Łódź; MA in Kraków; MN in Szczecin; MO in Piła; MWiM in Olsztyn), as well as research centres abroad (AN Ukraine in Kiev; AN Belarus in Mińsk; AN Russia in Moscow; AN Slovakia in Brno).

The samples from the collections of the archaeo-metric laboratory, Department of Chemistry, AMU (catalogue of finds) with its base in Śrem, were subject to specific physico-chemical analysis (Chapter III). Cutting edge methods of analysis were applied: infrared spectrophotometry using the Fourier transform (FTIR), thin layer chromatography (TLC), electron paramagnetic resonance (EPR), as well as the measurement of melting point temperature and analysis of melting point. These analyses were complemented by microscopic observations (polarised optical microscopy (POM), as well as scanning electron microscopy (SP), as well as in certain cases when necessary, mass spectrometry, MS, and nuclear magnetic resonance spectrometry were applied.

On account of the lack of possibility to compare the results of techno-archaeological analysis of wood tar materials known in the professional literature (other or incomplete laboratory analysis methods that did not allow to be qualified for any of the established technological groups, Chapter IV) with groups subject to comprehensive physico-chemical analysis in the AMU archaeo-metrical laboratory in Śrem, these samples were not considered in this part of the study.

Wood tar sample

Table 2

Range of temperatures of temperature of softening and melting points of birch (Db) and pine (Ds) tar samples received in modern times according to past technology in a two-chamber production set

Sample code	**Temperature of softening point**	**Temperature of melting point [°C]**	**Comments**
Birch tar (Db)	80 – 110	125 – 135	The analysed material had the consistency of thick ‘caramel’
Pine tar (Ds)	80 – 110	125 – 135	The analysed material had the consistency of thick ‘caramel’

Cycle of cultural systems of the Baltic drainage basin

Linear Pottery culture

Table 3

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
1	2	3	4
Sr 162	232	–	internal surface
Sr 167	–	–	internal surface
Sr 72	–	–	internal surface
Sr 73	–	–	external surface
Sr 74	145 – 165	–	internal surface
Sr 77	–	–	internal surface
Sr 79	145 – 175	–	external surface
Sr 80	180	–	internal surface
Sr 81	–	–	internal surface
Sr 82	210	–	internal surface
Sr 83	–	–	internal surface
Sr 87	–	–	internal surface
Sr 88-1	–	–	external surface
Sr 88-2	–	–	internal surface
Sr 89	221 – 265	–	internal surface
Sr 95	–	–	internal surface

1	2	3	4
Sr 96	178	–	internal surface
Sr 98	–	–	internal surface
Sr 90	–	–	internal surface
Sr 91	–	–	internal surface
Sr 92	–	–	internal surface
Sr 93	–	–	internal surface
Sr 94	215	–	internal surface
Sr 97	–	–	external surface

Late Band Pottery culture

Table 4

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin* (*Late Band Pottery culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 174	126 – 167, 220	–	internal surface
Sr 99	–	–	internal surface
Sr 100	210	–	internal surface

Funnel Beaker culture

Table 5a

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
1	2	3	4
Sr 140	95 – 105	125 – 142	internal surface
Sr 16	175	–	external surface
Sr 128	85 – 115	123 – 164	internal surface
Sr 41	112 – 136	148 – 189	wood tar coagulum
Sr 40	100 – 110	120 – 135	wood tar coagulum
Sr 9	168 – 185	–	external surface
Sr 66	98 – 115	150	external surface
Sr 137	115 – 125	145 – 178	external surface
Sr 33	100 – 115	125 – 145	wood tar coagulum
Sr 34	98 – 113	120 – 150	wood tar coagulum

1	2	3	4
Sr 35	178	–	internal surface
Sr 327	126 – 136	148 – 154	wood tar coagulum
Sr 212	126	–	external surface
Sr 215	108 – 128	–	internal surface
Sr 211	148 – 187	–	internal surface
Sr 213	–	–	internal surface
Sr 214	105 – 112	124 – 143	external surface
Sr 325-1	202 – 212	–	internal surface

Table 5b

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
1	2	3	4
Sr 325-2	200 – 220	–	internal surface
Sr 325-3	196 – 216	–	internal surface
Sr 175w	103 – 115	122 – 142	internal surface
Sr 175z	174	–	external surface
Sr 193	98 – 107	116 – 143	external surface
Sr 1	–	–	external surface
Sr 42	105 – 116	130 – 148	wood tar coagulum
Sr 43	100 – 110	125 – 140	wood tar coagulum
Sr 55	126 – 157	–	internal surface
Sr 56	112 – 123	128 – 147	external surface
Sr 28	102 – 118	128 – 145	external surface
Sr 30	115 – 125	136 – 148	wood tar coagulum
Sr 31	130 – 178	–	internal surface
Sr 252	121 – 146	–	external surface
Sr 198w	109 – 131	–	internal surface
Sr 198z	118 – 148	–	external surface
Sr 263	113 – 121	126 – 142	internal surface
Sr 264	110 – 121	134 – 148	internal surface
Sr 32-1	103 – 112	124 – 140	external surface
Sr 32-2	108 – 116	130 – 142	external surface

1	2	3	4
Sr 328	117 – 128, 270	–	internal surface
Sr 329w	93 – 110	117 – 130	internal surface
Sr 329z	100 – 108	116 – 132	external surface
Sr 46	96 – 115	120 – 140	ceramic ware fragment fracture
Sr 321	280	–	external surface
Sr 464	130 –145	–	external surface
Sr 465	92 – 100	105 – 115	internal surface
Sr 466	105 – 120	125 – 142	internal surface

Table 5c

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
1	2	3	4
Sr 467	220 – 240	–	internal surface
Sr 468	93 – 100	102 – 113	external surface
Sr 469-1	90 – 98	106 – 120	external surface
Sr 469-2	93 – 100	108 – 121	external surface
Sr 177-1	102 – 123	130 – 146	internal surface
Sr 177-2	100 – 115	120 – 142	internal surface
Sr 177-3w	123 – 148	165 – 195	internal surface
Sr 177-3z	156 – 172	–	external surface
Sr 37	182	–	external surface
Sr 192	–	–	internal surface
Sr 57	113	125 – 147	external surface
Sr 189	123 – 178	–	external surface
Sr 249	124	–	external surface
Sr 253	93 – 112	121 – 142	external surface
Sr 254	115 – 141	–	internal surface
Sr 3w	95 – 105	110 – 120	internal surface
Sr 3z	100 – 110	130 – 185	external surface
Sr 36	103 – 117	120 – 140	internal surface
Sr 12	100	153 – 190	external surface

1	2	3	4
Sr 5	120	195	external surface
Sr 284	132 – 148	–	external surface
Sr 324	210 – 265	–	external surface
Sr 8	180	–	external surface
Sr 219	123 – 174	–	external surface
Sr 13	295	–	external surface
Sr 23	–	–	external surface
Sr 24	140 – 156	178	external surface
Sr 58w	76 – 85	88 – 103	internal surface

Table 5d

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the C*ycle of cultural systems of the Baltic drainage basin *(Funnel Beaker culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 58z	80 – 85	90 – 105	external surface
Sr 59	80 – 87	90 – 100	external surface
Sr 68w	132 – 170	–	internal surface
Sr 68z	140 – 175	–	external surface
Sr 14	–	–	external surface
Sr 25	–	–	external surface
Sr 26	185	–	external surface
Sr 243	112 – 123	142 – 146	wood tar coagulum
Sr 67w	115	–	internal surface
Sr 67z	195	–	external surface

Globular Amphora culture

Table 6

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 517	125 – 150	200 – 236	external surface
Sr 18	240	–	external surface
Sr 19	210	–	external surface
Sr 141	257	–	external surface

Mierzanowice culture

Table 7

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 229	–	–	internal surface
Sr 166	92 – 108	170 – 193	wood tar coagula
Sr 227	–	–	internal surface
Sr 326	98 – 133	167 – 180	wood tar coagula

Trzciniec culture circle

Table 8

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec culture circle)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
1	2	3	4
Sr 268	–	–	internal surface
Sr 271	–	–	internal surface
Sr 272-1	176	–	internal surface
Sr 272-2	184 – 240	–	internal surface
Sr 459	125 – 132	143 – 160	internal surface
Sr 460	245 – 260	–	external surface
Sr 461	122 – 130	140 – 150	internal surface
Sr 462	125 – 155	160 – 195	external surface
Sr 463	94 – 110	114 – 130	internal surface
Sr 449	110 – 120	128 – 140	external surface
Sr 450	150 – 180	–	internal surface
Sr 447	–	–	internal surface
Sr 448	–	–	internal surface
Sr 451	110 – 123	148 – 168	external surface
Sr 452	128 – 145	154 – 165	external surface
Sr 453	90 – 98	108 – 120	external surface
Sr 454	–	–	external surface
Sr 455	130 – 148	155 – 190	external surface

1	2	3	4
Sr 456	140 – 172	–	external surface
Sr 457	85 – 95	110 – 120	internal surface
Sr 220	–	–	internal surface
Sr 223	–	–	external surface
Sr 224	–	–	internal surface
Sr 258	–	–	internal surface
Sr 225	–	–	internal surface
Sr 257	112 – 144	–	internal surface
Sr 439w	77 – 84	90 – 105	internal surface
Sr 439z	82 – 92	96 – 110	external surface
Sr 440	82 – 92	102 – 115	external surface
Sr 228	106 – 117	125 – 143	internal surface

Tumulus culture

Table 9

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Tumulus culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 171	–	–	internal surface
Sr 172	234	–	external surface

Lusatian culture

Table 10

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
1	2	3	4
Sr 441	105 – 126	130 – 143	external surface
Sr 443	152 – 176	–	external surface
Sr 444-1	102 – 110	115 – 140	internal surface
Sr 444-2	–	–	internal surface
Sr 71w	90 – 100	110 – 140	internal surface
Sr 71z	94 – 103	110 – 140	external surface
Sr 256w	122 – 135	144 – 176	internal surface

1	2	3	4
Sr 256z	–	–	external surface
Sr 267	248	–	internal surface
Sr 270	226	–	internal surface
Sr 374w	130 – 140	–	internal surface
Sr 374z	126 – 158	–	external surface
Sr 129w	–	–	internal surface
Sr 129z	–	–	external surface
Sr 130	160 – 190	–	external surface
Sr 131	290	–	external surface
Sr 132w	175	–	internal surface
Sr 132z	153 – 187		external surface
Sr 133w	–	–	internal surface
Sr 133z	–	–	external surface

Cycle of cultural systems of the steppe and forest steppe in Eastern Europe

Tripolye culture

Table 11

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of steppe and forest steppe culture systems of Eastern Europe (Tripolye culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 47	80 – 90	100 – 110	wood tar coagulum
Sr 184	76 – 80	85 – 120	wood tar coagulum

Pre-Yamnaya culture

Table 12

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of steppe and forest steppe culture systems of Eastern Europe (Pre-yamnaya culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 38	90 – 100	110 – 120	wood tar coagulum
Sr 39	95 – 105	110 – 125	wood tar coagulum

Catacomb culture

Table 13

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of steppe and forest steppe culture systems of Eastern Europe (Catacomb culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 51	92 – 112	126 – 142	wood tar coagulum
Sr 52	98 – 115	120 – 135	wood tar coagulum
Sr 53	102 – 118	124 – 152	wood tar coagulum
Sr 54	100 – 112	123 – 140	wood tar coagulum

Cycle of forest zone cultural systems of Eastern Europe

Dnieper-Donets culture

Table 14

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (Dnieper Donets culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 315w	232	–	internal surface
Sr 315z	243	–	external surface
Sr 317	–	–	internal surface
Sr 319	240 – 268	–	internal surface
Sr 318	210	–	internal surface

Zedmar culture

Table 15

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (Zedmar culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 230	–	–	internal surface
Sr 232w	172	–	internal surface
Sr 232z	227	–	external surface
Sr 233	132 – 167	–	internal surface
Sr 234	–	–	internal surface
Sr 235	–	–	internal surface

Comb culture

Table 16

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (Comb culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 231	172 – 210	–	internal surface

Neman culture

Table 17

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (Neman culture)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 255-1	220	–	external surface
Sr 255-2	112 – 130	–	external surface
Sr 188	226	–	external surface
Sr 520	–	–	internal surface
Sr 320	235 – 265	–	internal surface
Sr 355	–	–	external surface
Sr 356	–	–	internal surface
Sr 236	154	–	internal surface
Sr 237	–	–	internal surface
Sr 238	–	–	external surface

Trzciniec Cultural circle – eastern branch

Table 18

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (Trzciniec Cultural circle – eastern branch)*

Sample code	**Temperature of softening point [°C]**	**Temperature of melting point [°C]**	**Comments**
Sr 330	151 – 170	–	internal surface
Sr 331	188 – 192	–	internal surface
Sr 333	–	–	internal surface

North Belarus culture

Table 19

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of forest zone cultural systems of Eastern Europe (North Belarus culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 221-1	147 –178	–	internal surface
Sr 221-2	–	–	internal surface
Sr 221-3	–	–	internal surface
Sr 221-4	–	–	internal surface
Sr 221-5	–	–	internal surface
Sr 221-6	–	–	internal surface
Sr 221-7	147 – 170	–	internal surface
Sr 332	185	–	internal surface
Sr 334-1	–	–	internal surface
Sr 334-2	–	–	internal surface
Sr 334-3	–	–	internal surface

Cycle of cultural systems of the Carpathian Basin

Eastern Linear Pottery culture

Table 20

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Carpathian Basin (Eastern Linear Pottery culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 10	165	–	external surface
Sr 438	140 – 190	–	external surface

Bükk culture

Table 21

Range of temperatures for temperature of softening and melting points of archaeological pereparations representing *the Cycle of cultural systems of the Carpathian Basin (Bükk culture)*

Sample code	Temperature of softening point [°C]	Temperature of melting point [°C]	Comments
Sr 151	208	–	external surface

Wood tar sample

Table 22

Results of birch (Db) and pine (Ds) tar samples received in modern times according to past technology in a two-chamber production set

Solvent	Sample code	
	Birch tar (Db)	Pine tar (Ds)
Hexane (C_6H_{14})	+	+
Cyklohexane (C_6H_{12})	+	+
Carbon tetrachloride (CCl_4)	++	++
Dichloromethane (CH_2Cl_2)	+++	+++
Chloroform ($CHCl_3$)	+++	+++
Ethyl acetate ($C_4H_8O_2$)	++	++
Methanol (CH_3OH)	+	–
Acetone (C_3H_6O)	+++	+++
Tetrahydrofuran (C_4H_8O)	+++	+++
Toluene (C_7H_8)	++	++
Benzene (C_6H6)	–	–
Water (H_30^+)	–	–
Hydrochloric acid (HCl)	–	–
Sodium hydroxide (NaOH)	–	–
Ammonium thiocyanate (NH_4SCN)	–	–

Cycle of cultural systems of the Baltic drainage basin

Linear Pottery culture

Table 23a

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Solvent	**Sample code**											
	Sr 162	**Sr 167**	**Sr 72**	**Sr 73**	**Sr 74**	**Sr 77**	**Sr 79**	**Sr 80**	**Sr 81**	**Sr 82**	**Sr 83**	**Sr 87**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–	–	+	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	–	–	–	+	–	–	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–	–	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–	–	–	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–	–	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	+	+	+	+	+	++	–	++	+	++	–	+
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+	+	+	+	+	+	–	+	+	+	+++	+

Table 23b

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Solvent	Sample code											
	Sr 88–1	**Sr 88–2**	**Sr 89**	**Sr 95**	**Sr 96**	**Sr 98**	**Sr 90**	**Sr 91**	**Sr 92**	**Sr 93**	**Sr 94**	**Sr 97**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	+	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	+	++	–	–	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	+	++	–	–	–	–	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–	+	+	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	+	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	+	++	–	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	+	+	–	–	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–	–	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	++	+	+	–	–	+	+	+	++	+	–	+
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+	++	–	++	++	+	+	–	+	+	–	+

Late Band Pottery culture

Table 24

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Late Band Pottery culture)*

Solvent	**Sample code**		
	Sr 174	**Sr 99**	**Sr 100**
Hexane (C_6H_{14})	–	–	–
Cyklohexane (C_6H_{12})	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–
Chloroform ($CHCl_3$)	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–
Methanol (CH_3OH)	–	–	–
Acetone (C_3H_6O)	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–
Toluene (C_7H_8)	–	–	–
Benzene (C_6H_6)	–	–	–
Water (H_30^+)	–	–	–
Hydrochloric acid (HCl)	+	–	–
Sodium hydroxide (NaOH)	–	–	–
Ammonium thiocyanate (NH_4SCN)	+	+	+

Funnel Beaker culture

Table 25a

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 140	**Sr 16**	**Sr 128**	**Sr 41**	**Sr 40**	**Sr 9**	**Sr 66**	**Sr 137**	**Sr 33**	**Sr 34**	**Sr 35**	**Sr 327**
1	2	3	4	5	6	7	8	9	10	11	12	13
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	+	–	–	–	–	–	+	–	+	+	+	–
Dichloromethane (CH_2Cl_2)	+++	–	++	+	++	–	+++	++	+++	+++	+++	++

1	2	3	4	5	6	7	8	9	10	11	12	13
Chloroform ($CHCl_3$)	+++	–	++	++	++	–	+++	+++	+++	+++	+++	++
Ethyl acetate ($C_4H_8O_2$)	–	–	+	+	–	–	+	+	+	+	+	+
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	+	–	+	+	+	–	+	+	+	+	+	+
Tetrahydrofuran (C_4H_8O)	+++	+	++	++	+++	–	+++	+++	+++	+++	+++	+
Toluene (C_7H_8)	++	–	–	+	+	–	++	+	+	+	+	+
Benzene (C_6H_6)	+	–	+	+	–	–	++	–	+	+	+	+
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	+	–	–	–	+	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	–	+++	–	–	–	–	–	–	–	–	–	–

Table 25b

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 212	**Sr 215**	**Sr 211**	**Sr 213**	**Sr 214**	**Sr 325-1**	**Sr 325-2**	**Sr 325-3**	**Sr 175w**	**Sr 175z**	**Sr 193**	**Sr 1**
1	2	3	4	5	6	7	8	9	10	11	12	13
Hexane (C_6H_{14})	–	–	–	–	–	+	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	+	–	–	–	–	+	+	–	+	–	–	–
Dichloromethane (CH_2Cl_2)	+	–	+	–	+	++	+	++	+++	++	++	–
Chloroform ($CHCl_3$)	+	–	+	–	+	++	+	++	+++	++	++	–
Ethyl acetate ($C_4H_8O_2$)	+	–	–	–	–	++	+	++	++	+	+	–

1	2	3	4	5	6	7	8	9	10	11	12	13
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	+	–	–	++	+	+	+	–	+	–
Tetrahydrofuran (C_4H_8O)	+	–	+	–	+	+++	+	++	+++	++	+++	–
Toluene (C_7H_8)	+	–	+	–	–	+	–	+	+	+	+	–
Benzene (C_6H_6)	+	–	–	–	–	+	+	+	+	+	+	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	+	–	+	–	–	–	–	–	–	–	+
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+++	+	+	+	+++	–	–	–	+	+	+	+++

Table 25c

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 42	**Sr 43**	**Sr 55**	**Sr 56**	**Sr 28**	**Sr 30**	**Sr 31**	**Sr 252**	**Sr 198w**	**Sr 198z**	**Sr 263**	**Sr 264**
1	2	3	4	5	6	7	8	9	10	11	12	13
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	+	+	–	++	++	–	–	–	–	+	+
Dichloromethane (CH_2Cl_2)	+++	+++	++	+++	+++	+++	–	+	++	++	++	+++
Chloroform ($CHCl_3$)	+++	++	++	+++	+++	+++	–	+	++	++	++	+++
Ethyl acetate ($C_4H_8O_2$)	–	+	+	+	+	++	–	–	–	–	+	+
Methanol (CH_3OH)	–	–	–	–	–	+	–	–	–	–	–	–
Acetone (C_3H_6O)	+	+	–	+	–	+	–	–	+	+	–	–

1	2	3	4	5	6	7	8	9	10	11	12	13
Tetrahydrofuran (C_4H_8O)	+++	+++	+++	+++	+++	+++	–	+	+++	+++	++	+++
Toluene (C_7H_8)	+	+	+	+	+	+	–	+	+	+	+	+
Benzene (C_6H_6)	+	+	+	+	+	+	–	+	+	+	+	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	+	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	+	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	–	–	–	–	–	–	+	–	+	+	–	–

Table 25d

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 32-1	**Sr 32-2**	**Sr 328**	**Sr 329w**	**Sr 329z**	**Sr 46**	**Sr 321**	**Sr 464**	**Sr 465**	**Sr 466**	**Sr 467**	**Sr 468**
1	2	3	4	5	6	7	8	9	10	11	12	13
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	++	–	–	–	–	–	–	–	++	–	–	++
Dichloromethane (CH_2Cl_2)	+++	++	+	++	++	++	–	+	++	+	–	+++
Chloroform ($CHCl_3$)	+++	+++	+	+++	+++	++	–	–	+++	+++	–	+++
Ethyl acetate ($C_4H_8O_2$)	++	–	–	–	–	+	–	–	++	++	–	+
Methanol (CH_3OH)	+	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	+	–	–	–	–	+	–	+	+	–	–	++
Tetrahydrofuran (C_4H_8O)	+++	+++	+	++	++	+++	–	–	+++	++	–	++
Toluene (C_7H_8)	+	–	–	–	–	+	–	–	++	++	–	++
Benzene (C_6H_6)	+	–	–	–	–	+	–	–	++	+	–	+

1	2	3	4	5	6	7	8	9	10	11	12	13
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	+	–
Ammonium thiocyanate (NH_4SCN)	–	–	–	–	–	–	+	–	+	+	+++	–

Table 25e

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 469-1	**Sr 469-2**	**Sr 177-1**	**Sr 177-2**	**Sr 177-3w**	**Sr 177-3z**	**Sr 37**	**Sr 192**	**Sr 57**	**Sr 189**	**Sr 249**	**Sr 253**
1	2	3	4	5	6	7	8	9	10	11	12	13
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	+	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	++	–	–	–	–	–	–	+	–	–	+
Dichloromethane (CH_2Cl_2)	++	+++	+	++	+	–	+	–	+++	+	–	++
Chloroform ($CHCl_3$)	+++	+++	++	++	++	+	+	–	+++	+	–	++
Ethyl acetate ($C_4H_8O_2$)	++	+++	+	+	+	–	–	–	+	+	–	+
Methanol (CH_3OH)	+	–	–	+	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	+	++	+	+	+	–	+	–	+	–	–	–
Tetrahydrofuran (C_4H_8O)	++	+++	+	++	+	+	+	–	+++	+	–	+++
Toluene (C_7H_8)	++	+	–	–	+	–	–	–	+	–	–	+
Benzene (C_6H_6)	+	+	–	–	+	–	–	–	+	+	–	+
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	+	–	–	–	–

1	2	3	4	5	6	7	8	9	10	11	12	13
Sodium hydroxide (NaOH)	++	+	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+	+	++	++	+++	+	–	+	–	++	++	+++

Table 25f

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 254	**Sr 3w**	**Sr 3z**	**Sr 36**	**Sr 12**	**Sr 5**	**Sr 284**	**Sr 324**	**Sr 8**	**Sr 219**	**Sr 13**	**Sr 23**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	+	–	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	+	++	+	+++	++	++	+	–	–	++	–	–
Chloroform ($CHCl_3$)	+	++	+	+++	++	++	+	–	–	++	–	–
Ethyl acetate ($C_4H_8O_2$)	–	+	–	+	+	–	–	–	–	++	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	+	–	+	+	–	–	+	–	–
Tetrahydrofuran (C_4H_8O)	+	++	+	+++	++	+++	+	–	–	+++	–	–
Toluene (C_7H_8)	–	+	–	+	–	+	–	–	–	+	–	–
Benzene (C_6H_6)	–	+	–	+	–	+	–	–	–	+	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+++	–	+++	–	+++	–	+++	+++	+	+++	+++	+++

Table 25g

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Solvent	**Sample code**											
	Sr 24	**Sr 58w**	**Sr 58z**	**Sr 59**	**Sr 68w**	**Sr 68z**	**Sr 14**	**Sr 25**	**Sr 26**	**Sr 243**	**Sr 67w**	**Sr 67z**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	+	+	–	+	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	+	+++	+++	+++	+++	+	–	–	–	+	–	–
Chloroform ($CHCl_3$)	+	+++	+++	+++	+++	+	–	–	–	+	–	–
Ethyl acetate ($C_4H_8O_2$)	–	+	+	+	–	–	–	–	–	+	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	+	–	–	–	–	–	+	–	–
Tetrahydrofuran (C_4H_8O)	+	+++	+++	+++	++	–	–	–	–	+	–	–
Toluene (C_7H_8)	–	+	+	+	–	+	–	–	–	+	–	–
Benzene (C_6H_6)	–	+	+	+	–	+	–	–	–	+	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+++	+	+	–	–	–	+	+++	+++	+	+	+

Globular Amphora culture

Table 26

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Solvent	**Sample code**			
	Sr 517	**Sr 18**	**Sr 19**	**Sr 141**
Hexane (C_6H_{14})	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–
Dichloromethane (CH_2Cl_2)	++	–	–	–
Chloroform ($CHCl_3$)	++	–	–	–
Ethyl acetate ($C_4H_8O_2$)	+	–	–	–
Methanol (CH_3OH)	–	–	–	–
Acetone (C_3H_6O)	+	–	–	–
Tetrahydrofuran (C_4H_8O)	+++	–	–	–
Toluene (C_7H_8)	+	–	–	–
Benzene (C_6H_6)	+	–	–	–
Water (H_30^+)	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	++
Sodium hydroxide (NaOH)	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	–	+++	+++	+++

Mierzanowice culture

Table 27

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Solvent	**Sample code**			
	Sr 229	**Sr 166**	**Sr 227**	**Sr 326**
1	2	3	4	5
Hexane (C_6H_{14})	–	+	–	–
Cyklohexane (C_6H_{12})	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	+++	–	++
Chloroform ($CHCl_3$)	–	+++	–	++
Ethyl acetate ($C_4H_8O_2$)	–	–	–	+
Methanol (CH_3OH)	–	–	–	–
Acetone (C_3H_6O)	–	–	–	+

1	2	3	4	5
Tetrahydrofuran (C_4H_8O)	–	+++	–	++
Toluene (C_7H_8)	–	+	–	+
Benzene (C_6H_6)	–	+	–	+
Water (H_30^+)	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–
Sodium hydroxide (NaOH)	+	–	+	–
Ammonium thiocyanate (NH_4SCN)	+	–	+	–

Trzciniec Cultural circle

Table 28a

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Solvent	**Sample code**									
	Sr 268	**Sr 271**	**Sr 272-1**	**Sr 272-2**	**Sr 459**	**Sr 460**	**Sr 461**	**Sr 462**	**Sr 463**	**Sr 449**
Hexane (C_6H_{14})	–	–	–	–	–		–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	+	–	+++	+++
Dichloromethane (CH_2Cl_2)	–	–	–	–	++	–	++	+	+++	+++
Chloroform ($CHCl_3$)	–	–	–	–	+++	–	+++	+	+++	+++
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	+	–	+	–	++	++
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	+	–	++	++
Tetrahydrofuran (C_4H_8O)	–	–	–	–	+++	–	++	+	++	+++
Toluene (C_7H_8)	–	–	–	–	++	–	+	–	++	++
Benzene (C_6H_6)	–	–	–	–	+	–	++	–	++	+
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	+	+	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	+	–	+	–	–
Ammonium thiocyanate (NH_4SCN)	+	+	+++	+++	+	+	+	+	+	+

Table 28b

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Solvent	Sample code									
	Sr 450	**Sr 447**	**Sr 448**	**Sr 451**	**Sr 452**	**Sr 453**	**Sr 454**	**Sr 455**	**Sr 456**	**Sr 457**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	++	+	++	–	++	+	+++
Dichloromethane (CH_2Cl_2)	–	–	–	++	+++	+++	–	+++	+	+++
Chloroform ($CHCl_3$)	–	–	–	+++	+++	+++	–	++	+	+++
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	+	+	–	++	–	+
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	++	+++	++	–	+	–	++
Tetrahydrofuran (C_4H_8O)	–	–	–	+	+++	+++	–	+++	+	++
Toluene (C_7H_8)	–	–	–	+	++	+	–	+	–	+
Benzene (C_6H_6)	–	–	–	+	+	+	–	+	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	+	+	+	–	–	–	+	–	+	–
Ammonium thiocyanate (NH_4SCN)	+	+	+	+	+	+	+++	+	+	+

Table 28c

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Solvent	Sample code									
	Sr 220	**Sr 223**	**Sr 224**	**Sr 258**	**Sr 225**	**Sr 257**	**Sr 439w**	**Sr 439z**	**Sr 440**	**Sr 228**
1	2	3	4	5	6	7	8	9	10	11
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	++	++	++	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–	–	++	+++	++	+++
Chloroform ($CHCl_3$)	–	–	–	–	–	–	+++	+++	+++	+++
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–	++	+	+	+

1	2	3	4	5	6	7	8	9	10	11
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	+	++	++	++
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–	–	+++	++	+++	+++
Toluene (C_7H_8)	–	–	–	–	–	–	+	+	+	+
Benzene (C_6H_6)	–	–	–	–	–	–	+	+	+	+
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	+	+	+	+	+	+	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+++	+++	+++	+++	+++	+	–	–	+	–

Tumulus culture

Table 29

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Tumulus culture)*

Solvent	**Sample code**	
	Sr 171	**Sr 172**
Hexane (C_6H_{14})	–	–
Cyklohexane (C_6H_{12})	–	–
Carbon tetrachloride (CCl_4)	–	–
Dichloromethane (CH_2Cl_2)	–	–
Chloroform ($CHCl_3$)	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–
Methanol (CH_3OH)	–	–
Acetone (C_3H_6O)	–	–
Tetrahydrofuran (C_4H_8O)	–	–
Toluene (C_7H_8)	–	–
Benzene (C_6H_6)	–	–
Water (H_30^+)	–	–
Hydrochloric acid (HCl)	+	++
Sodium hydroxide (NaOH)	–	–
Ammonium thiocyanate (NH_4SCN)	+	+

Lusatian culture

Table 30a

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Solvent	Sample code									
	Sr 441	**Sr 443**	**Sr 444-1**	**Sr 444-2**	**Sr 71w**	**Sr 71z**	**Sr 256w**	**Sr 256z**	**Sr 267**	**Sr 270**
Hexane (C_6H_{14})	–	–	–	–	–		–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	++	–	–	–	+	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	+++	–	+	–	++	++	++	–	–	–
Chloroform ($CHCl_3$)	++	–	+	+	+++	++	++	–	–	–
Ethyl acetate ($C_4H_8O_2$)	+	–	–	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	+++	–	+	–	+++	++	++	–	–	–
Toluene (C_7H_8)	+	–	–	–	+	+	+	–	–	–
Benzene (C_6H_6)	+	–	–	–	+	+	+	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	+	–
Sodium hydroxide (NaOH)	–	+	–	–	–	–	–	+	–	–
Ammonium thiocyanate (NH_4SCN)	+	+++	+	+	+	+	+	+	+	+++

Table 30b

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Solvent	Sample code									
	Sr 374w	**Sr 374z**	**Sr 129w**	**Sr 129z**	**Sr 130**	**Sr 131**	**Sr 132w**	**Sr 132z**	**Sr 133w**	**Sr 133z**
1	2	3	4	5	6	7	8	9	10	11
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	+	++	–	–	–	–	–	–	–	–
Chloroform ($CHCl_3$)	++	++	–	–	–	–	–	–	–	–

1	2	3	4	5	6	7	8	9	10	11
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	+	+	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	++	+	–	–	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–	–	–	–	–	–
Benzene (C_6H_6)	++	–	–	–	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–	–	–	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	+++	+	+++	+++	+	+	+	+	+++	+

Cycle of cultural systems of the steppe and forest steppe in Eastern Europe

Tripolye culture

Table 31

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Solvent	**Sample code**	
	Sr 47	**Sr 184**
Hexane (C_6H_{14})	–	+
Cyklohexane (C_6H_{12})	–	+
Carbon tetrachloride (CCl_4)	–	++
Dichloromethane (CH_2Cl_2)	+++	+++
Chloroform ($CHCl_3$)	+++	+++
Ethyl acetate ($C_4H_8O_2$)	+	++
Methanol (CH_3OH)	–	–
Acetone (C_3H_6O)	+	++
Tetrahydrofuran (C_4H_8O)	+++	+++
Toluene (C_7H_8)	+	+++
Benzene (C_6H_6)	+	++
Water (H_30^+)	–	–
Hydrochloric acid (HCl)	–	–
Sodium hydroxide (NaOH)	–	–
Ammonium thiocyanate (NH_4SCN)	–	–

Pre-Yamnaya culture

Table 32

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Pre-Yamnaya culture)*

Solvent	**Sample code**	
	Sr 38	**Sr 39**
Hexane (C_6H_{14})	–	–
Cyklohexane (C_6H_{12})	–	–
Carbon tetrachloride (CCl_4)	+	+
Dichloromethane (CH_2Cl_2)	+++	+++
Chloroform ($CHCl_3$)	+++	+++
Ethyl acetate ($C_4H_8O_2$)	+	+
Methanol (CH_3OH)	–	–
Acetone (C_3H_6O)	+	+
Tetrahydrofuran (C_4H_8O)	+++	+++
Toluene (C_7H_8)	+	+
Benzene (C_6H_6)	+	+
Water (H_30^+)	–	–
Hydrochloric acid (HCl)	–	–
Sodium hydroxide (NaOH)	–	–
Ammonium thiocyanate (NH_4SCN)	–	–

Catacomb culture

Table 33

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Catacomb culture)*

Solvent	**Sample code**			
	Sr 51	**Sr 52**	**Sr 53**	**Sr 54**
1	2	3	4	5
Hexane (C_6H_{14})	–	+	–	–
Cyklohexane (C_6H_{12})	–	–	–	–
Carbon tetrachloride (CCl_4)	–	+	+	+
Dichloromethane (CH_2Cl_2)	+++	+++	+++	+++
Chloroform ($CHCl_3$)	+++	+++	+++	+++
Ethyl acetate ($C_4H_8O_2$)	–	+	+	+
Methanol (CH_3OH)	–	–	–	–
Acetone (C_3H_6O)	+	+	+	+

1	2	3	4	5
Tetrahydrofuran (C_4H_8O)	+++	+++	+++	+++
Toluene (C_7H_8)	+	+	+	+++
Benzene (C_6H_6)	+	+	+	+
Water (H_30^+)	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	–
Ammonium thiocyanate (NH_4SCN)	–	–	–	–

The Cycle of cultural systems of the forest zone in Eastern Europe

Dnieper-Donets culture

Table 34

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (Dnieper-Donets culture)*

Solvent	**Sample code**				
	Sr 315w	**Sr 315z**	**Sr 317**	**Sr 319**	**Sr 318**
Hexane (C_6H_{14})	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–
Sodium hydroxide (NaOH)	+	–	++	+++	++
Ammonium thiocyanate (NH_4SCN)	+	–	–	+	+

Zedmar culture

Table 35

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (Zedmar culture)*

Solvent	**Sample code**					
	Sr 230	**Sr 232w**	**Sr 232z**	**Sr 233**	**Sr 234**	**Sr 235**
Hexane (C_6H_{14})	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–
Hydrochloric acid (HCl)	–	–	–	–	–	–
Sodium hydroxide (NaOH)	+	–	–	+	+++	++
Ammonium thiocyanate (NH_4SCN)	+	–	–	–	+	+

Comb culture

Table 36

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (Comb culture)*

Solvent	**Sample code**
	Sr 231
1	2
Hexane (C_6H_{14})	–
Cyklohexane (C_6H_{12})	–
Carbon tetrachloride (CCl_4)	–
Dichloromethane (CH_2Cl_2)	–
Chloroform ($CHCl_3$)	–
Ethyl acetate ($C_4H_8O_2$)	–

1	2
Methanol (CH_3OH)	–
Acetone (C_3H_6O)	–
Tetrahydrofuran (C_4H_8O)	–
Toluene (C_7H_8)	–
Benzene (C_6H_6)	–
Water (H_30^+)	–
Hydrochloric acid (HCl)	–
Sodium hydroxide (NaOH)	+
Ammonium thiocyanate (NH_4SCN)	+

Neman culture

Table 37

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (Neman culture)*

Solvent	**Sample code**									
	Sr 255-1	**Sr 255-2**	**Sr 188**	**Sr 520**	**Sr 320**	**Sr 355**	**Sr 356**	**Sr 236**	**Sr 237**	**Sr 238**
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	–	–	–	–	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	+	+	+	–	–	+	–	–	–	–
Sodium hydroxide (NaOH)	–	–	–	+	++	–	+	+	+	+
Ammonium thiocyanate (NH_4SCN)	+	+	+	–	–	++	–	+	+	+++

Trzciniec Cultural circle – eastern branch

Table 38

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (Trzciniec Cultural circle – eastern branch)*

Solvent	**Sample code**		
	Sr 330	**Sr 331**	**Sr 333**
Hexane (C_6H_{14})	–	–	–
Cyklohexane (C_6H_{12})	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–
Chloroform ($CHCl_3$)	–	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–	–
Methanol (CH_3OH)	–	–	–
Acetone (C_3H_6O)	–	–	–
Tetrahydrofuran (C_4H_8O)	+	–	–
Toluene (C_7H_8)	–	–	–
Benzene (C_6H_6)	–	–	–
Water (H_30^+)	–	–	–
Hydrochloric acid (HCl)	+	–	+
Sodium hydroxide (NaOH)	+	–	+
Ammonium thiocyanate (NH_4SCN)	+++	–	–

North Belarus culture

Table 39

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the forest zone in Eastern Europe (North Belarus culture)*

Solvent	**Sample code**										
	Sr 221-1	**Sr 221-2**	**Sr 221-3**	**Sr 221-4**	**Sr 221-5**	**Sr 221-6**	**Sr 221-7**	**Sr 332**	**Sr 334-1**	**Sr 334-2**	**Sr 334-3**
1	2	3	4	5	6	7	8	9	10	11	12
Hexane (C_6H_{14})	–	–	–	–	–	–	–	–	–	–	–
Cyklohexane (C_6H_{12})	–	–	–	–	–	–	–	–	–	–	–
Carbon tetrachloride (CCl_4)	–	–	–	–	–	–	–	–	–	–	–
Dichloromethane (CH_2Cl_2)	–	–	–	–	–	–	–	–	–	–	–
Chloroform ($CHCl_3$)	–	–	–	–	–	–	–	–	–	–	–

1	2	3	4	5	6	7	8	9	10	11	12
Ethyl acetate ($C_4H_8O_2$)	–	–	–	–	–	–	–	–	–	–	–
Methanol (CH_3OH)	–	–	–	–	–	–	–	–	–	–	–
Acetone (C_3H_6O)	–	–	–	–	–	–	–	–	–	–	–
Tetrahydrofuran (C_4H_8O)	–	–	–	–	–	–	–	–	–	–	–
Toluene (C_7H_8)	–	–	–	–	–	–	–	–	–	–	–
Benzene (C_6H_6)	–	–	–	–	–	–	–	–	–	–	–
Water (H_30^+)	–	–	–	–	–	–	–	–	–	–	–
Hydrochloric acid (HCl)	+	–	+	+	–	–	–	–	–	–	+
Sodium hydroxide (NaOH)	+	+	+	+	+	+	+	+	+	++	++
Ammonium thiocyanate (NH_4SCN)	+	+	+	+	+	+	+	+	+	+	+

Cycle of cultural systems of the Carpathian Basin

Eastern Linear Pottery culture

Table 40

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Carpathian Basin (Eastern Linear Pottery culture)*

Solvent	**Sample code**	
	Sr 10	**Sr 438**
1	2	3
Hexane (C_6H_{14})	–	–
Cyklohexane (C_6H_{12})	–	–
Carbon tetrachloride (CCl_4)	–	–
Dichloromethane (CH_2Cl_2)	–	–
Chloroform ($CHCl_3$)	–	–
Ethyl acetate ($C_4H_8O_2$)	–	–
Methanol (CH_3OH)	–	–
Acetone (C_3H_6O)	–	–
Tetrahydrofuran (C_4H_8O)	–	–
Toluene (C_7H_8)	–	–
Benzene (C_6H_6)	–	–
Water (H_30^+)	–	–

1	2	3
Hydrochloric acid (HCl)	–	–
Sodium hydroxide (NaOH)	–	–
Ammonium thiocyanate (NH_4SCN)	+++	+++

Bükk culture

Table 41

Results of solubility of archaeological preparations *representing the Cycle of cultural systems of the Carpathian Basin (Bükk culture)*

Solvent	**Sample code**
	Sr 151
Hexane (C_6H_{14})	–
Cyklohexane (C_6H_{12})	–
Carbon tetrachloride (CCl_4)	–
Dichloromethane (CH_2Cl_2)	–
Chloroform ($CHCl_3$)	–
Ethyl acetate ($C_4H_8O_2$)	–
Methanol (CH_3OH)	–
Acetone (C_3H_6O)	–
Tetrahydrofuran (C_4H_8O)	–
Toluene (C_7H_8)	–
Benzene (C_6H_6)	–
Water (H_30^+)	–
Hydrochloric acid (HCl)	+
Sodium hydroxide (NaOH)	–
Ammonium thiocyanate (NH_4SCN)	+++

Wood tar samples

Table 42

Value of coefficient R_f of comparative sample components for wood tar substances:birch (Db), pine (Ds), oak (Dd), beech (Dbu), spruce (Dśw), alder (Do), hornbeam (Dg), ash (Dj) obtained in modern times according to past technology in a two-chamber production set

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Db	0,26f	0,38f	0,46a	0,6a	–	0,81a
Ds	–	0,38f	0,46a, f	0,6a	0,75a	–
Dd	–	–	–	0,56a	–	–
Dbu	–	–	–	–	–	–
Dśw	–	–	0,42a	0,52a	–	–
Do	–	–	–	–	–	–
Dg	–	–	0,42a	–	–	–
Dj	–	–	0,46a	0,54a	–	–

a – absorption; f – fluoresence; a, f – absorption and fluoresence

Cycle of cultural systems of the Baltic drainage basin

Linear Pottery culture

Table 43

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 79	0,24f	–	–	–	–	–
Sr 95	0,27f	–	–	–	–	–
Sr 96	0,26f	–	–	–	–	–

f – fluoresence

Late Band Pottery culture

Table 44

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Late Band Pottery culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 174	0,25f	–	–	–	–	–

f – fluoresence

Funnel Beaker culture

Table 45a

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 140	0,24f	0,37f	0,48a	–	–	–
Sr 128	0,25f	–	–	–	–	–
Sr 41	0,28f	–	–	–	–	–
Sr 40	0,24f	–	–	–	–	–
Sr 66	0,26f	–	–	–	–	–
Sr 137	0,27f	–	–	–	–	–
Sr 33	0,26f	0,38f	0,46a	–	–	–
Sr 34	0,26f	0,38f	0,46a	–	–	–
Sr 35	0,26f	0,38f	0,46a	–	–	–
Sr 327	0,26f	–	–	–	–	–
Sr 211	0,25f	–	–	–	–	–
Sr 325-1	0,24f	–	–	–	–	–
Sr 325-3	0,24f	–	–	–	–	–
Sr 175w	0,25f	–	–	–	–	–
Sr 175z	0,25f	–	–	–	–	–
Sr 193	0,26f	–	–	–	–	–
Sr 42	0,25f	–	–	–	–	–
Sr 43	0,24f	0,37f	0,48a	–	–	–
Sr 55	0,26f	–	–	–	–	–
Sr 56	0,26f	–	–	–	–	–
Sr 28	0,28f	–	–	–	–	–
Sr 30	0,26f	0,37f	0,46a	–	–	–

a – absorption; f – fluoresence

Table 45b

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	Development phase					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 198w	0,27f	–	–	–	–	–
Sr 198z	0,27f	–	–	–	–	–
Sr 263	0,26f	–	–	–	–	–
Sr 264	0,26f	–	–	–	–	–
Sr 32-1	0,24f	–	–	–	–	–
Sr 32-2	0,24f	–	–	–	–	–
Sr 328	0,27f	–	–	–	–	–
Sr 329w	0,25f	–	–	–	–	–
Sr 329z	0,25f	–	–	–	–	–
Sr 46	0,23f	–	–	–	–	–
Sr 465	0,26f	–	–	–	–	–
Sr 466	0,28f	–	–	–	–	–
Sr 468	0,27f	–	–	–	–	–
Sr 469-1	0,26f	–	–	–	–	–
Sr 469-2	0,26f	–	–	–	–	–
Sr 177-1	0,25f	–	–	–	–	–
Sr 177-2	0,25f	–	–	–	–	–
Sr 177-3w	0,25f	–	–	–	–	–
Sr 177-3z	0,25f	–	–	–	–	–
Sr 37	0,26f	0,38f	0,46a	–	–	–
Sr 57	0,26f	–	–	–	–	–

a – absorption; f – fluoresence

Table 45c

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	Development phase					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
1	2	3	4	5	6	7
Sr 253	0,26f	–	–	–	–	–
Sr 3w	0,24f	0,36f	0,48a	–	–	–
Sr 3z	0,24f	0,36f	0,48a	–	–	–
Sr 36	0,26f	0,38f	0,46a	–	–	–

1	2	3	4	5	6	7
Sr 12	0,24f	–	–	–	–	–
Sr 5	0,26f	–	–	–	–	–
Sr 219	0,26f	–	–	–	–	–
Sr 24	0,24f	0,35f	0,47a	–	–	–
Sr 58w	0,26f	–	–	–	–	–
Sr 58z	0,26f	–	–	–	–	–
Sr 59	0,26f	–	–	–	–	–
Sr 68w	0,26f	0,34f	0,46a	–	–	–
Sr 68z	0,26f	0,34f	0,46a	–	–	–
Sr 243	0,26f	–	–	–	–	–

a – absorption; f – fluoresence

Globular Amphora culture

Table 46

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 517	0,26f	–	–	–	–	–

f – fluoresence

Mierzanowice culture

Table 47

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 166	0,26f	–	–	–	–	–
Sr 326	0,26f	–	–	–	–	–

f – fluoresence

Trzciniec Cultural circle

Table 48

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 459	0,24f	–	–	–	–	–
Sr 461	0,27f	–	–	–	–	–
Sr 463	0,26f	–	–	–	–	–
Sr 449	0,25f	–	–	–	–	–
Sr 451	0,24f	–	–	–	–	–
Sr 452	0,24f	–	–	–	–	–
Sr 453	0,26f	–	–	–	–	–
Sr 455	0,25f	–	–	–	–	–
Sr 456	0,25f	–	–	–	–	–
Sr 457	0,26f	–	–	–	–	–
Sr 439w	0,28f	–	–	–	–	–
Sr 439z	0,28f	–	–	–	–	–
Sr 440	0,27f	–	–	–	–	–
Sr 228	0,26f	–	–	–	–	–

f – fluoresence

Lusatian culture

Table 49

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 441	0,26f	–	–	–	–	–
Sr 444-1	0,27f	–	–	–	–	–
Sr 444-2	0,26f	–	–	–	–	–
Sr 71w	0,24f	–	–	–	–	–
Sr 71z	0,24f	–	–	–	–	–
Sr 256w	0,26f	–	–	–	–	–
Sr 374w	0,25f	–	–	–	–	–
Sr 374z	0,25f	–	–	–	–	–

f – fluoresence

The Cycle of cultural systems of the steppe and forest steppe in Eastern Europe

Tripolye culture

Table 50

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 47	0,23f	0,38f	0,48a	–	–	–
Sr 184	0,25f	0,36f	0,46a	–	–	–

a – absorption; f – fluoresence

Pre-Yamnaya culture

Table 51

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Pre-Yamnaya culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 38	0,26f	0,38f	0,48a	–	–	–
Sr 39	0,26f	0,38f	0,48a	–	–	–

a – absorption; f – fluoresence

Catacomb culture

Table 52

Values of coefficient R_f of comparative archaeological samples representing *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Catacomb culture)*

Sample code	**Development phase**					
	Hexane (C_6H_{14}) : Carbon tetrachloride (CCl_4) 3:1 (v:v)					
Sr 51	0,27f	0,37f	0,47a	–	–	–
Sr 52	0,26f	0,39f	0,48a	–	–	–
Sr 53	0,29f	0,37f	0,46a	–	–	–
Sr 54	0,26f	0,38f	0,48a	–	–	–

a – absorption; f – fluoresence

Birch bark

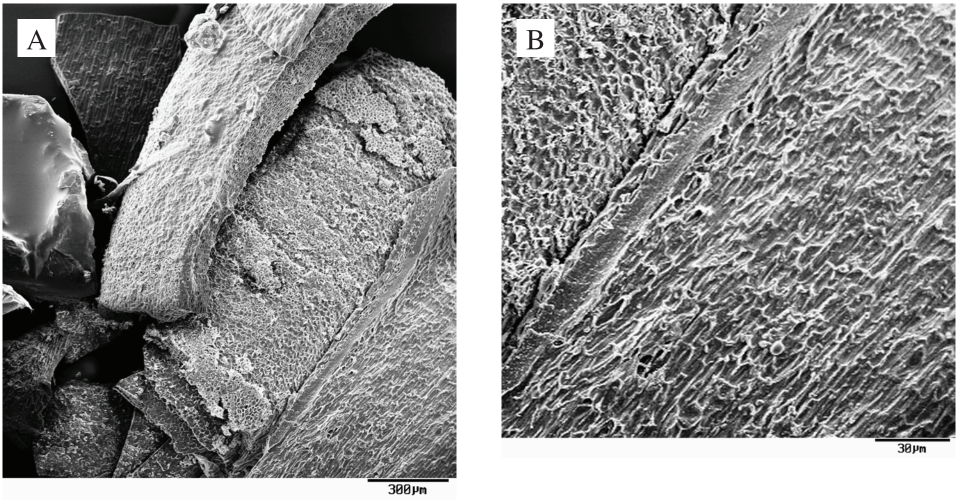


Photo. 1. Scanning electron mikroscopy (SEM) for contemporary birch bark: (a) x 200, (b) enlargement x 400

Pine

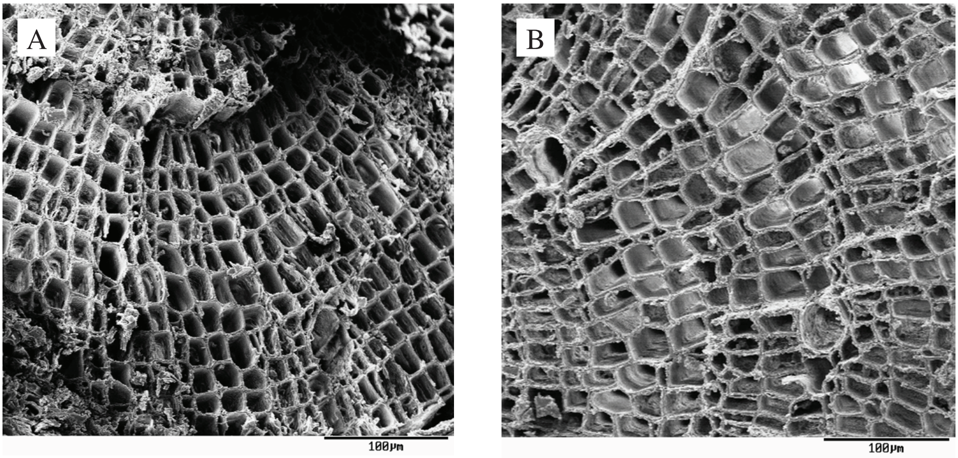


Photo. 2. SEM for contemporary pine: (a) enlargement x 250, (b) enlargement x 350

Cycle of cultural systems of the Baltic drainage basin

Linear Pottery culture

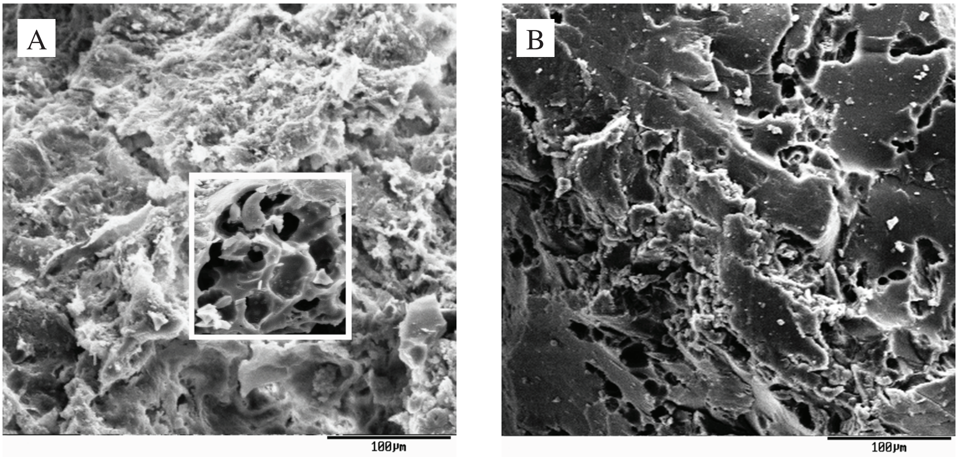


Photo. 3. SEM for sample Sr 167: (a) enlargement x 250, (b) enlargement x 250

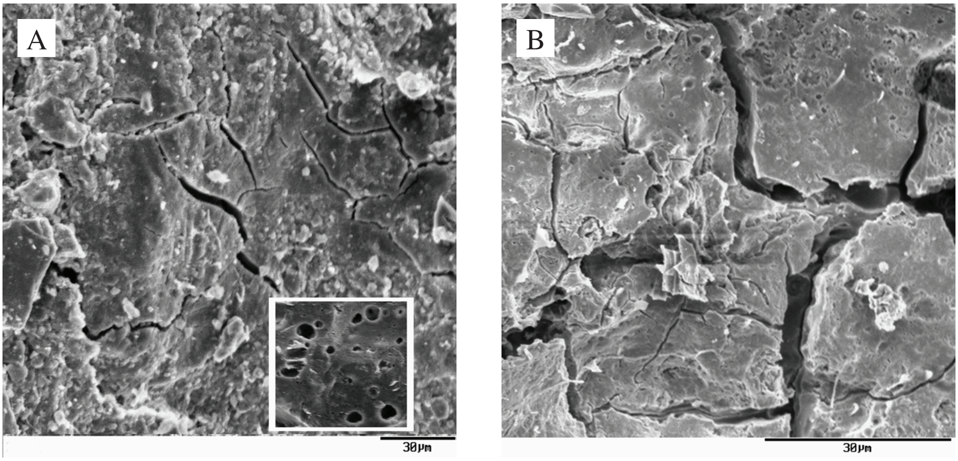


Photo. 4. SEM for sample Sr 74: (a) enlargement x 500, (b) enlargement x 1000

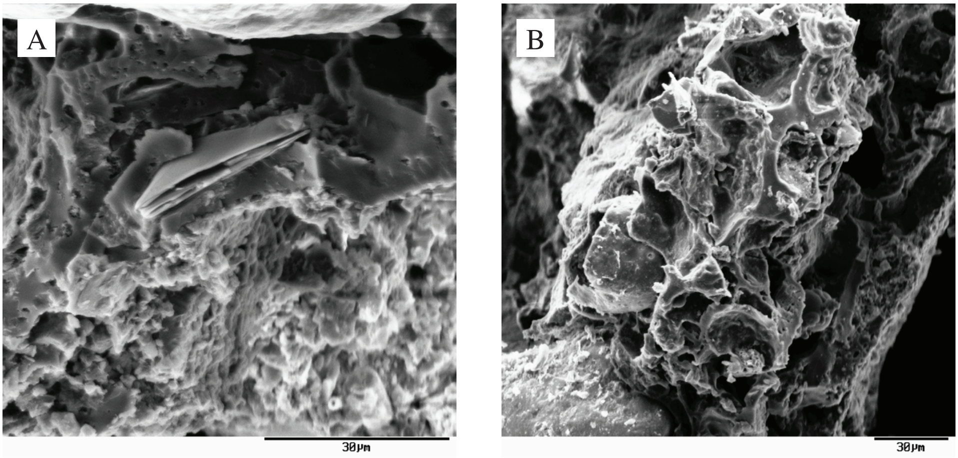


Photo. 5. SEM for sample Sr 81: (a) enlargement x 500, (b) enlargement x 1250

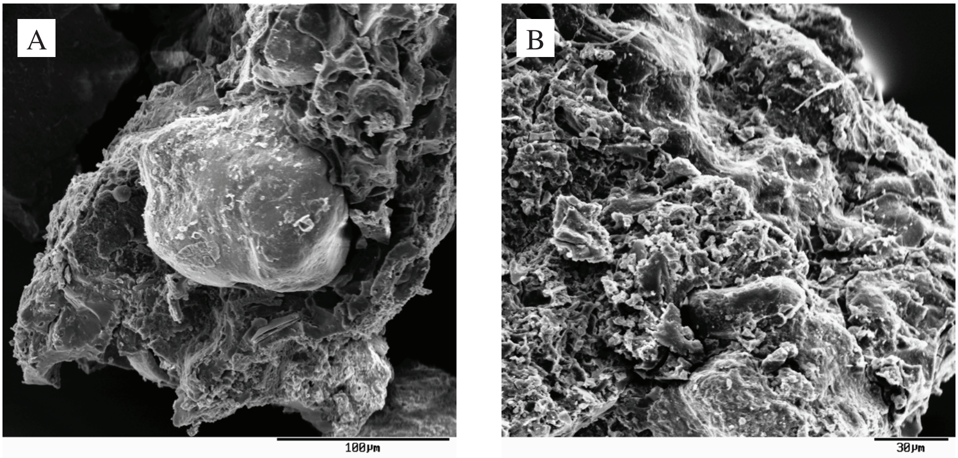


Photo. 6. SEM for sample Sr 83: (a) enlargement x 350, (b) enlargement x 500

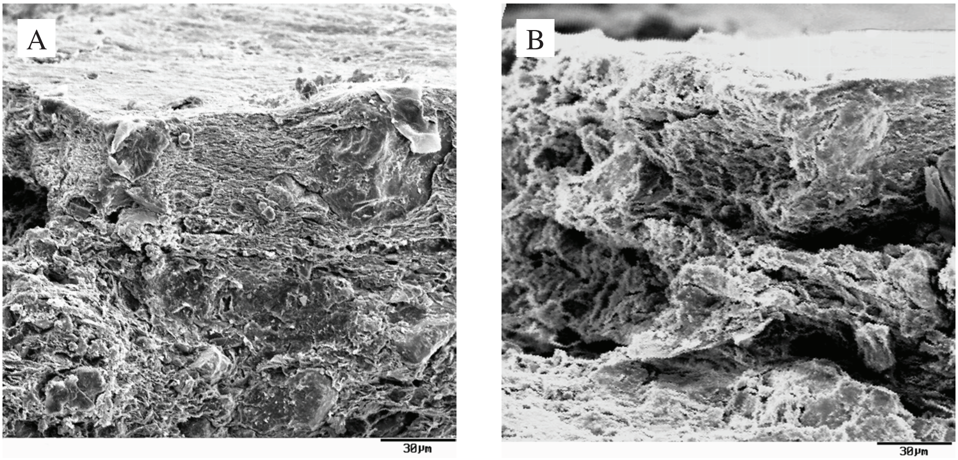


Photo. 7. SEM for sample Sr 88-1: (a) enlargement x 500, (b) enlargement x 750

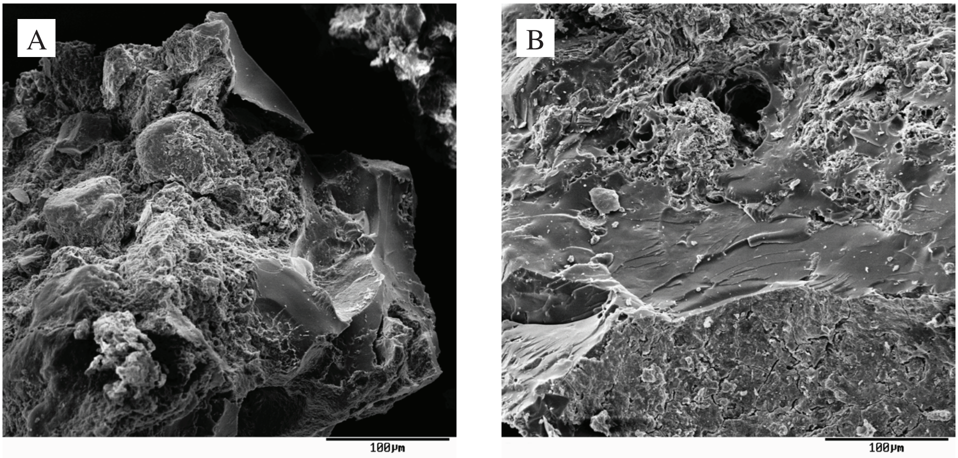


Photo. 8. SEM for sample Sr 95: (a) enlargement x 250, (b) enlargement x 250

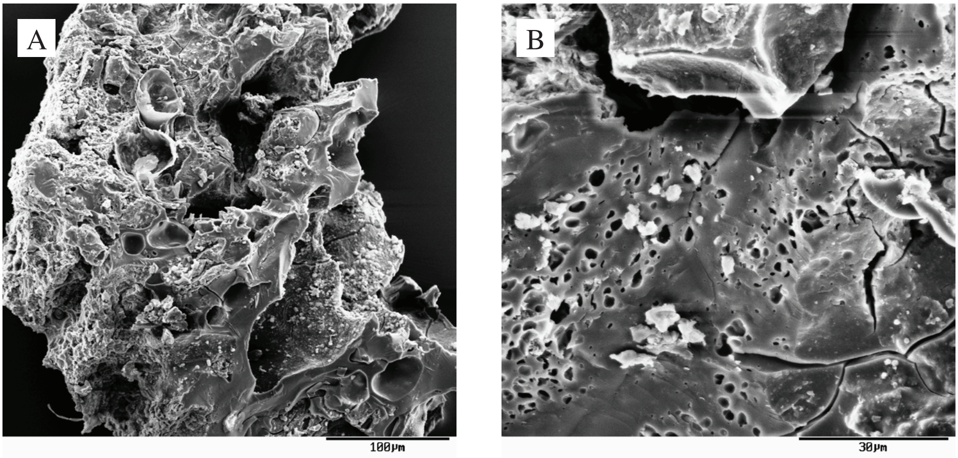


Photo. 9. SEM for sample Sr 98: (a) enlargement x 250, (b) enlargement x 1000

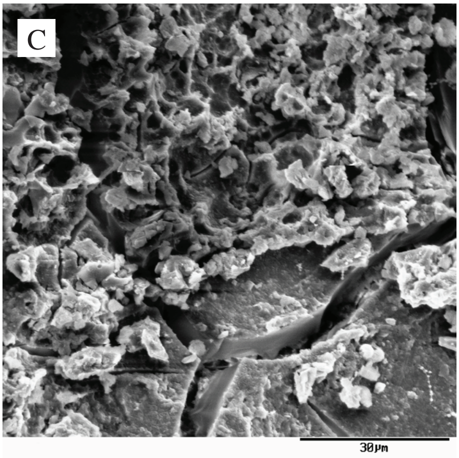
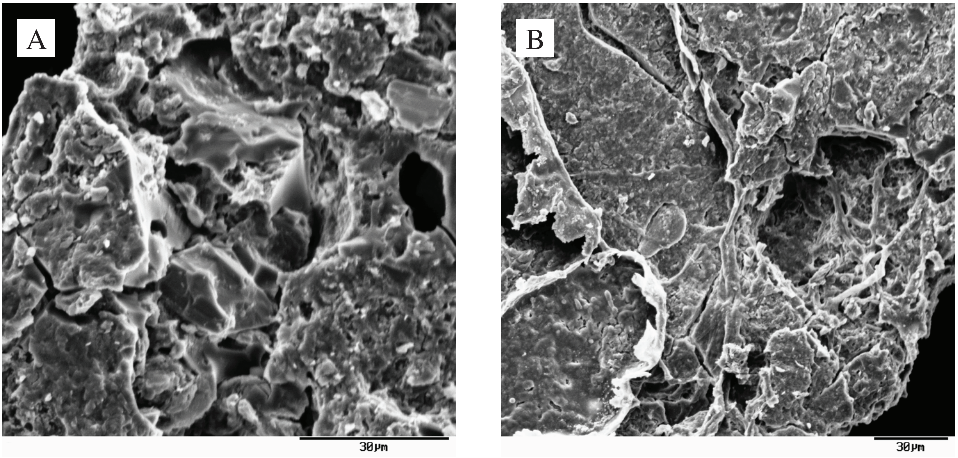
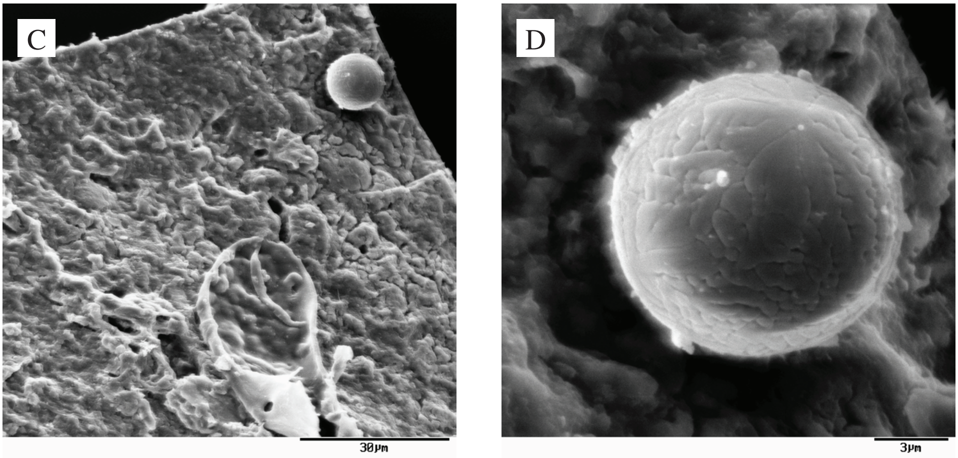


Photo. 9. SEM for sample Sr 98: (c) enlargement x 1000



P h o t o . 10. SEM for sample Sr 90: (a) enlargement x 1000, (b) enlargement x 1000



P h o t o . 10. SEM for sample Sr 90: (c) enlargement x 1000, (d) enlargement x 5000

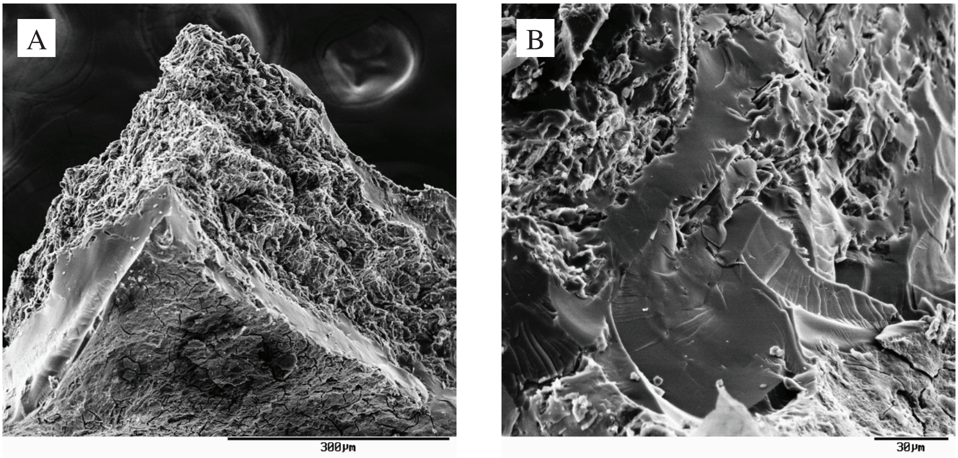


Photo. 11. SEM for sample Sr 91: (a) enlargement x 150, (b) enlargement x 500

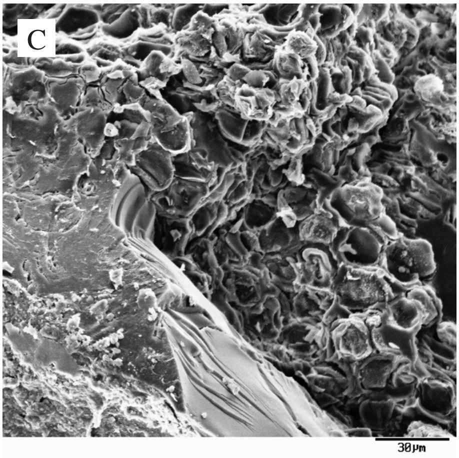


Photo. 11. SEM for sample Sr 91: (c) enlargement x 500

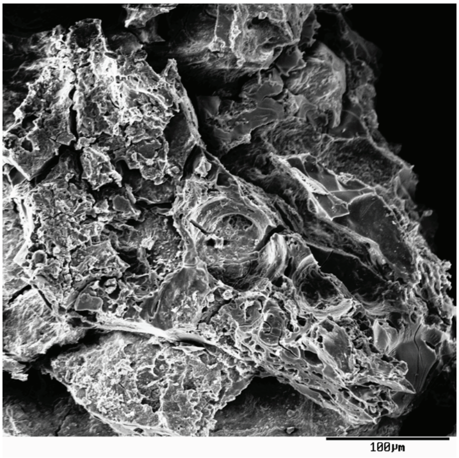


Photo. 12. SEM for sample Sr 92 – enlargement x 250

Late Band Pottery culture

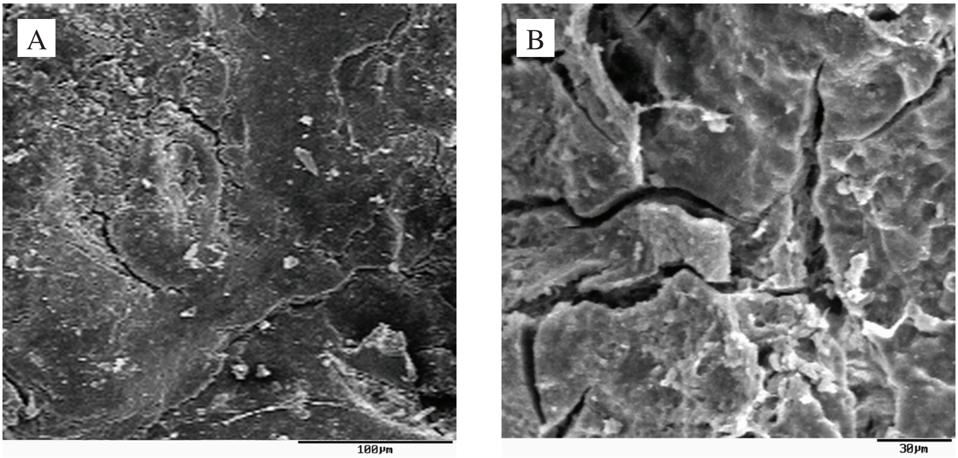
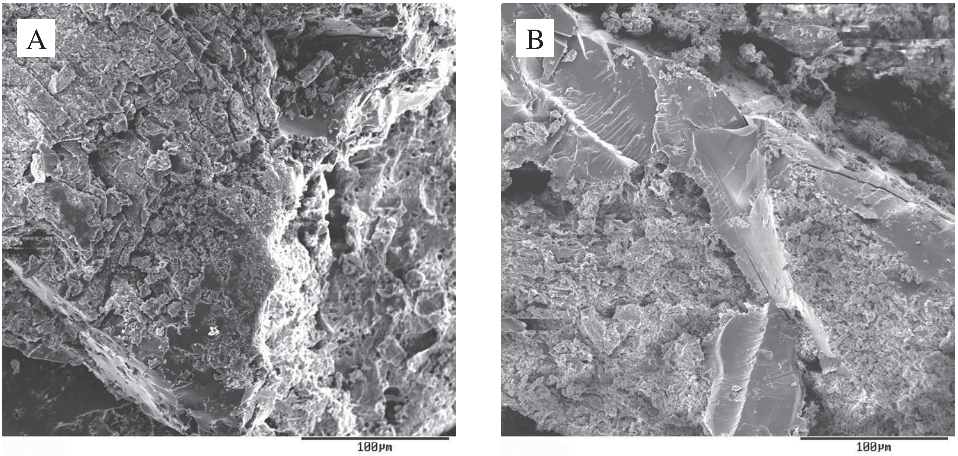
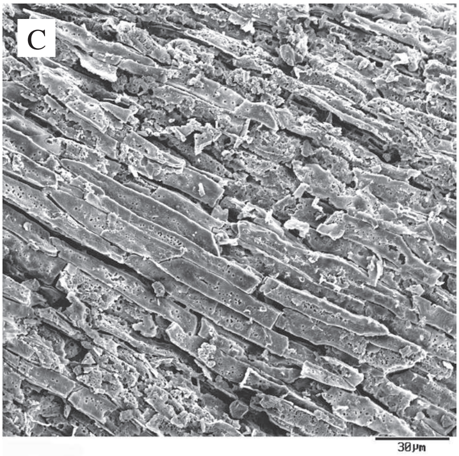


Photo. 13. SEM for sample Sr 174: (a) enlargement x 250, (b) enlargement x 1000

Funnel Beaker culture



P h o t o . 14. SEM for sample Sr 34: (a) enlargement x 250, (b) enlargement x 250



P h o t o . 14. SEM for sample Sr 34: (c) enlargement x 500

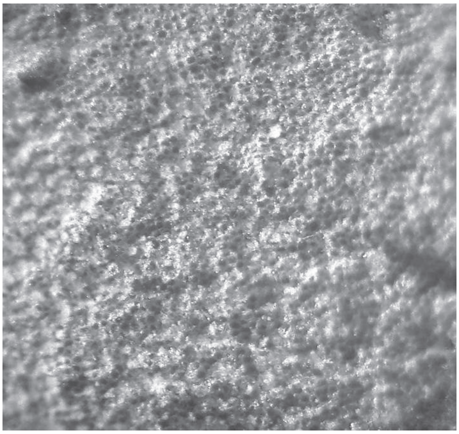


Photo. 15. Polarized optical microscopy (POM) for sample Sr 35 – enlargement x 240

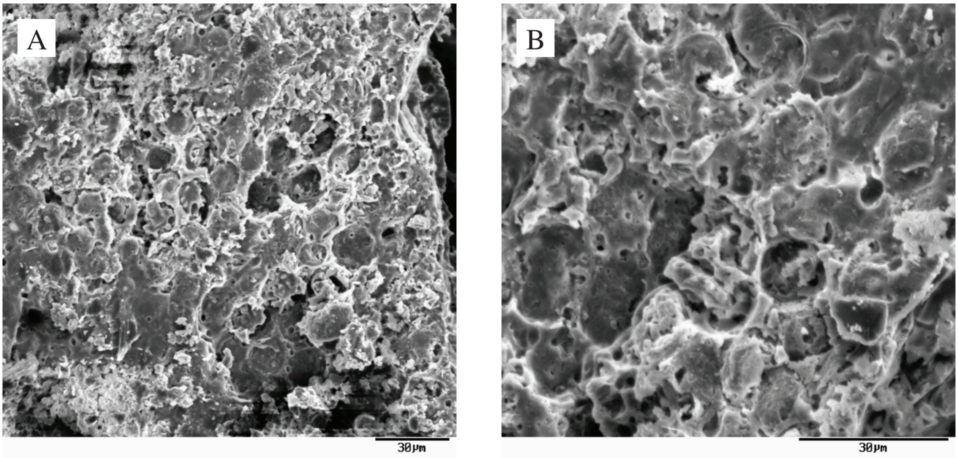


Photo. 16. SEM for sample Sr 327: (a) enlargement x 250, (b) enlargement x 1000

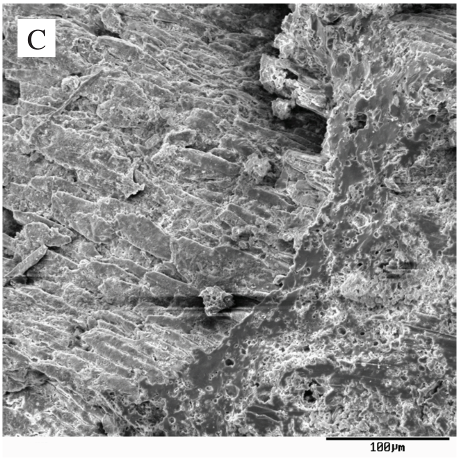


Photo. 16. SEM for sample Sr 327: (c) enlargement x 500

Photo. 17. POM for sample Sr 214 – enlargement x 120

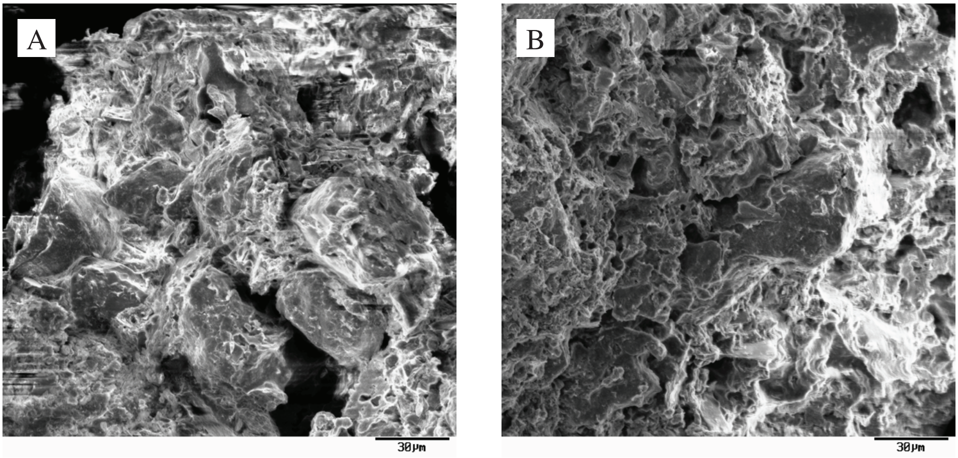


Photo. 18. SEM for sample Sr 325-3: (a) enlargement x 500, (b) enlargement x 500

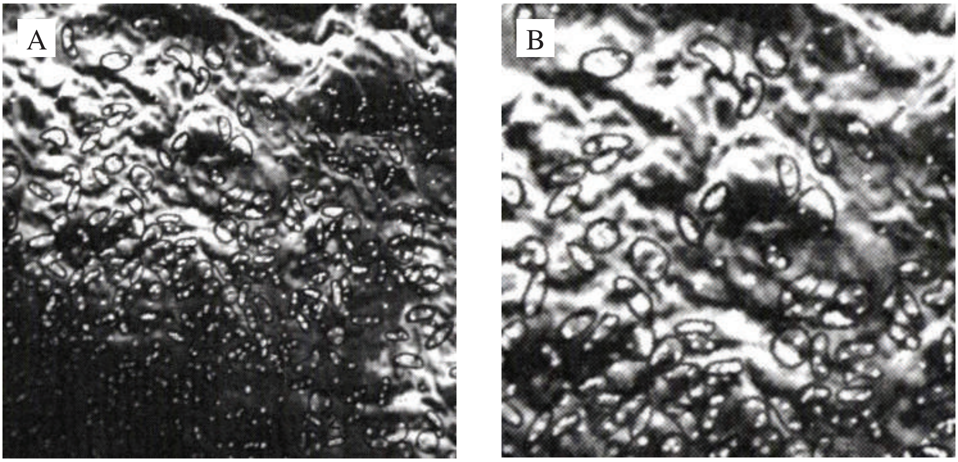


Photo. 19. SEM for sample Sr 1: (a) enlargement x 1000, (b) enlargement x 2500

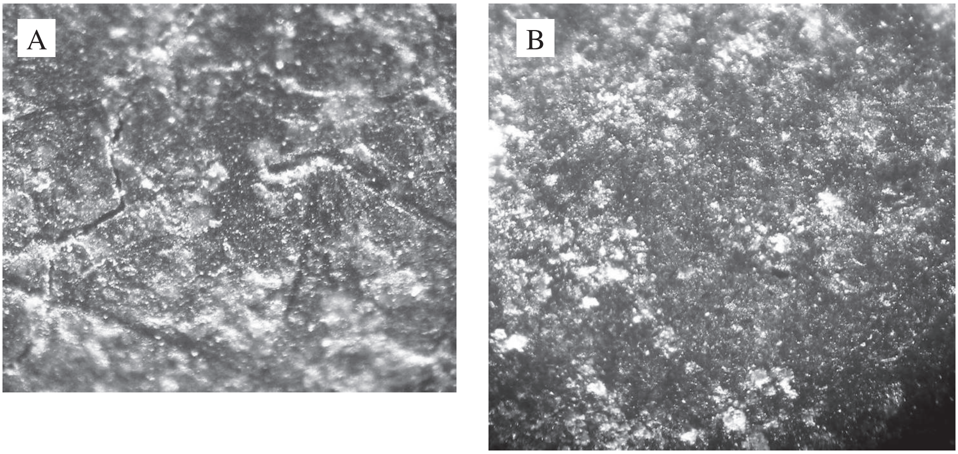


Photo. 20. POM for sample Sr 1: (a) enlargement x 200, (b) enlargement x 120

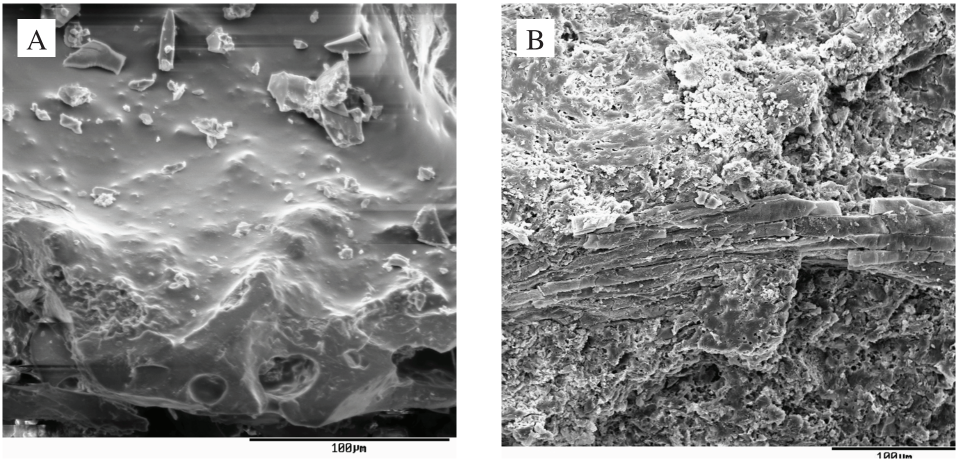


Photo. 21. SEM for sample Sr 43: (a) enlargement x 250, (b) enlargement x 250

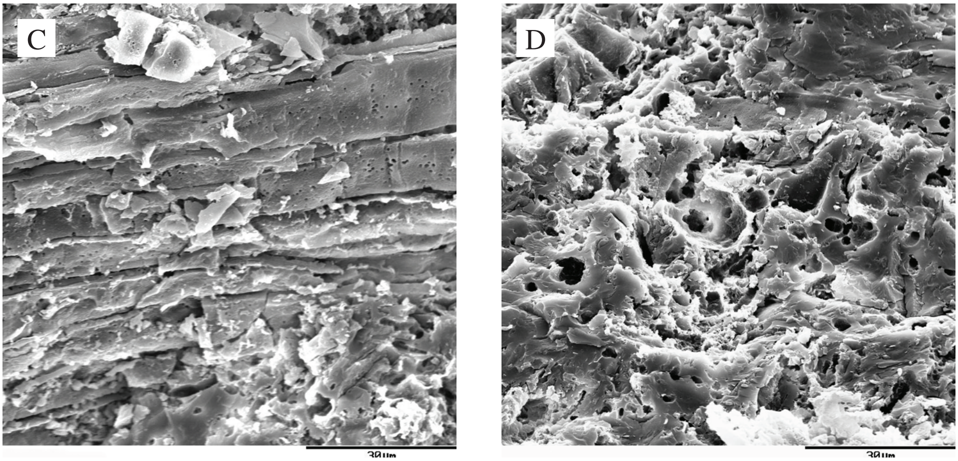


Photo. 21. SEM for sample Sr 43: (c) enlargement x 1000, (d) enlargement x 1000

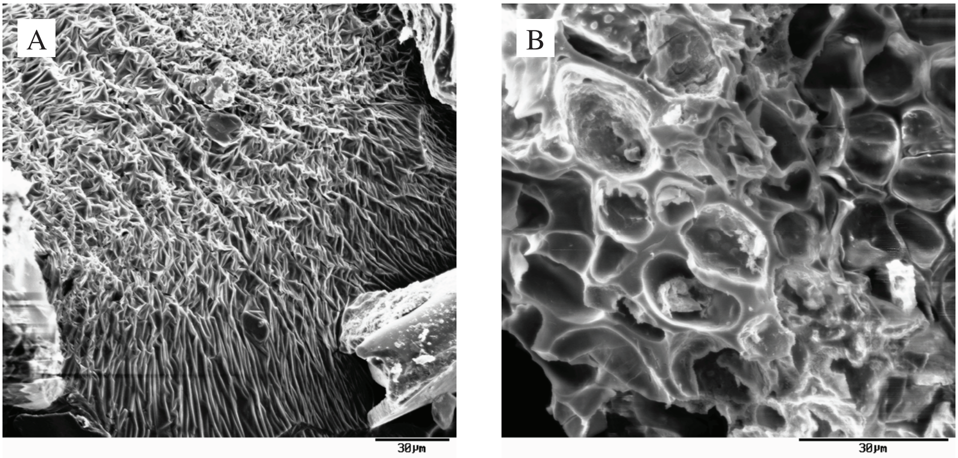


Photo. 22. SEM for sample Sr 30: (a) enlargement x 500, (b) enlargement x 1000

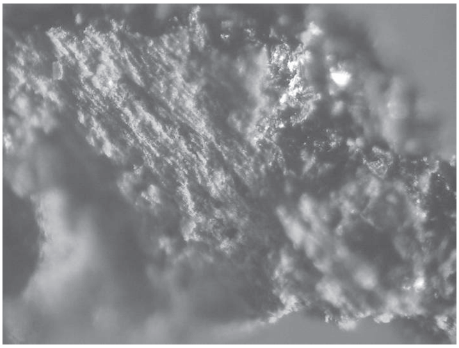


Photo. 23. POM for sample Sr 30 – enlargement x 200

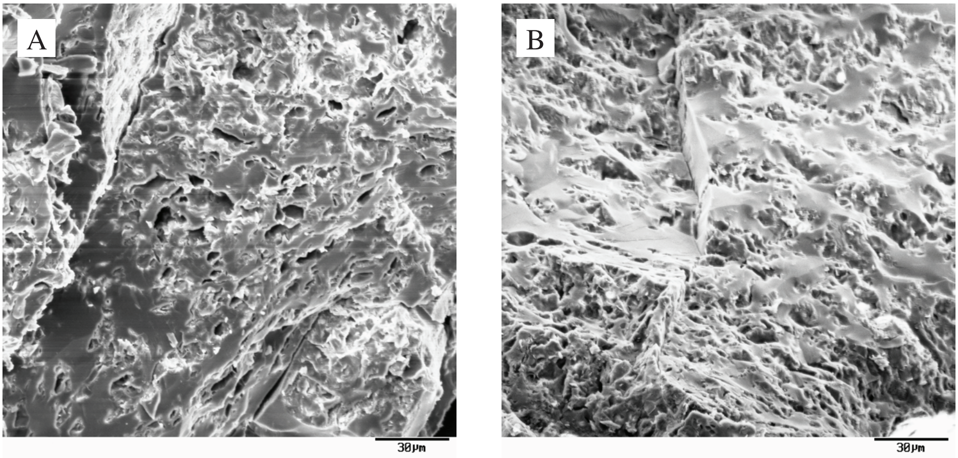


Photo. 24. SEM for sample Sr 32-2: (a) enlargement x 500, (b) enlargement x 500

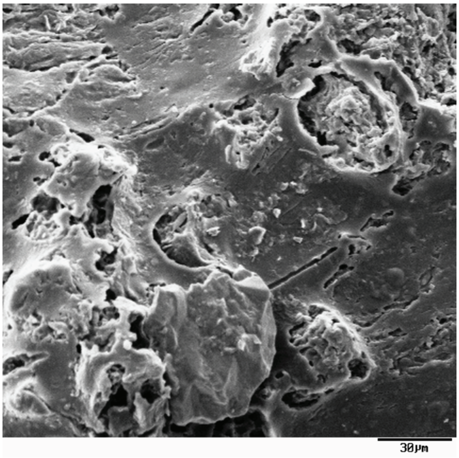


Photo. 25. SEM for sample Sr 467 – enlargement x 500

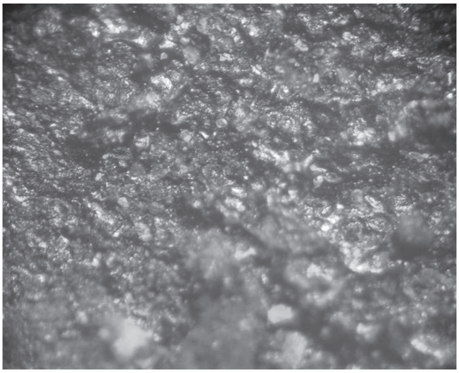
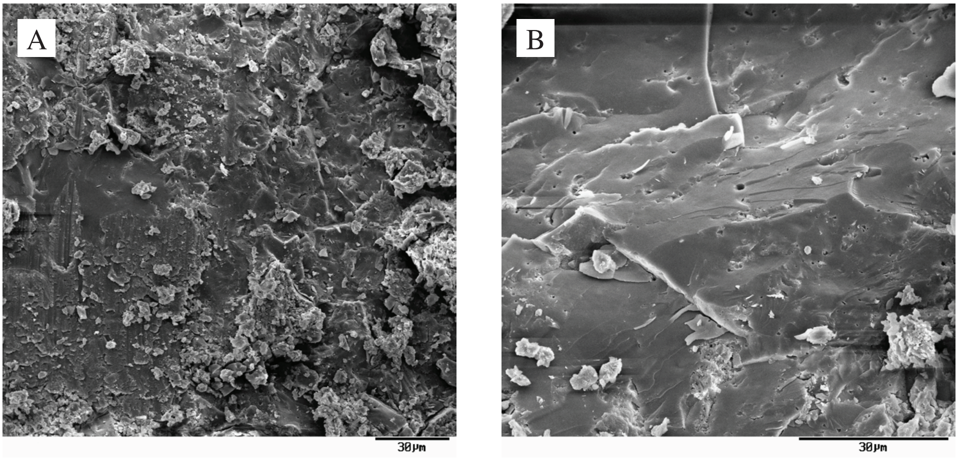
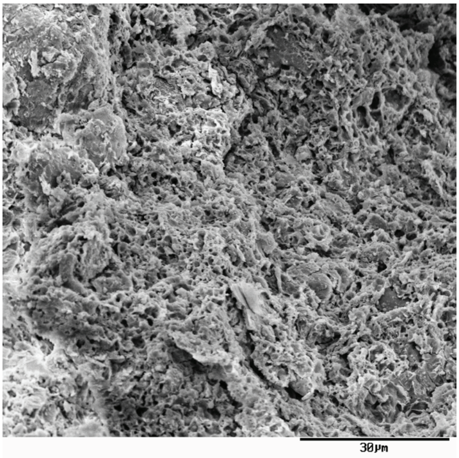


Photo. 26. POM for sample Sr 467 – enlargement x 120



P h o t o . 27. SEM for sample Sr 469-1: (a) enlargement x 500, (b) enlargement 1000



P h o t o . 28. SEM for sample Sr 469-2 – enlargement x 1000

Photo. 29. POM for sample Sr 469-2 – enlargement x 240

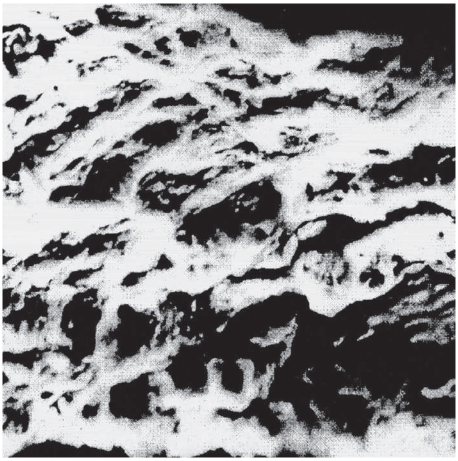


Photo. 30. SEM for sample Sr 3z – enlargement x 500

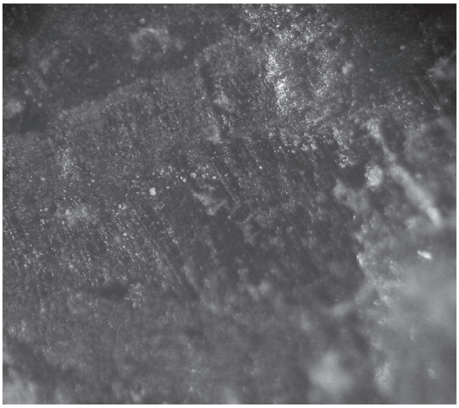


Photo. 31. POM for sample Sr 12 – enlargement x 240

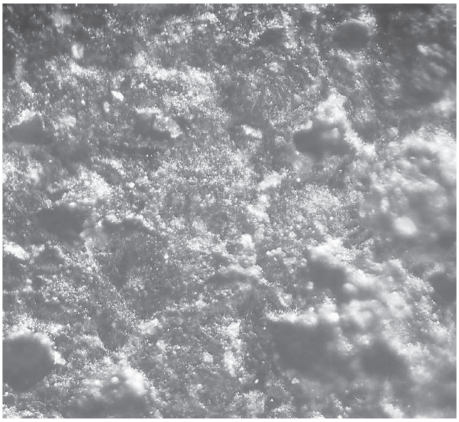


Photo. 32. POM for sample Sr 284 – enlargement x 120

Photo. 33. POM for sample Sr 8 – enlargement x 120

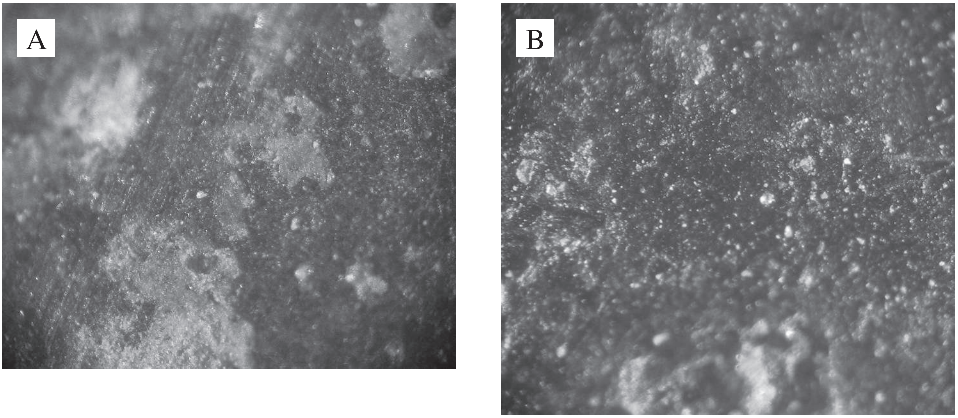


Photo. 34. POM for sample Sr 23: (a) enlargement x 120, (b) enlargement x 240

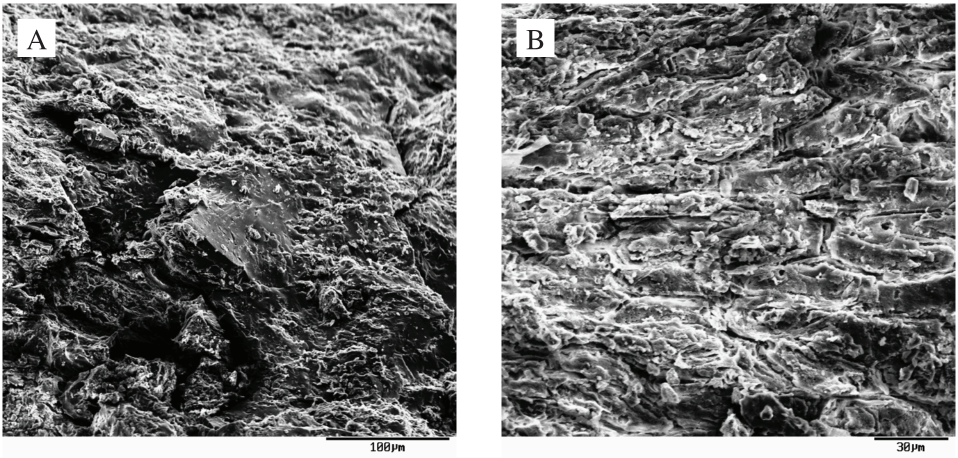


Photo. 35. SEM for sample Sr 58z: (a) enlargement x 250, (b) enlargement x 500

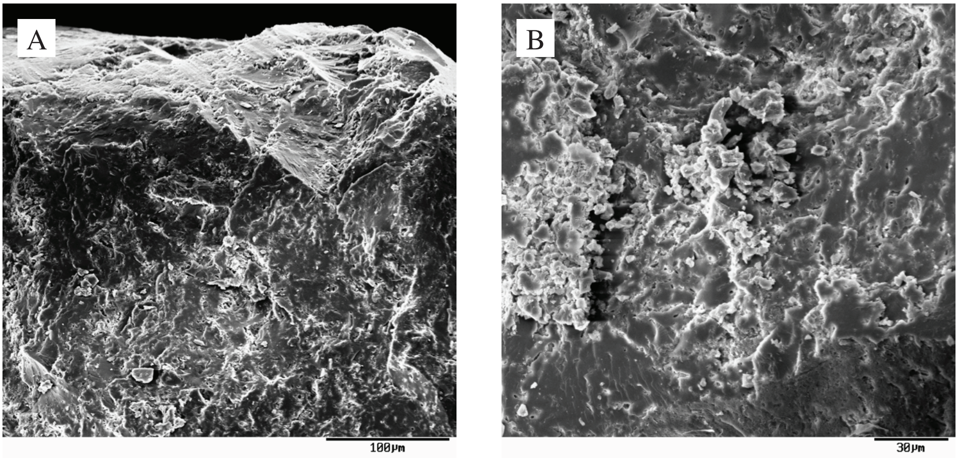


Photo. 36. SEM for sample Sr 59: (a) enlargement x 250, (b) enlargement x 500

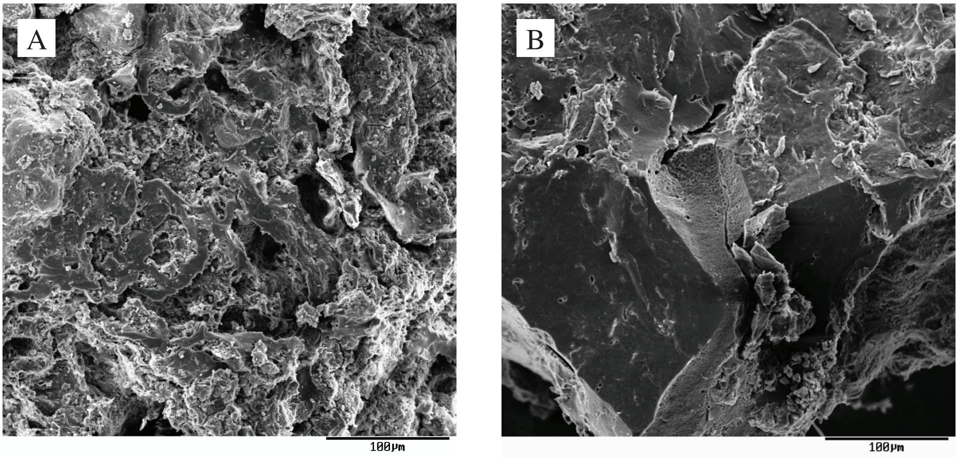


Photo. 37. SEM for sample Sr 68w: (a) enlargement x 250, (b) enlargement x 250

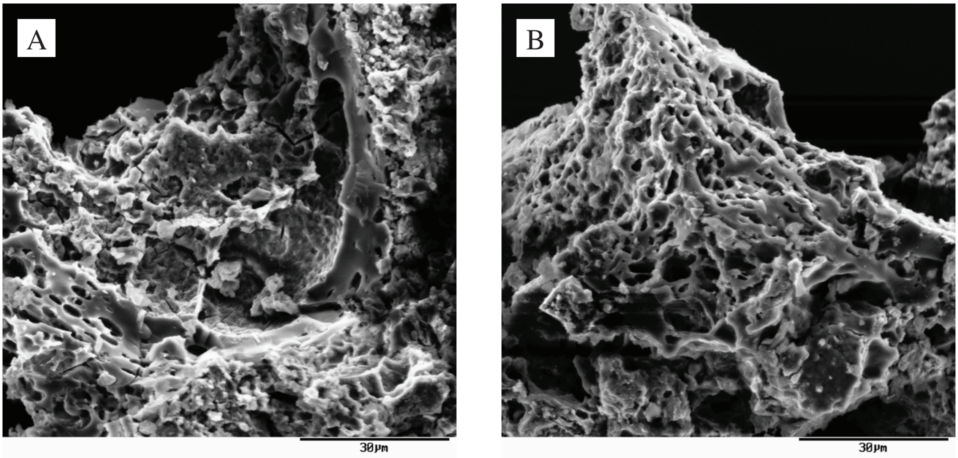


Photo. 38. SEM for sample Sr 67w: (a) enlargement x 1000, (b) enlargement x 1000

Globular Amphora culture

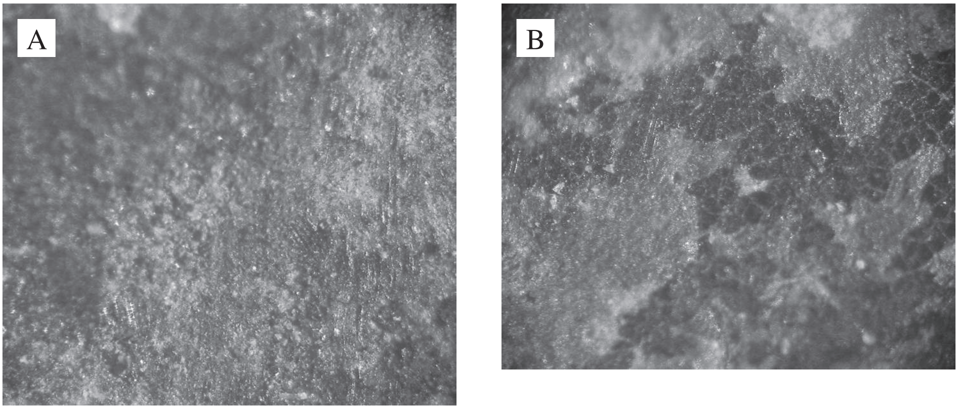


Photo. 39. POM for sample Sr 19: (a) enlargement x 200, (b) enlargement x 300

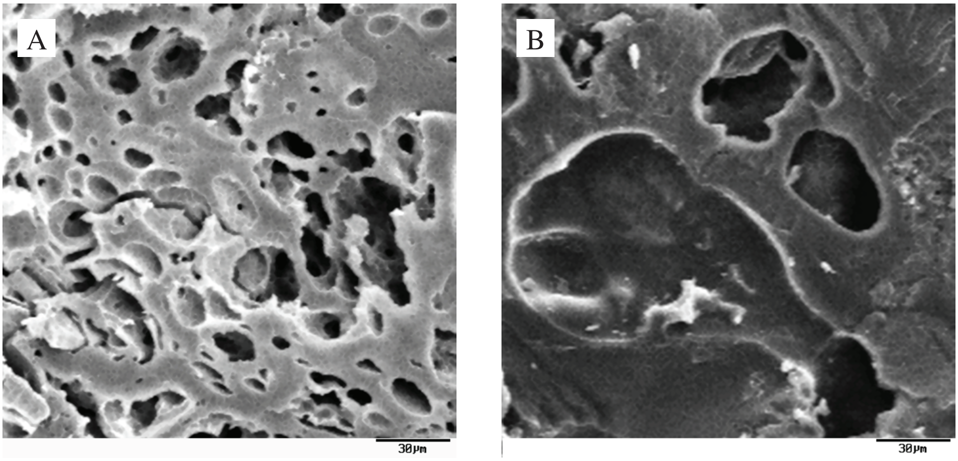


Photo. 40. SEM for sample Sr 141: (a) enlargement x 250, (b) enlargement x 1000

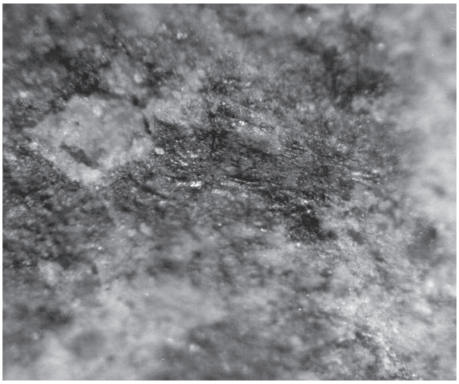


Photo. 41. POM for sample Sr 141 – enlargement x 240

Mierzanowice culture

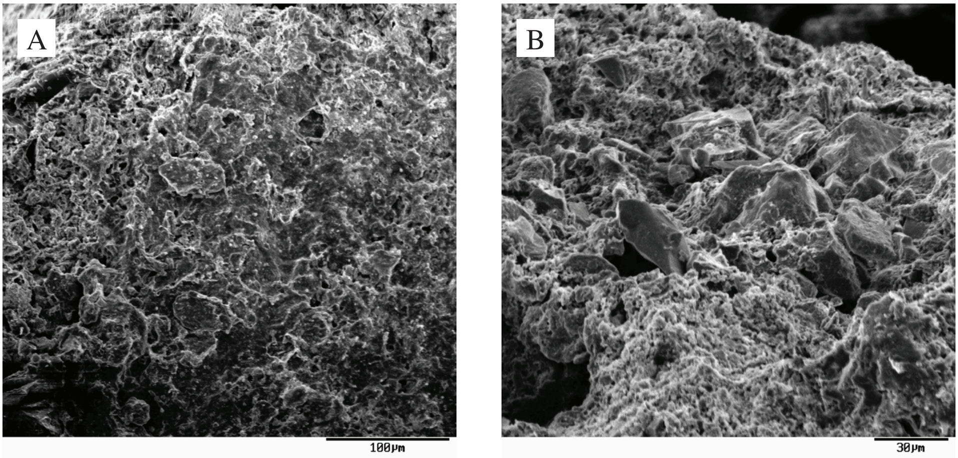


Photo. 42. SEM for sample Sr 326: (a) enlargement x 250, (b) enlargement x 500

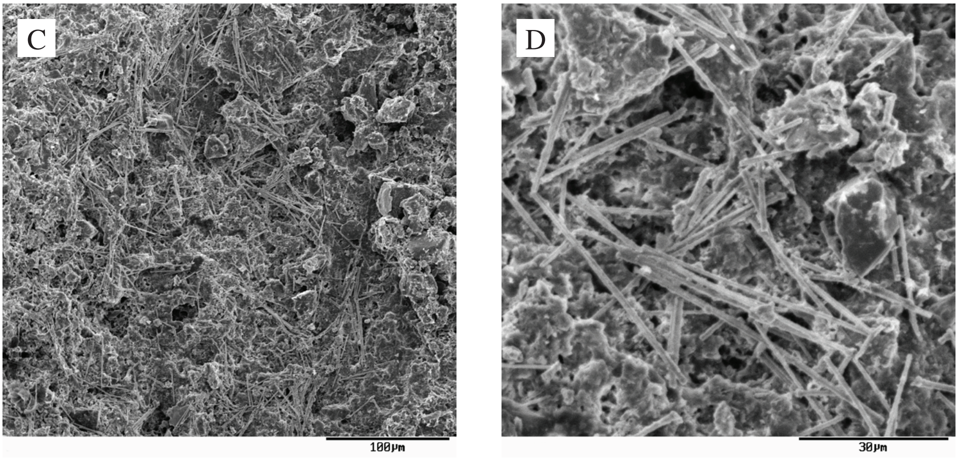


Photo. 42. SEM for sample Sr 326: (c) enlargement x 250, (d) enlargement x 1000

Tumulus culture

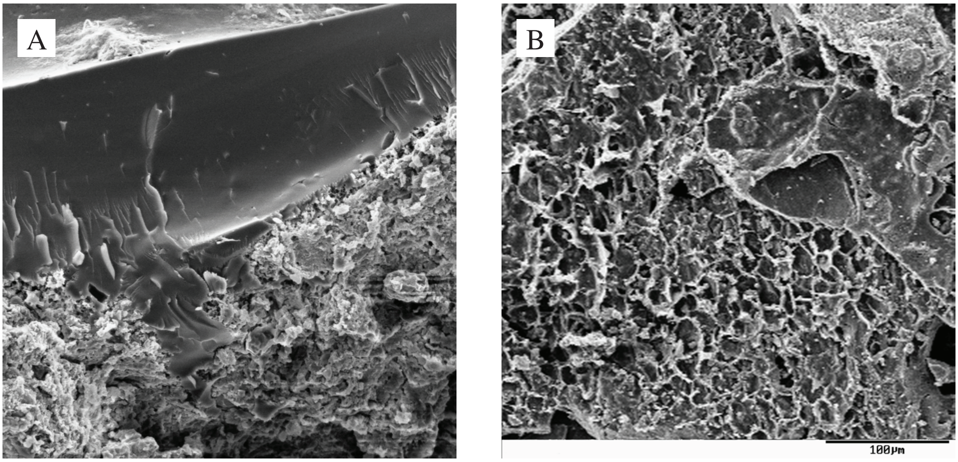


Photo. 43. SEM for sample Sr 172: (a) enlargement x 500, (b) enlargement x 250

Trzciniec Cultural circle

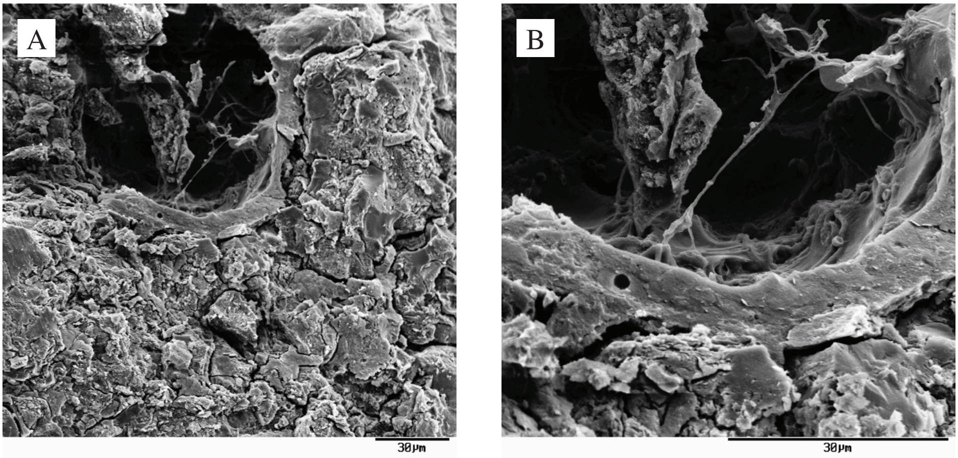


Photo. 44. SEM for sample Sr 448: (a) enlargement x 500, (b) enlargement x 1500

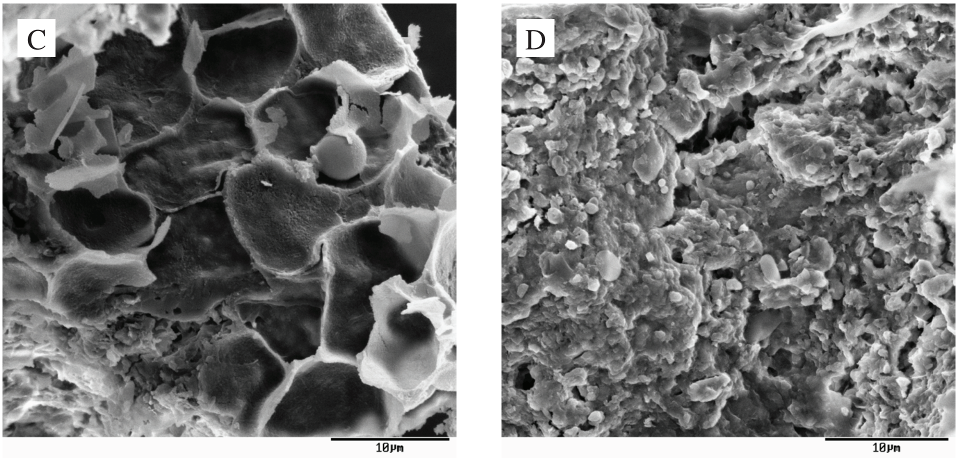


Photo. 44. SEM for sample Sr 448: (c) enlargement x 2400, (d) enlargement x 2500

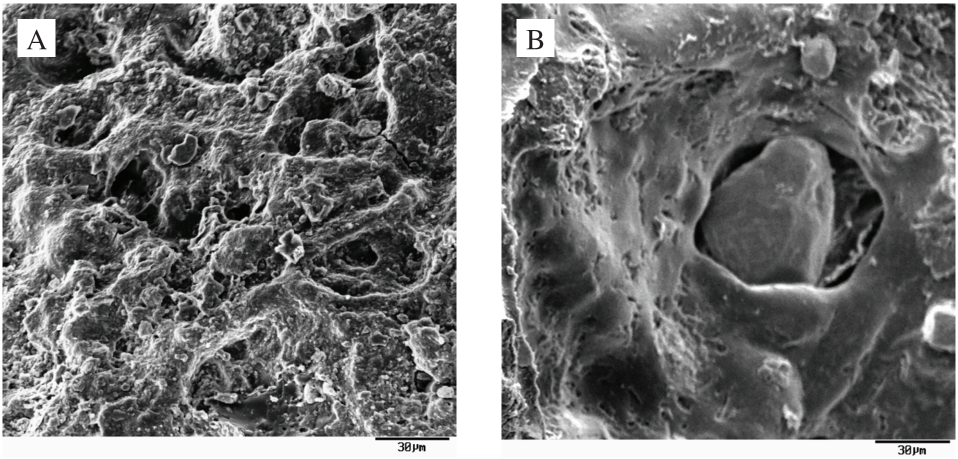


Photo. 45. SEM for sample Sr 454: (a) enlargement x 500, (b) enlargement x 600

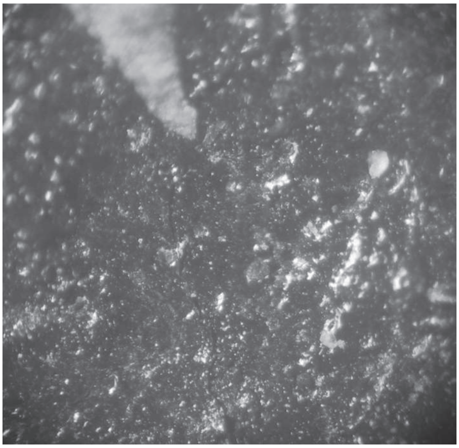


Photo. 46. POM for sample Sr 258 – enlargement x 120

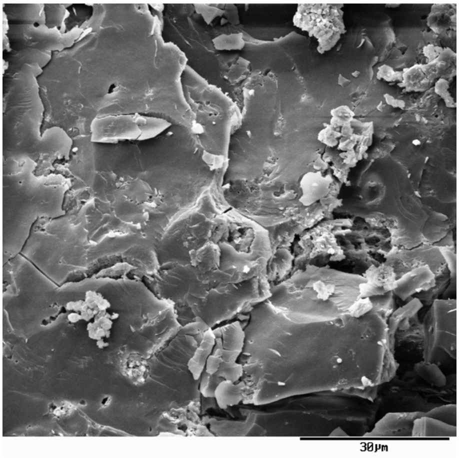


Photo. 47. SEM for sample Sr 439w – enlargement x 1000

Lusatian culture

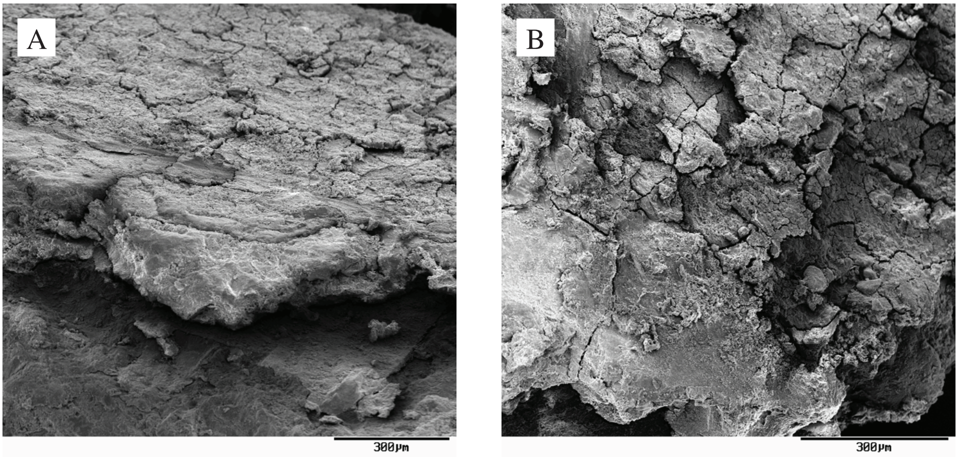


Photo. 48. SEM for sample Sr 443: (a) enlargement x 80, (b) enlargement x 100

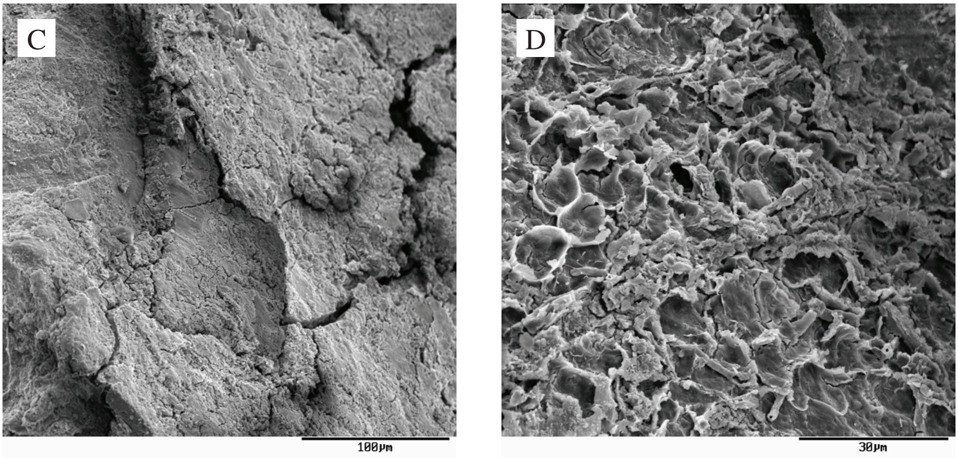


Photo. 48. SEM for sample Sr 443: (c) enlargement x 300, (d) enlargement x 1000

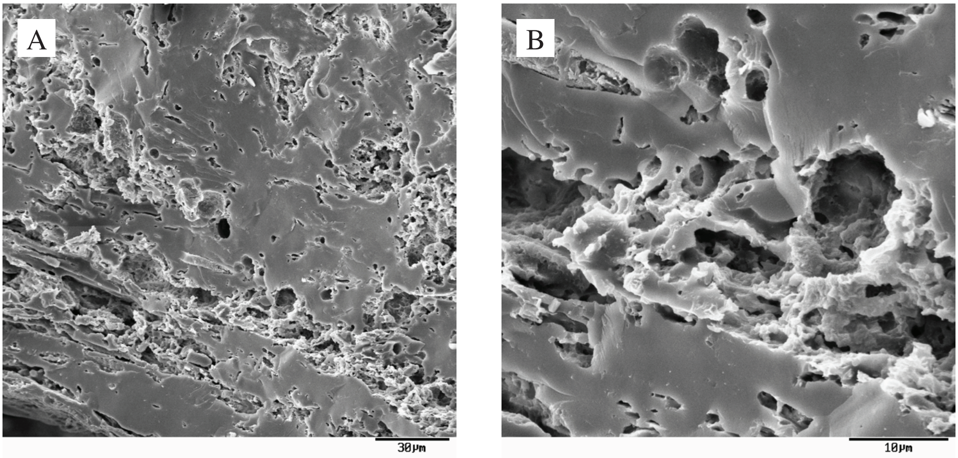


Photo. 49. SEM for sample Sr 444-1: (a) enlargement x 500, (b) enlargement x 2000

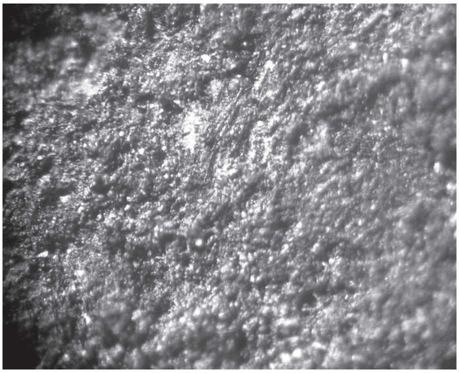


Photo. 50. POM for sample Sr 270 – enlargement x 240

Cycle of cultural systems of the steppe and forest steppe of the Baltic drainage basin

Tripolye culture

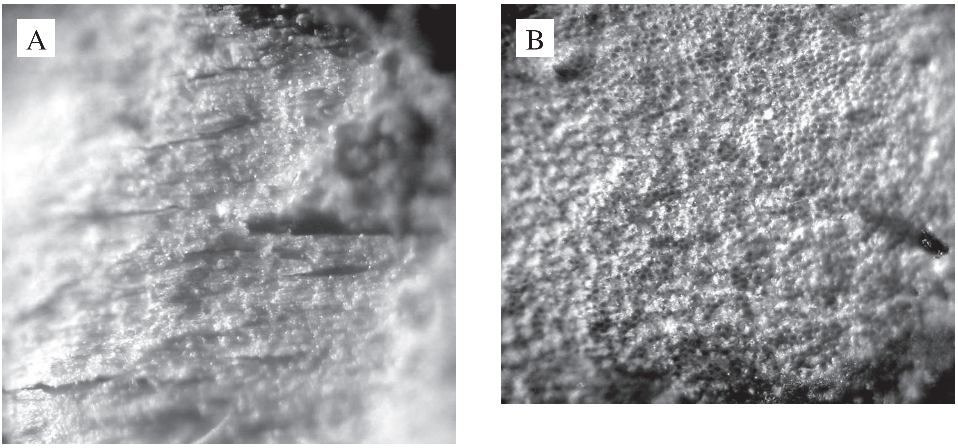


Photo. 51. POM for sample Sr 47: (a) enlargement x 120, (b) enlargement x 240

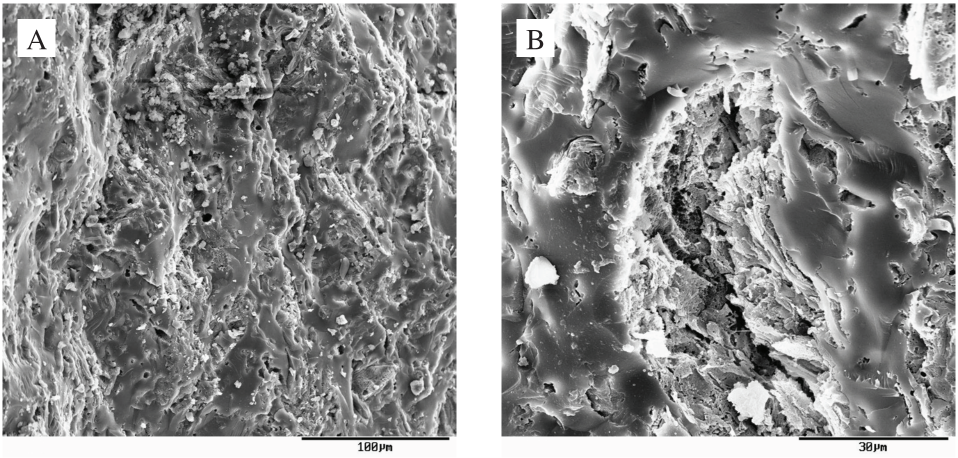


Photo. 52. SEM for sample Sr 184: (a) enlargement x 250, (b) enlargement x 500

Pre-Yamnaya culture

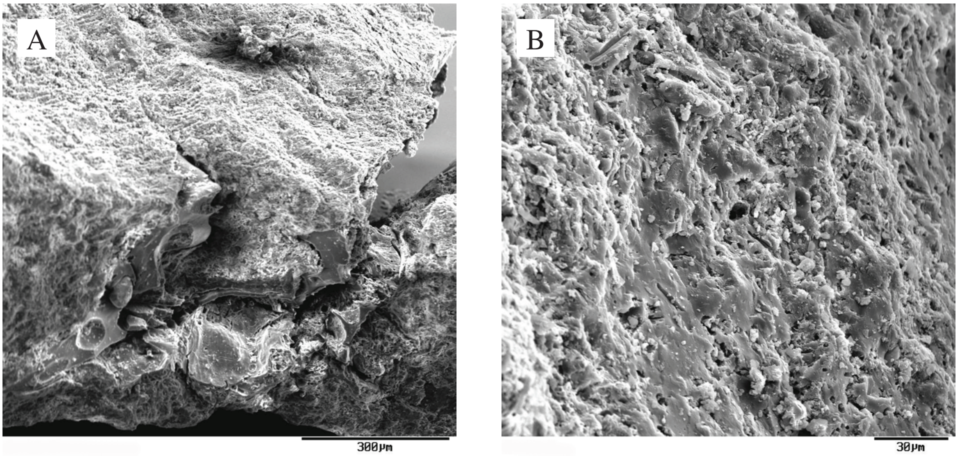


Photo. 53. SEM for sample Sr 39: (a) enlargement x 130, (b) enlargement x 500

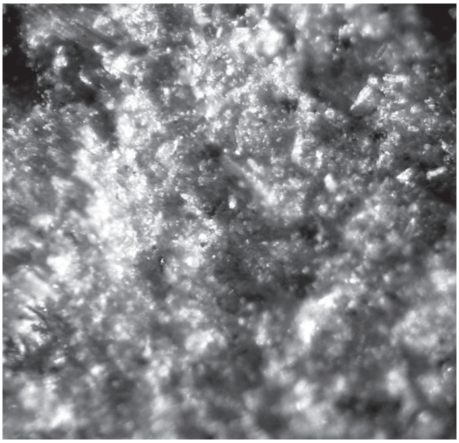


Photo. 54. POM for sample Sr 39 – enlargement x 120

Tumulus culture

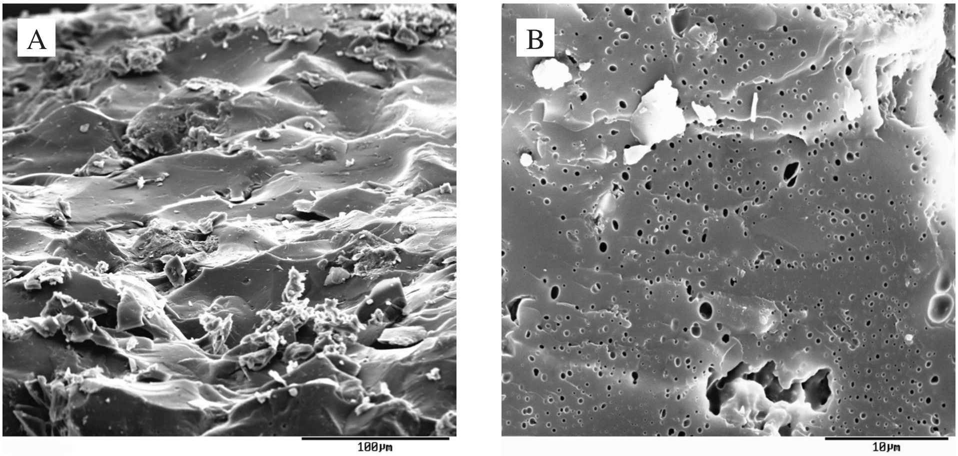


Photo. 55. SEM for sample Sr 54: (a) enlargement x 250, (b) enlargement x 1000

Cycle of the cultural systems of the forest zone in Eastern Europe

Dnieper-Donets culture

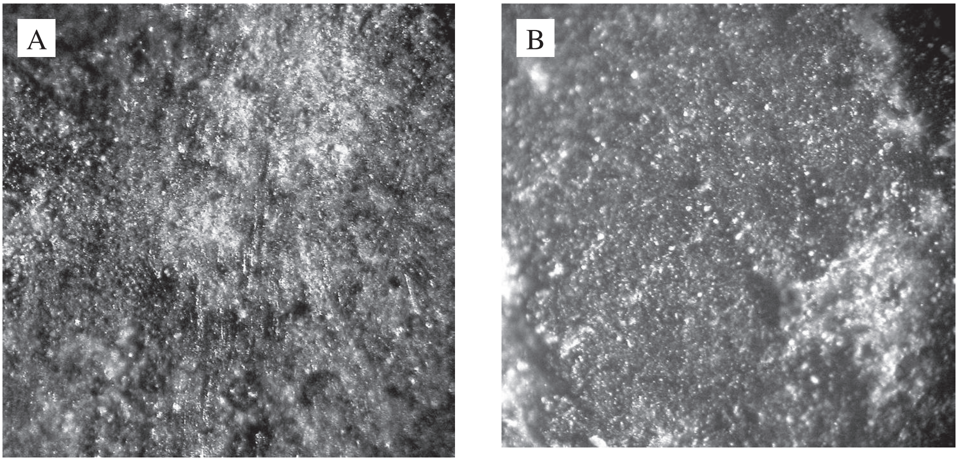


Photo. 56. POM for sample Sr 315z: (a) enlargement x 120, (b) enlargement x 100

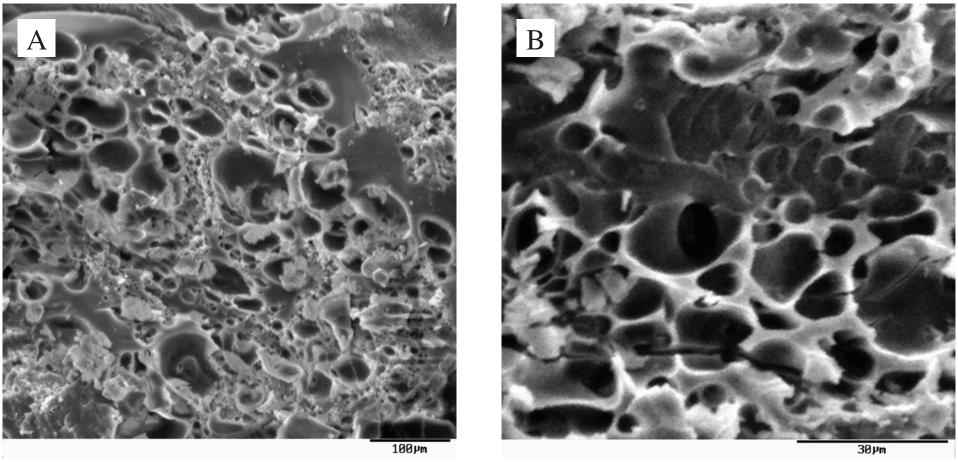


Photo. 57. SEM for sample Sr 318: (a) enlargement x 500, (b) enlargement x 1500

Zedmar culture

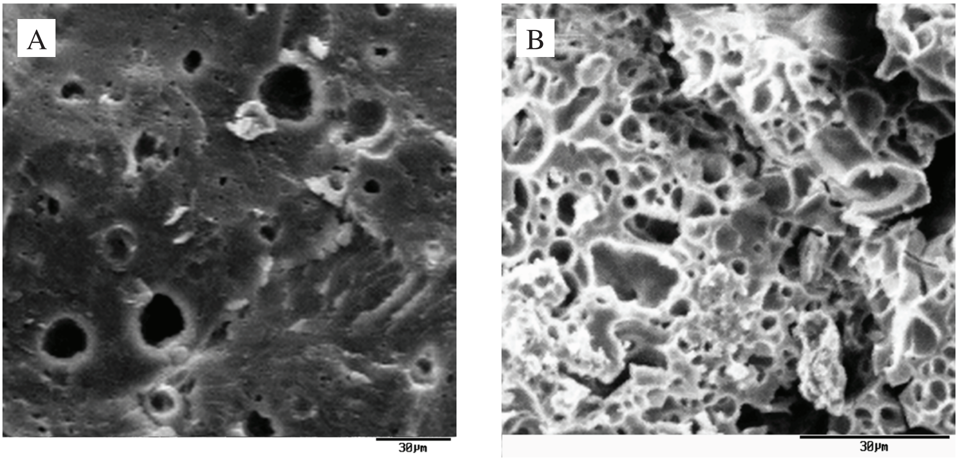


Photo. 58. SEM for sample Sr 232w: (a) enlargement x 650, (b) enlargement x 1000

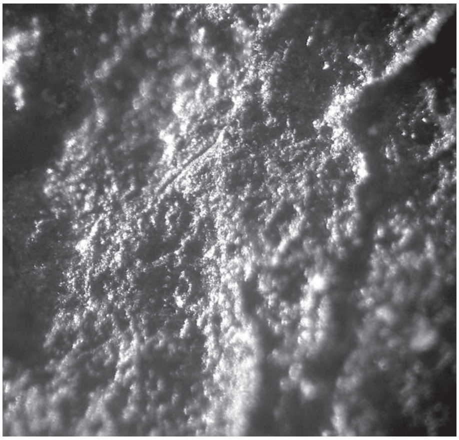
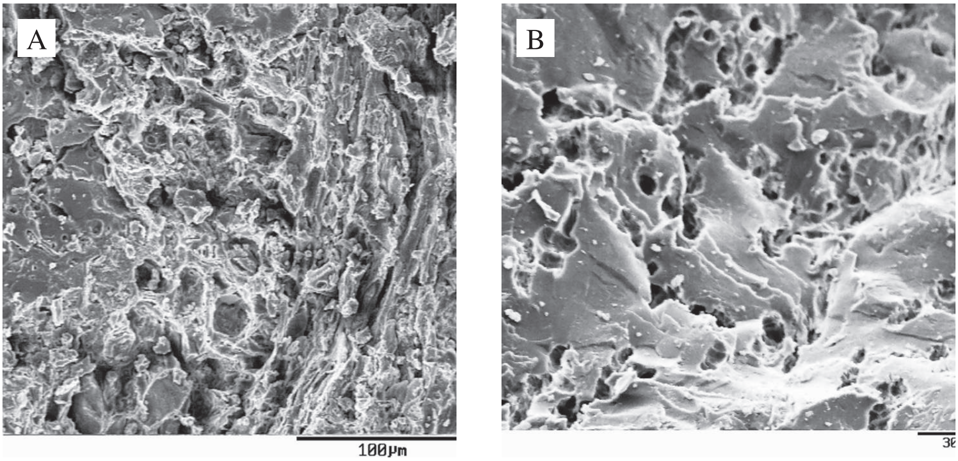


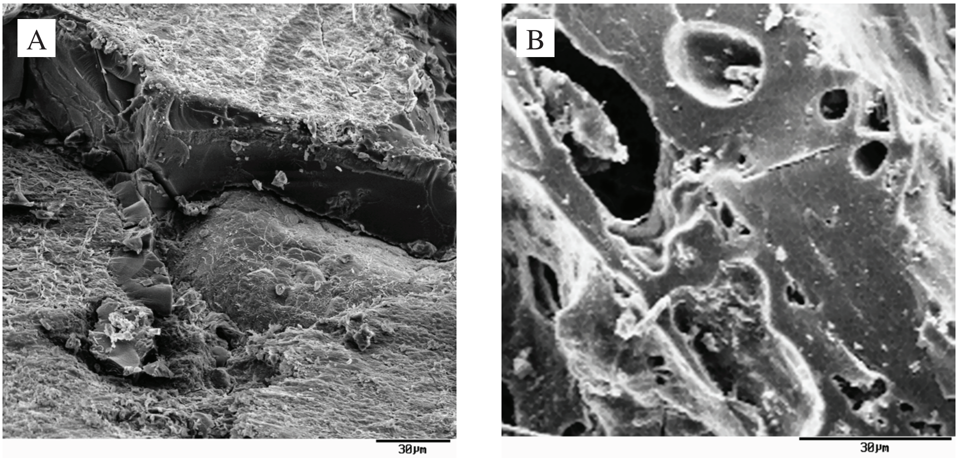
Photo. 59. POM for sample Sr 232z – enlargement x 240

Comb culture



P h o t o . 60. SEM for sample Sr 231: (a) enlargement x 250, (b) enlargement x 500

Neman culture



P h o t o . 61. SEM for sample Sr 255-1: (a) enlargement x 500, (b) enlargement x 1000

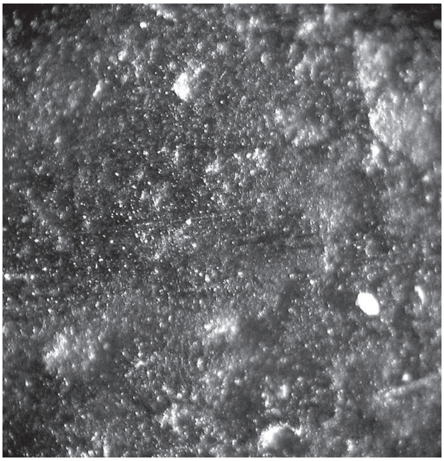


Photo. 62. POM for sample Sr 255-1 – enlargement x 350

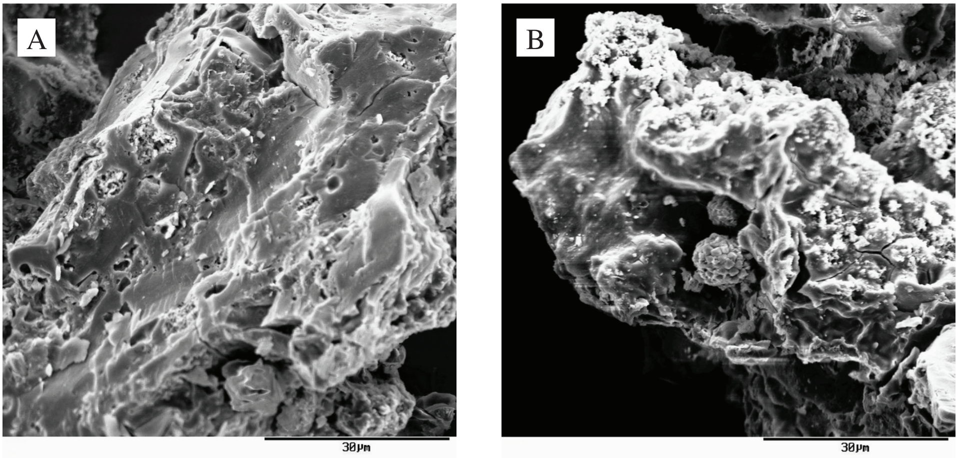
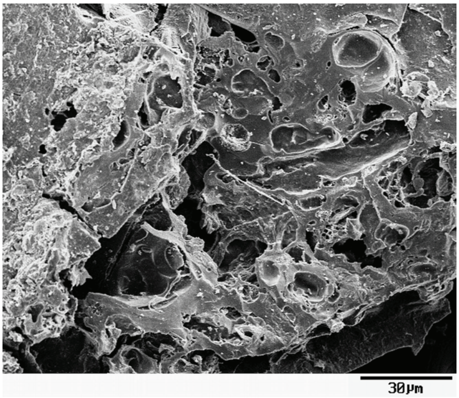
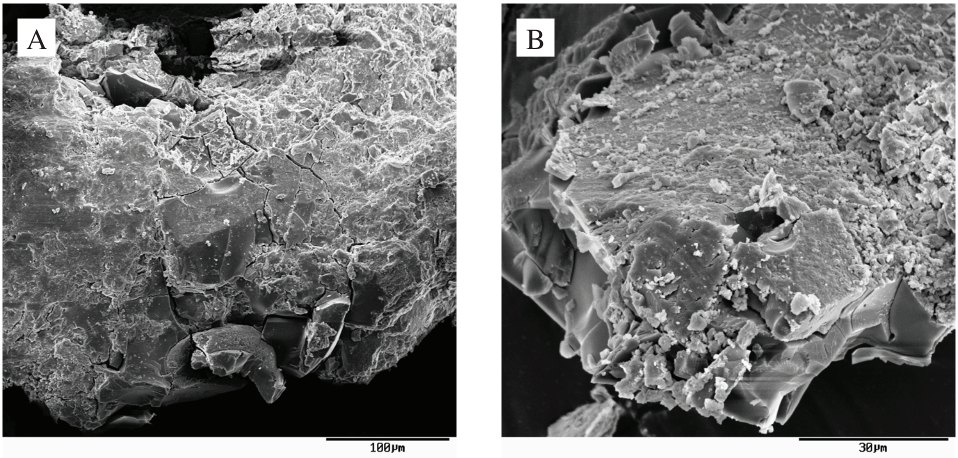


Photo. 63. SEM for sample Sr 188: (a) enlargement x 500, (b) enlargement x 500



P h o t o . 64. SEM for sample Sr 238 – enlargement x 600

Trzciniec Cultural circle – eastern branch



P h o t o . 65. SEM for sample Sr 330: (a) enlargement x 250, (b) enlargement x 1000

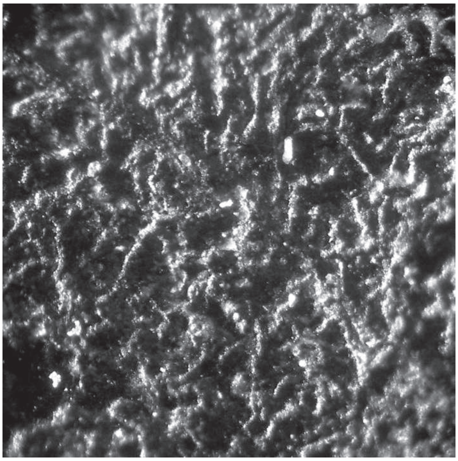


Photo. 66. POM for sample Sr 330 – enlargement x 120

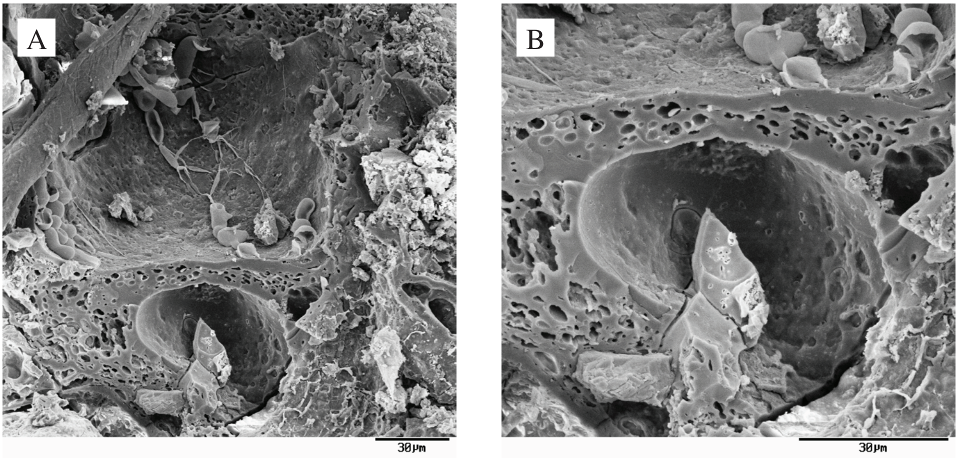


Photo. 67. SEM for sample Sr 333: (a) enlargement x 500, (b) enlargement x 1000

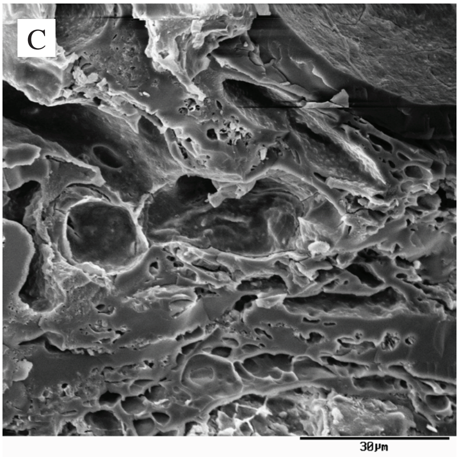


Photo. 67. SEM for sample Sr 333: (c) enlargement x 1000

North Belarus culture

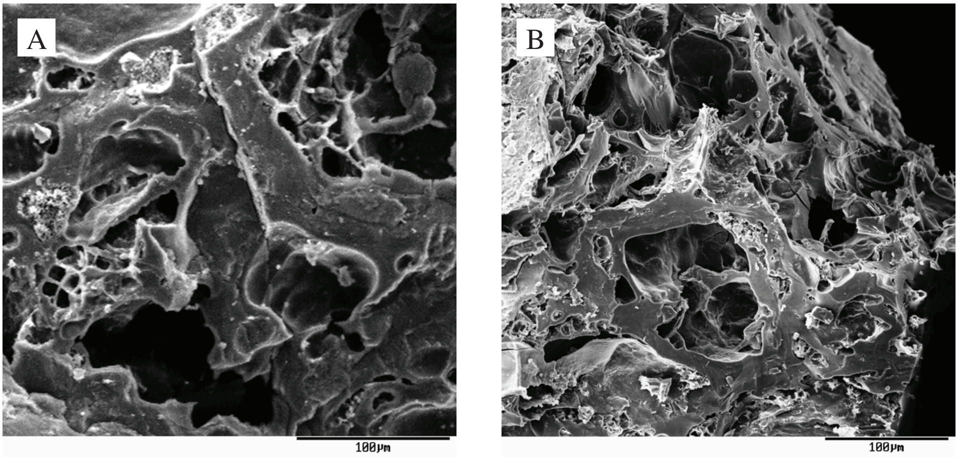


Photo. 68. SEM for sample Sr 221-5: (a) enlargement x 250, (b) enlargement x 250

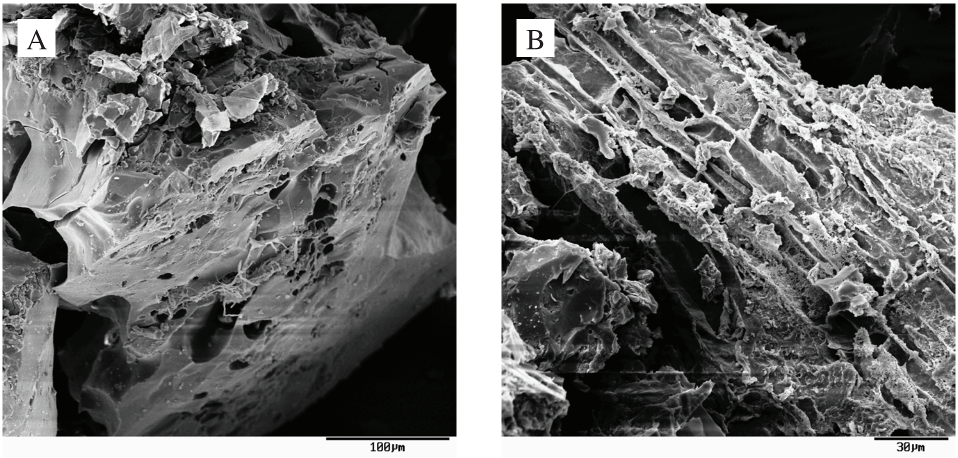


Photo. 69. SEM for sample Sr 332: (a) enlargement x 250, (b) enlargement x 1000

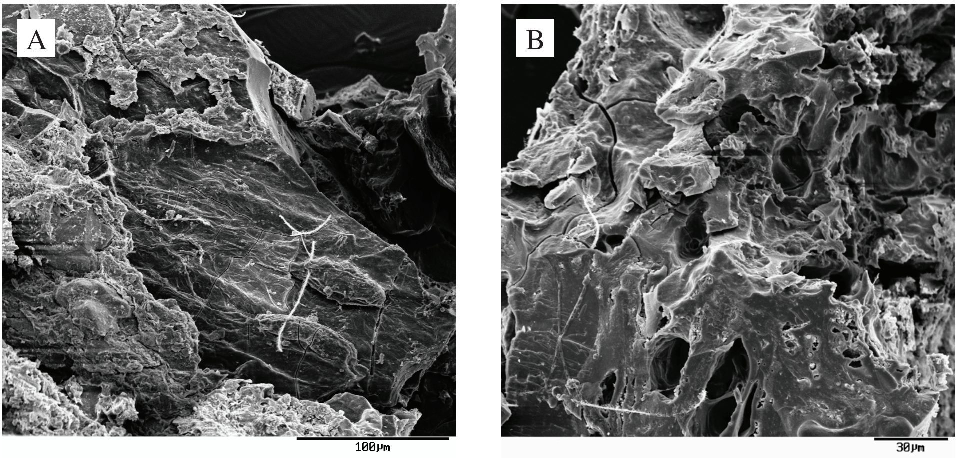


Photo. 70. SEM for sample Sr 334-1: (a) enlargement x 300, (b) enlargement x 500

Cycle of cultural systems of the Carpathian Basin

Eastern Linear Pottery culture

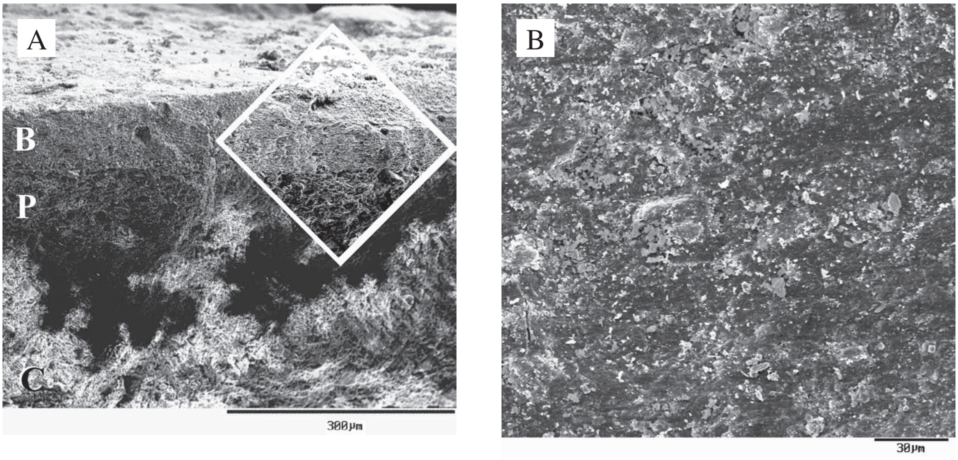


Photo. 71. SEM for sample Sr 438: (a) enlargement x 340, (b) enlargement x 500

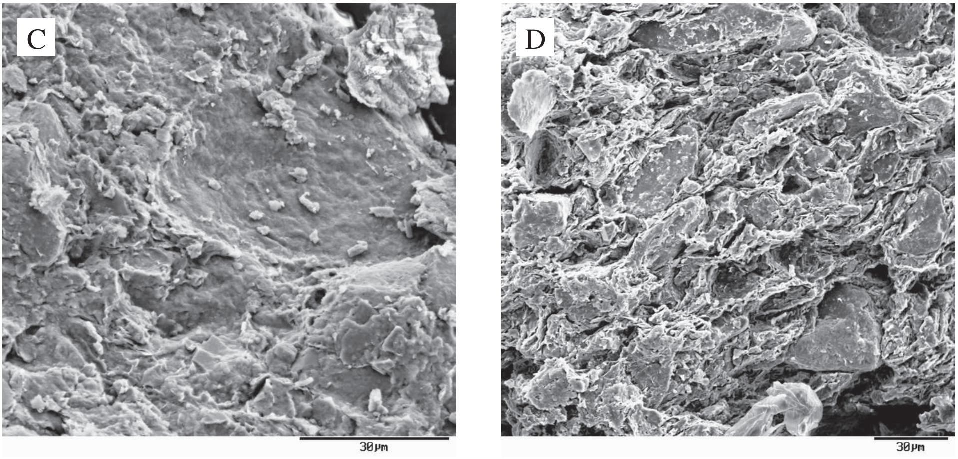


Photo. 71. SEM for sample Sr 438: (c) enlargement x 250, (d) enlargement x 500

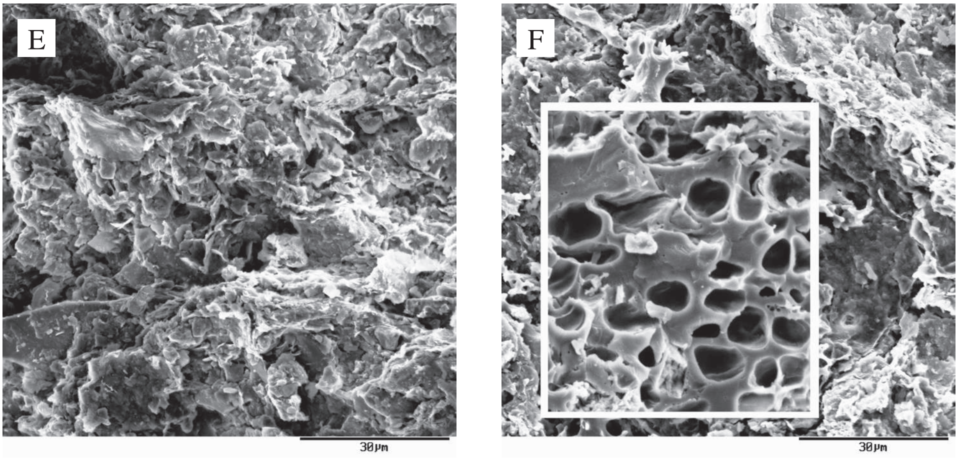


Photo. 71. SEM for sample Sr 438: (e) enlargement x 1000, (f) enlargement x 1000

Bükk culture

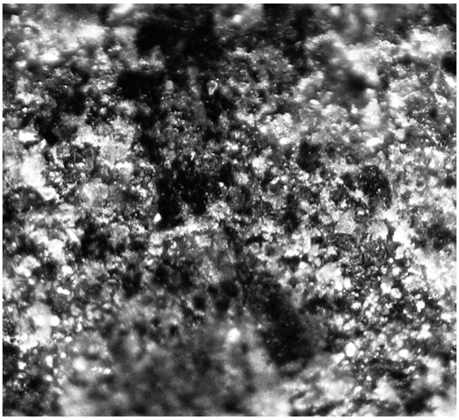


Photo. 72. POM for sample Sr 151 – enlargement x 200

Wood tar samples

Table 53

Infrared spectrophotometry results (FTIR) for wood tar samples: birch (Db), pine (Ds), oak (Dd), beech (Dbu), spruce (Dśw), alder (Do), hornbeam (Dg), ash (Dj) obtained in modern times according to past technology in a two-chamber production set

Sample code	**Db**	**Ds**	**Dd**	**Dbu**	**Dśw**	**Do**	**Dg**	**Dj**
Wavenumber [cm^{-1}]	3371	3351	3401	3402	3402	3401	3391	3401
	3069	3057			3017		3011	
		2958	2962	2961	2957	2958	2962	2961
	2927	2928	2930	2937	2923	2929	2936	2937
	2854	2869	2854	2856	2850	2853	2873	2849
	1734	1726		1738	1734	1737	1737	1738
	1709	1694	1709	1717	1709	1707	1698	1708
	1653			1653	1650	1650	1650	1650
	1640					1643		1643
	1608	1602	1613	1616	1604	1613	1614	1613
	1539		1562	1559	1547		1555	1556
	1515	1514	1511	1517	1514	1515		1515
		1498	1482	1482		1482	1482	1482
	1456	1461	1462	1464	1463	1463	1463	1462
	1377	1383	1360	1362	1384	1366	1360	1365
	1239	1270	1264	1241	1269	1276	1265	1275
	1178	1175			1123		1153	1152
	1107	1108	1107	1105		1106	1106	1108
	1034	1037		1035	1036	1034	1037	1037
	884	886						
		857	849			850		
		821	813	826	820	826	815	827
	757	755	767	765	755	763	756	763
	730		720	720			718	718
	668	668		668	668		665	
	546	564	516	554	541	590	530	548

Only the main peaks were shown in the above table.

Cycle of cultural systems of the Baltic drainage basin

Linear Pottery culture

Table 54a

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	**Sr 162**	**Sr 167**	**Sr 72**	**Sr 73**	**Sr 74**	**Sr 77**	**Sr 79**	**Sr 80**	**Sr 81**	**Sr 82**	**Sr 83**	**Sr 87**
Wavenumber [cm^{-1}]	3160	3370	3343	3324	3339	3208	3421	3207	3307	3193	3428	3195
	2914	2913	2920	2920	2923	2921	2924	2918	2919	2921	2922	2922
	2846	2853	2849	2848	2849	2851	2851	2851	2849	2852	2850	2851
							1734				1734	
						1703	1709		1700		1705	1703
				1631		1657			1653		1647	
							1617				1616	
	1579	1572	1576		1584	1582		1573	1576	1579	1558	1585
							1507					
	1454	1426	1449			1442	1457		1448		1457	1444
	1384		1394	1390	1382	1402	1375	1381	1395	1384	1387	1381
			1257		1233	1273	1228	1245	1251	1244	1234	1228
		1154	1154	1159	1153		1150	1165	1155	1153	1162	1155
	1062			1078	1075	1067	1072	1080	1081	1071	1093	1084
	1029	1029	1029	1017	1033	1033	1034	1033	1015	1030	1027	1036
					912		913	912		912		
	873	**873**	**879**		878	873	**881**				**884**	
		788	798	794	795	794	796	788	799	795	793	797
	763	775	779	777	777	777	778	778		779	775	778
								758	745			
		712	**726**	723			**729**	721	720	721	**721**	727
	664	695	694	694	694	693	694	695	695	682	695	695
					668		667	666	664	661	667	665
	601	603	602	597	598	603	603	601		604	596	606
	552	554	556		553	563	559	552				553
	467	468	473	469	470	469	464	469	473	465	468	465

Only the main peaks were shown in the above table.

Table 54b

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	**Sr 88-1**	**Sr 88-2**	**Sr 89**	**Sr 95**	**Sr 96**	**Sr 98**	**Sr 90**	**Sr 91**	**Sr 92**	**Sr 93**	**Sr 94**	**Sr 97**
Wavenumber [cm^{-1}]	3391	3428	3209	3428	3391	3196	3177	3214	3234	3162	3197	3351
					3065		3064					3063
	2927	2929	2919	2924	2923	2922	2915	2919	2921	2914	2918	2929
	2856	2854	2849	2815	2851	2853	2845	2850	2850	2846	2847	2844
		1726		1728	1733							
		1702		1709	1708							
										1653		
		1622			1616							
	1589		1573			1576	1558	1576	1582	1576	1576	1582
								1559		1559		
	1451	1455		1453	1456	1451	1436	1448		1456		
	1397	1387	1384	1377	1376	1381	1376	1387	1383	1374	1386	1386
			1223	1273	1229	1243	1262	1256		1241	1229	
	1162	1157	1156	1157	1155	1154	1178	1158	1157			
	1071	1085	1073	1076	1077	1078	1101	1083	1078	1067	1072	1078
	1033	1021	1026	1029	1036	1034	1034	1025	1028	1039	1023	1029
	912			911	912	911	914	913	914			911
					883	876	**880**	**880**	**878**	**880**	874	**878**
							836					
	799	798	799		796	795		799	794	787	795	793
	777	777	745	779	778	778	777		777	775		776
							754	745			746	
		726		726	**727**		**735**	**720**	**723**	**728**		**723**
	695	694	694	694	695	693	694	694	695	683	685	694
					668	668	664	661	664	668	662	
	644	645		648	646	644		649		648		644
	600		600	603	601	602	604	598	604	602	596	601
	551	565	550			551	556			557	548	
	468	467	474	469	465	468	469	473	470	465	472	467

Only the main peaks were shown in the above table.

Late Band Pottery culture

Table 55

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Late Band Pottery culture)*

Sample code	**Sr 174**	**Sr 99**	**Sr 100**
Wavenumber [cm^{-1}]	3414	3336	3335
	3065		
	2924	2918	2926
	2851	2852	2548
	1734		
	1635	1650	1653
	1617		
		1563	1576
	1457	1451	1437
	1376	1386	1387
	1243	1246	
	1174	1162	1167
	1106		
		1068	1059
	1032	1028	1035
	881	837	863
			797
			777
	720	723	
	692	687	693
		602	606
	539	545	
	468	472	469

Only the main peaks were shown in the above.table

Funnel Beaker culture

Table 56a

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 140**	**Sr 16**	**Sr 128**	**Sr 41**	**Sr 40**	**Sr 9**	**Sr 66**	**Sr 137**	**Sr 33**	**Sr 34**	**Sr 35**	**Sr 327**
Wavenumber [cm^{-1}]	3392	3367	3447	3345	3392	3368	3432	3421	3419	3445	3447	3402
	3063	3065	3067	3068	3060	3067	3062	3064	3064	3068	3063	3070
	2924	2925	2927	2923	2924	2926	2924	2926	2927	2925	2926	2926
	2852	2852	2852	2851	2852	2851	2852	2852	2853	2854	2853	2853
	1734	1734	1730	1733	1724	1735	1733	1733	1734	1733	1734	1732
	1717	1710	1707	1707	1707	1707	1708	1713	1706	1711	1709	1711
	1653	1648	1635	1653	1653	1655	1652	1653		1639	1653	1640
	1616	1623	1621	1604	1604	1602	1603	1603	1614	1593	1603	1602
	1507		1507					1506			1506	
	1457	1456	1457	1456	1456	1453	1456	1457	1457	1456	1457	1455
	1375	1387	1386	1376	1377	1374	1376	1376	1376	1376	1375	1377
	1242	1237	1261	1251	1249		1252	1235	1245	1245	1243	1246
	1174	1168	1167	1171	1173	1164	1166	1163	1176	1175	1175	1175
	1106	1085	1075	1103	1102	1086	1102	1103	1096	1096	1104	1107
	1033	1035	1039	1032	1032	1039	1030	1045	1032	1031	1030	1035
	882	**876**	**881**	**884**	**884**	**880**	**883**	**881**	**884**	**883**	**884**	**882**
	806	797	800	820	810	798	798	803	804	796	799	812
		778	781		780	765	778			777		
	730	**727**	**730**	**730**	**727**	**729**	**730**	**727**	**730**	**729**	**730**	**729**
	693	693	693		692	694	695	692	697	695	691	661
	662		662	668	658	662	667	668	661	664	668	
	596	606	596		597	602	604	591	602	600		
	515	525	516	512	514		518	514		512	526	547
	473	471	468	470	468	472	473	454	469	467	468	474

Only the main peaks were shown in the above table.

Table 56b

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 212**	**Sr 215**	**Sr 211**	**Sr 213**	**Sr 214**	**Sr 325-1**	**Sr 325-2**	**Sr 325-3**	**Sr 175w**	**Sr 175z**	**Sr 193**	**Sr 1**
Wavenumber [cm^{-1}]	3391	3344	3302	3374	3233	3402	3416	3428	3402	3441	3323	3431
	3065		3063		3067	3065	3068	3069	3062	3065	3061	
	2924	2908	2924	2925	2924	2924	2925	2926	2926	2926	2926	2919
	2852	2840	2852	2851	2852	2852	2852	2852	2854	2853	2853	2844
	1732		1732		1732	1733	1732	1732	1729	1733	1732	
	1709		1710		1711	1709	1710	1711	1708	1712	1709	
	1657		1631		1640		1640	1640		1641	1642	1653
	1620			1620	1620	1639	1613		1603	1608		
		1581	1598									
	1556		1554		1551	1552		1552	1558			
	1514				1535	1514	1514	1514		1506	1514	
	1453	1477	1454	1472	1461	1461	1461	1462	1457	1455	1462	
	1384	1396	1376	1402	1384	1377	1376	1376	1378	1376	1384	1384
	1242		1246	1211	1236	1236	1243	1243	1243	1247	1234	
	1164		1174	1123	1170	1163	1174	1175	1174	1175	1163	1169
	1084	1068	1107	1076	1083	1103	1103	1104	1105	1106	1097	1072
	1036	1034	1034	1028	1031	1030	1031	1031	1033	1031	1031	1026
	882	**874**	**882**	**877**	**881**	**882**	**883**	**884**	**884**	**883**	**883**	
	798	794			800		798	798	800	817	802	798
	776	777	786		781	780	780	779	779	778	779	778
	728	**713**	**727**		**731**	**724**	**729**	**728**	**729**	**729**	**727**	
	691	693	695		694	694	694	700	692	698	693	695
	668	665	668	668	668	664	663	664		661	663	667
	602	603					602	599		593		604
	534	558	538	556		539	535	546	534	545	522	
	485	470	476	436	466	469	470	470	468	479	478	473

Only the main peaks were shown in the above table.

Table 56c

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 42**	**Sr 43**	**Sr 55**	**Sr 56**	**Sr 28**	**Sr 30**	**Sr 31**	**Sr 252**	**Sr 198w**	**Sr 198z**	**Sr 263**	**Sr 264**
Wavenumber [cm^{-1}]	3444	3430	3334	3325	3307	3409	3297	3386	3369	3282	3401	3403
	3069	3061	3065	3061	3064	3063	3057	3067	3064	3060	3065	3063
	2927	2926	2925	2925	2924	2925	2935	2925	2924	2923	2925	2926
	2853	2854	2852	2853	2852	2853	2838	2853	2851	2852	2853	2853
	1732	1732	1731	1732	1734	1730		1734	1731	1731	1733	1733
	1709	1709	1711	1710	1707	1708	1700	1709	1710	1709	1711	1710
	1641	1640	1633	1642	1653	1650	1643	1653	1658	1640	1637	1637
	1605	1613	1604	1605	1636	1607	1609	1616	1631		1596	1608
				1573	1576		1576		1605	1605		
	1558	1552	1552	1551	1559		1558			1556		1558
		1505	1514		1516	1514			1554	1536	1511	
	1456	1455	1454	1461	1456	1454	1457	1456	1454	1461	1456	1456
	1385	1376	1377	1377	1376	1377	1387	1375	1376	1377	1376	1376
	1250	1248	1249	1237	1250	1245	1285	1246	1254	1228	1244	1245
	1171	1175	1173	1174	1170	1175		1174	1174	1165	1174	1175
	1102	1107	1087		1102	1109	1075	1104	1102	1105	1103	1106
	1033	1034		1034	1034	1030	1038	1031	1043	1028	1032	1032
	884	**884**	**880**	**884**	**884**	**884**		**880**	**878**	**885**	**885**	**884**
	798	818		821	809	792	786	800			793	799
		780	782				768		781	782	777	776
	731	**730**	**730**	**730**	**730**	**730**		**729**	**728**	**726**	**729**	**730**
	694	695	695	694	694		685		693	695	694	695
	668	662	662	664	668	665	660	668	661	660		
	605				605				578	551	604	596
	537	533	516	522		539	527	525		513	520	520
	476	469	463	474	476	468	472	472	466	476	467	472

Only the main peaks were shown in the above table.

Table 56d

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 32-1**	**Sr 32-2**	**Sr 328**	**Sr 329w**	**Sr 329z**	**Sr 46**	**Sr 321**	**Sr 464**	**Sr 465**	**Sr 466**	**Sr 467**	**Sr 468**
Wavenumber [cm^{-1}]	3420	3429	3402	3422	3423	3403	3424	3152	3340	3201	3161	3340
	3061	3062	3061	3062	3063	3061		3056	3069	3067		3062
	2926	2926	2924	2926	2926	2925	2925	2919	2926	2925	2920	2926
	2854	2854	2852	2853	2854	2854	2855	2849	2853	2852	2852	2853
	1734	1732	1731	1733	1732	1731			1733	1732		1734
	1706	1710	1709	1710	1710	1709		1696	1710	1709	1692	1710
	1637		1639	1639	1640	1632			1653			1652
						1619	1626		1640	1639		1624
		1608	1602	1608	1608			1576	1616	1602	1599	
	1559	1552	1556			1555						
			1536						1558		1551	1558
	1457	1455	1461	1456	1455	1455	1460	1444	1457	1462	1445	1457
	1376	1376	1376	1377	1376	1376	1396	1371	1376	1377	1365	1376
	1244	1245	1239	1248	1244	1260		1243	1244			1245
	1163	1176	1164	1175	1175	1173		1161	1174	1166	1155	1176
	1105	1104	1085	1108	1107	1103	1085	1082	1105	1081	1080	1105
	1030	1036	1031	1035	1036	1039	1032	1039	1034	1039	1036	1035
	884	**884**	**884**	**883**	**884**	**882**		**876**	**883**	**882**	**874**	**883**
	797		800	812	811		798	797	797	796	796	794
	775	780	777		780	780	778	778	778	778	778	779
	729	**729**	**729**	**729**	**730**	**730**			**730**	**730**		**729**
	691	692	694		693	693		694	694	694	694	694
	665	664	664	664	664	665	671		667	665	664	668
	541	544	539	546	546	577					601	
		507		505			514	538	541		526	538
	469	472	473	469	473	467	472	468	463	459	468	463

Only the main peaks were shown in the above table.

Table 56e

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	Sr 469-1	Sr 469-2	Sr 177-1	Sr 177-2	Sr 177-3w	Sr 177-3z	Sr 37	Sr 192	Sr 57	Sr 189	Sr 249	Sr 253
Wavenumber $[cm^{-1}]$	3351	3392	3446	3368	3346	3413	3400	3289	3306	3306	3444	3404
	3068	3063	3067	3064	3069		3063		3059	3063		3064
	2926	2925	2926	2926	2924	2927	2925	2924	2925	2924		2925
	2853	2853	2853	2853	2854	2851	2853	2851	2853	2852		2852
	1732	1733	1733		1733		1728	1737	1732	1732		1734
	1710	1706	1710	1700	1717		1703	1709	1709	1710		1707
		1654	1638	1652	1646	1645	1656	1659				1653
	1633	1635	1616		1602	1617		1640	1638	1641	1641	1616
	1605	1616		1576	1576		1597	1591	1605	1605	1607	1576
			1558	1559	1533	1558	1573					1558
		1558			1506		1556	1547	1551	1552		
	1456	1457	1457	1457	1457	1447	1453	1461	1454	1461	1479	1456
	1377	1377	1380	1375	1377	1395	1384		1377	1376	1369	1376
	1247	1242	1243	1238	1248		1233	1221	1233	1234	1224	1229
	1172	1166	1174	1161	1145	1157	1159		1172	1163	1172	1152
	1105	1084	1106	1094	1087	1085	1087	1085	1104	1105	1097	1099
	1036	1041	1032	1032	1033	1032	1036	1022	1027	1028	1015	1031
	883	**882**	**883**	**885**	**882**		**883**	**873**	**881**	**884**	**873**	**885**
	798	798		798	799	798	798	800			791	794
	779	779	775	773	777	778	780		782			777
	729	**730**	**730**	**724**	**726**	**726**	**728**	**714**	**730**	**723**		**729**
	695	694	691	692		694	694	695	692	692	693	694
	645	668		671	668		664	664	661	660	668	668
			598			601	604		603		555	601
	545	531	546	534	529	527	564	557	551	554		526
	463	468	471	473	474	468	468	479	469	474	461	471

Only the main peaks were shown in the above table.

Table 56f

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 254**	**Sr 3w**	**Sr 3z**	**Sr 36**	**Sr 12**	**Sr 5**	**Sr 284**	**Sr 324**	**Sr 8**	**Sr 219**	**Sr 13**	**Sr 23**
Wavenumber [cm^{-1}]	3361	3408	3445	3422	3437	3418	3417	3417	3447	3174	3426	3416
	3067	3064	3065	3067	3067	3063				3063		
	2925	2925	2927	2926	2925	2926	2925	2925	2927	2925	2926	2925
	2852	2854	2854	2853	2853	2851	2854	2855	2857	2853	2854	2854
	1733	1734	1734	1733	1732	1733			1730	1730		1727
	1707	1709	1700	1710	1709	1700	1709		1700	1707	1700	1709
	1647	1639	1654	1641	1656	1653	1657			1653	1657	1658
	1596		1639	1616	1626	1620	1639	1621	1617		1613	1640
	1576	1605					1571			1600		
	1558	1552	1552	1556		1556	1552			1558	1548	1552
	1456	1454	1457	1456	1455	1457	1451	1395	1457	1457	1461	1461
	1376	1375	1384	1376	1377	1374	1376	1383	1383	1379	1383	1377
	1235			1244	1234				1239	1253		1231
	1166			1175	1159	1175	1158		1138	1154	1158	1157
	1087			1105	1092		1071	1079		1084	1079	1075
	1032	1035	1034	1035	1035	1033	1036	1030	1048	1043	1030	1030
	884	**880**	**880**	**883**	**883**	**881**	**883**	**883**		**884**	**872**	
	794	798	795	797	798		798	798	798	800		797
	777	777		777	778	776	779	777		777	777	777
	729	**729**	**729**	**729**	**728**	**731**	**728**	**728**	**728**	**728**	**726**	**727**
	694	691		692	695	691	695	695		694	695	695
	668		668	668	661	660		661	664	668	665	
		538	542	547	534		533	552			529	533
	514					521	517	513	510	507		
	466	469	471	468	468	470	468	469	464	473	469	470

Only the main peaks were shown in the above table.

Table 56g

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Funnel Beaker culture)*

Sample code	**Sr 24**	**Sr 58w**	**Sr 58z**	**Sr 59**	**Sr 68w**	**Sr 68z**	**Sr 14**	**Sr 25**	**Sr 26**	**Sr 243**	**Sr 67w**	**Sr 67z**
Wavenumber [cm^{-1}]	3384	3435	3445	3434	3404	3337	3251	3443	3430	3420	3325	3335
	3065	3069	3063	3058			3056	3070	3068	3070		
							2953				2944	
	2924	2927	2927	2926	2926	2922	2924	2929	2927	2926		2922
	2851	2854	2853	2853	2855	2851	2854	2854	2854	2853	2839	2848
	1733	1732	1733	1732			1734	1727	1737	1733		
	1709	1709	1709	1709	1700		1700	1709	1709	1711		
					1653		1653		1666			
	1638	1640	1639	1639		1638		1643		1635		
	1603	1614	1605	1604				1602	1597	1616		
		1582	1580	1582	1576	1585					1581	1585
					1559		1532	1555		1558		
	1456	1454	1455	1455	1457	1442	1457	1461	1461	1456		
	1375	1384	1385	1384	1387	1376	1377	1376	1377	1376	1409	1387
	1247	1250	1244	1250	1248	1263	1209	1229	1227	1247		
	1171	1171	1171	1171	1162	1169		1158	1144	1176	1126	1162
	1082	1103	1103	1103	1086			1072	1078	1106		
	1029	1033	1033	1032	1030	1029	1027	1036	1030	1033	1031	1029
	883	**884**	**884**	**884**	**873**	**877**		**884**	**884**	**881**	**864**	**857**
		809	792	810	794		797	799	799	810	794	
	781	782	782	781	781	778	763	776	780	770	757	
	725	**730**	**729**	**729**			**729**	**728**	**728**	**729**		
	691	694	693	692	694	692		695	693	697	692	693
	660		668	668	668	665	664	663	664		667	
	547	547	541	539	526	545	520	534	529	544	553	542
	468	460	475	475	472	468	483	478	473	472	475	471

Only the main peaks were shown in the above table.

Globular Amphora culture

Table 57

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Sample code	**Sr 517**	**Sr 18**	**Sr 19**	**Sr 141**
Wavenumber [cm^{-1}]	3420	3338	3417	3358
	3069			
	2929	2925	2926	2923
	2850	2850	2855	2852
	1730			
	1710	1708		1708
	1651			
			1635	
	1602			1596
		1584		
			1507	1506
			1491	
	1450		1436	1455
	1380	1390	1383	1376
	1250	1241		1260
	1170	1162	1122	1173
		1087	1084	1103
	1030	1029	1030	1036
	880		837	**885**
	797		798	798
	775	778	779	777
	730	725		**731**
	695	693	702	695
	668		664	665
	603	606	601	
	460	468	469	470

Only the main peaks were shown in the above table.

Mierzanowice culture

Table 58

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Sample code	**Sr 229**	**Sr 166**	**Sr 227**	**Sr 326**
Wavenumber [cm^{-1}]	3340	3340	3341	3408
	3193			
				3070
		2926		2926
		2853		2853
	2349		2352	
	2289		2285	
		1732		1732
		1710		1711
		1642		1640
	1597	1600	1583	1608
				1513
	1453	1454		1455
	1374	1377	1382	1376
	1280	1250		1250
	1175	1176		1175
	1089	1106	1087	1107
	1032	1029	1031	1034
	912			
	875	**884**	880	**883**
	799		798	799
	779		778	777
		730		**729**
	695	692	695	694
			601	600
	516	523	532	534
	471	478	470	469

Only the main peaks were shown in the above table.

Trzciniec Cultural circle

Table 59a

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Sample code	Sr 268	Sr 271	Sr 272-1	Sr 272-2	Sr 459	Sr 460	Sr 461	Sr 462	Sr 463	Sr 449
Wavenumber [cm^{-1}]	3348	3354	3447	3373	3356	3353	3393	3338	3394	3210
					3064		3068	3068	3069	3064
	2913	2952	2914	2936	2925	2929	2927	2925	2925	2923
	2851	2826	2819	2825	2853	2854	2853	2852	2853	2852
					1734		1733	1734	1733	1733
					1707		1710	1711	1711	1706
	1636	1653	1650	1653	1653		1641	1645	1640	1653
	1607	1605	1610	1602	1616	1589	1603	1593	1604	1595
	1580	1576	1577							
		1559		1557	1559					
	1415	1457	1421	1438	1457	1441	1457	1456	1456	1456
	1393	1395	1394	1388	1377	1387	1377	1388	1376	1376
	1228				1254	1269	1245	1249	1244	1235
	1165	1172	1166	1162	1173	1172	1174	1167	1174	1171
	1099	1100	1099	1075	1106	1111	1102	1098	1106	1105
	1038	1046	1049	1030	1029	1036	1033	1029	1033	1035
	871				**886**	**875**	**883**	**873**	**882**	**886**
	796	799	798		820		797	796	804	798
	776	776	775	778	777	788	779	778	778	779
					730	**721**	**730**	**730**	**730**	**729**
	693	694	691	694			694	694	694	695
	666	668	668	667	668	670	667			668
	648		652		634	630	637	636	636	636
			582		575	586	578	598		
		536		542	537	539			537	538
	469	475	461	474	472	472	468	467	469	469

Only the main peaks were shown in the above table.

Table 59b

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Sample code	**Sr 450**	**Sr 447**	**Sr 448**	**Sr 451**	**Sr 452**	**Sr 453**	**Sr 454**	**Sr 455**	**Sr 456**	**Sr 457**
Wavenumber [cm^{-1}]	3187	3201	3194	3354	3340	3422	3447	3313	3229	3193
				3069	3068	3065		3069	3064	3066
	2930	2952	2925	2926	2927	2926	2958	2927	2920	2924
	2869	2865	2855	2854	2853	2853	2864	2853	2849	2852
				1733	1734	1732		1734		1733
	1700			1711	1717	1709	1700	1717		1708
			1693						1698	
		1653		1653	1653	1641	1653	1653		1653
	1585	1616	1590	1603	1597	1611		1600	1578	1596
		1559			1559		1559	1559	1544	
	1429	1457	1418	1456	1457	1455	1457	1457	1454	1456
	1388	1374	1384	1384	1376	1377	1382	1376	1378	1376
	1253	1260	1286	1246	1243	1243		1249	1254	1244
		1166	1155	1162	1173	1173	1165	1174	1165	1172
	1100	1084	1083	1086	1105	1106	1090	1105	1082	1106
	1032	1035	1035	1047	1035	1034	1042	1033	1034	1035
	882			**881**	**882**	**883**		**885**	**875**	**883**
	794	797	798	799	798	799	798	813	796	804
	777	776	767	778			778	782	778	779
	725			**729**	**729**	**730**		**728**	**722**	**730**
	694			694	694	695	694	695	694	693
	664	668	670		668	667	668	668	663	668
	605			604			603		607	602
	557		543		545					
	470	477	476	473	467	471	476	467	466	467

Only the main peaks were shown in the above table.

Table 59c

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Cultural circle)*

Sample code	**Sr 220**	**Sr 223**	**Sr 224**	**Sr 258**	**Sr 225**	**Sr 257**	**Sr 439w**	**Sr 439z**	**Sr 440**	**Sr 228**
Wavenumber [cm^{-1}]	3430	3156	3343	3338	3396	3369	3406	3381	3397	3331
						3070	3070	3070	3071	3068
	2937	2945	2929	2943	2927	2924	2926	2926	2926	2927
	2868	2874		2882						
			2848		2856	2852	2854	2854	2854	2853
							1733	1732	1732	1732
						1703	1709	1708	1709	1710
	1640	1656	1657	1658	1632	1657	1641	1639	1640	1640
				1604			1609	1604	1606	1601
		1567		1579		1583				
	1429	1426	1416	1414	1426	1453	1456	1455	1455	1455
	1386	1384	1376	1392		1377	1384	1384	1383	1376
					1275	1244	1252	1240	1252	1244
	1158	1144	1158	1163	1157	1169	1176	1173	1175	1176
				1127			1107			1103
		1086		1097		1084	1084	1088	1084	
	1034	1017	1032	1033	1037	1035	1044	1047	1045	1032
	874	874	874	872	876	**877**	**882**	**881**	**881**	**881**
	798	794	797	800	798	800	813	800	800	
	779	775	778	782	779				778	774
						731	**729**	**730**	**730**	**730**
	694	695	695	693	695			695	695	693
	665	664		668	665	663	668	668		
		603				600		604		604
		584					580			
						564		564		563
				644			545	546		
	529	516	528	512	514	521		511	515	
	472	464	472	461	473	477	467	471	469	469

Only the main peaks were shown in the above table.

Tumulus culture

Table 60

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Tumulus culture)*

Sample code	**Sr 171**	**Sr 172**
Wavenumber [cm^{-1}]		
	3395	3344
	2915	2921
	2843	2852
		1734
		1700
	1652	1653
	1610	1616
		1559
	1401	1419
		1376
		1261
	1157	1168
	1087	
	1045	1035
	994	
		876
	798	
	776	
	719	**723**
	688	695
	671	673
	571	567
	479	471

Only the main peaks were shown in the above table.

Lusatian culture

Table 61a

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Sr 441**	**Sr 443**	**Sr 444-1**	**Sr 444-2**	**Sr 71w**	**Sr 71z**	**Sr 256w**	**Sr 256z**	**Sr 267**	**Sr 270**
Wavenumber [cm^{-1}]	3316	3387	3365	3161	3447	3447	3337	3366	3327	3211
	3067				3070	3070				3063
	2927	2922	2919	2919	2925	2927	2922	2942	2942	2938
	2853	2851	2851	2850	2853	2854	2851	2838	2829	2831
	1732				1734	1734				
	1712		1709	1703	1718	1710	1701			1704
	1642	1653	1631		1653	1653			1652	
	1600	1616	1595	1589			1602	1604		
		1559			1559	1559	1579	1569	1559	1579
	1461	1457	1461	1451	1457	1457	1451	1417	1472	
	1376	1387	1343	1377	1375	1375	1380	1359	1394	1402
	1244	1263		1244	1247	1247	1261	1248		
	1173	1157	1168	1172	1171	1176	1166	1163	1164	
	1087	1089	1082			1107	1100	1098	1096	1096
	1046	1034	1036	1035	1038	1034	1031	1035	1026	1033
	982									
	880				**873**	**882**	873	873	873	
							813			
	798	798	796	799	796			792	792	798
		778	779	778						
	729				**730**	**730**				
		693	694	694				695	686	674
	665	668	665	664	668	667		665	668	658
		641					648	647	643	
								603		
	562			550	577	564	560	563		544
	510	512	520	509			519		511	
	461	472	460	455	462	458	462	468	461	459

Only the main peaks were shown in the above table.

Table 61b

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Sr 374w**	**Sr 374z**	**Sr 129w**	**Sr 129z**	**Sr 130**	**Sr 131**	**Sr 132w**	**Sr 132z**	**Sr 133w**	**Sr 133z**
Wavenumber [cm^{-1}]			3640	3624	3600	3300				
	3305	3292		3296			3300	3306	3300	3345
	3062	3063								
		2956		2950	2945					
	2926	2929	2922			2926	2925	2926	2927	
	2855	2868	2850		2850	2852	2852	2853	2854	
				2800						
	1734				1735	1737	1730		1733	1734
	1717		1709				1708	1709	1710	
		1700								
	1653			1665						
		1604	1599	1599	1599	1605	1599		1600	
	1559							1599		1599
		1496								
	1457	1458	1461			1462	1455	1454	1461	1457
	1375	1381		1394	1384	1384	1384		1384	1384
	1238	1246				1250	1250		1250	1250
	1166	1174				1172	1170		1150	
		1104			1100	1100	1100		1105	1093
	1041	1036	1030	1031	1037	1030	1036	1036	1030	1030
	881	**886**				**880**	**880**		**880**	843
	799	796	799	799	799			798		
		778	780	780	780			780		
		756								
	727					**722**	**730**		**720**	
	695	694						695		
	668	663								668
	532	528	533	528	522	510				
	471	492	490	485	480	485	480	480	480	

Only the main peaks were shown in the above table.

Cycle of cultural systems of the steppe and forest steppe in Eastern Europe

Tripolye culture

Table 62

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	**Sr 47**	**Sr 184**
Wavenumber [cm^{-1}]	3415	3338
	3065	3070
	2926	2921
	2853	2853
	1733	
	1710	
		1688
	1640	
	1614	1597
	1455	1440
	1376	1376
	1244	1238
	1176	1181
	1107	1104
	1032	1032
	983	
	883	**876**
		841
		811
	730	**745**
		711
		693
	668	668
	546	534
	463	469

Only the main peaks were shown in the above table.

Pre-Yamnaya culture

Table 63

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Pre-Yamnaya culture)*

Sample code	**Sr 38**	**Sr 39**
Wavenumber [cm^{-1}]	3392	3446
	3071	3068
	2926	2926
	2852	2853
	1734	1734
	1718	1718
	1653	
	1616	1617
	1559	
	1456	1457
	1376	1376
	1247	1247
	1176	1175
	1107	1107
	1031	1034
	981	
	884	**883**
		841
	817	811
	729	**729**
	547	545
	462	468

Only the main peaks were shown in the above table.

Catacomb culture

Table 64

Infrared spectrophotometry results of archaeological samples representing *the Cycle of culture systems of the steppe and forest steppe in Eastern Europe (Catacomb culture)*

Sample code	**Sr 51**	**Sr 52**	**Sr 53**	**Sr 54**
1	2	3	4	5
Wave-number [cm^{-1}]	3402	3402	3402	3408
	3069		3067	3062
	2924	2924	2923	2925

1	2	3	4	5
Wavenumber [cm^{-1}]	2851	2851	2851	2853
	1732	1733	1732	1733
	1712	1710	1709	1711
	1603	1619	1620	1605
	1463	1463	1463	1456
	1376	1376	1376	1377
	1249	1248	1254	1248
	1175	1174	1174	1175
	1104	1106	1106	1106
	1034	1043	1045	1031
		978	982	
	881	**882**	**881**	**884**
				819
	781	782	781	
	730	**729**	**728**	**730**
		601	597	
	571	564		548
	468	467	462	467

Only the main peaks were shown in the above table.

Cycle of cultural systems of the forest zone in Eastern Europe

Dnieper-Donets culture

Table 65

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (Dnieper-Donets culture)*

Sample code	**Sr 315w**	**Sr 315z**	**Sr 317**	**Sr 319**	**Sr 318**
1	2	3	4	5	6
Wavenumber [cm^{-1}]	3346	3392	3369	3390	3392
	2926	2930	2927	2928	2926
	2856	2857	2856	2855	2856
			1620		
	1602	1596	1608	1609	1609
	1447	1446	1461		
	1383	1382	1377	1382	1387
	1249	1242	1248	1251	1243

1	2	3	4	5	6
Wavenumber [cm^{-1}]		1161	1121		
	1084		1085	1078	1074
	1042	1036	1041	1045	1048
	914	926	916	913	913
	794	794	799	799	799
			777	775	781
			695		684
	673	673	672	672	672
	636	625			
	548		534	546	535
	467	475	473	473	473

Only the main peaks were shown in the above table.

Zedmar culture

Table 66

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (Zedmar culture)*

Sample code	**Sr 230**	**Sr 232w**	**Sr 232z**	**Sr 233**	**Sr 234**	**Sr 235**
1	2	3	4	5	6	7
Wavenumber [cm^{-1}]	3323	3191	3361	3184	3338	3206
	2925	2917	2922		2929	2923
				2906		
	2852	2848	2851	2846	2856	2852
					1700	
		1653	1652	1653	1653	
	1636	1635				1637
				1576		1595
		1559	1554		1559	
	1429	1436	1452	1447		1431
					1419	
	1399	1387	1376	1384		1384
				1237		1243
	1166	1130	1128	1150		1150
	1087	1077	1082	1093		1094
	1037	1033	1032	1031	1030	1031

1	2	3	4	5	6	7
Wavenumber [cm^{-1}]	875	873	874	873	875	873
	797	789	799	785	798	789
	779	776	777		779	
				756		758
	695	695	694	696	695	698
			668	664	646	656
	603	604	602	601	603	602
	559	558	552	559	555	558
	473	469	470	471	473	467

Only the main peaks were shown in the above table.

Comb culture

Table 67

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (Comb culture)*

Sample code	**Sr 231**
Wavenumber [cm^{-1}]	3199
	2921
	2850
	1700
	1653
	1617
	1436
	1400
	1384
	1138
	1088
	1035
	762
	672
	602
	559
	473

Only the main peaks were shown in the above table.

Neman culture

Table 68

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (Neman culture)*

Sample code	Sr 255-1	Sr 255-2	Sr 188	Sr 520	Sr 320	Sr 355	Sr 356	Sr 236	Sr 237	Sr 238
Wavenumber [cm^{-1}]	3329	3389	3399	3385	3392	3365	3323	3177	3188	3152
	2974									
	2929	2925	2924	2914	2932	2922	2925	2915	2916	2907
	2848	2856	2848	2853	2856	2851	2868	2834	2848	2840
	1710	1708								
						1700	1700			
		1693				1695		1693	1688	1689
						1653	1653			
			1620		1608			1614	1614	1653
	1582	1578		1583		1576				1576
		1463		1464	1449	1457	1437	1426	1426	1445
	1395		1401	1394			1399			1395
		1371	1384		1383	1375	1375	1354	1381	
	1265	1247		1268	1253			1286		1287
			1142	1169			1152	1150	1152	1145
	1090	1102	1117	1107	1078	1083	1090	1088	1089	1090
	1048	1036	1039	1033	1042	1035	1038	1017	1017	1025
					915					
	880		874		835				879	881
		800	798	796	800			818		798
	769	774		778					777	775
			740			759	753	748	748	
						721	721			
	668	668	670	694	672	694	695	660	695	662
	604		602	600		599	604	601	600	598
	585	582								
	475	461	479	466	468	465	472	491	491	488

Only the main peaks were shown in the above table.

Trzciniec Cultural circle – eastern branch

Table 69

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (Trzciniec Cultural circle – eastern branch)*

Sample code	**Sr 330**	**Sr 331**	**Sr 333**
Wavenumber [cm^{-1}]	3395	3376	3353
	2924	2925	2924
	2853	2864	2853
	1703	1709	1703
	1657	1657	
	1609	1597	1590
		1555	
	1453	1461	1460
	1377	1384	1377
	1231	1256	1245
	1164	1163	1172
	1084	1078	1054
	1041	1036	1048
	798	798	794
	779	778	775
	696	694	694
	664	664	662
	601		
	534	534	534
	475	479	480

Only the main peaks were shown in the above table.

North Belarus culture

Table 70

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the forest zone in Eastern Europe (North Belarus culture)*

Sample code	**Sr 221-1**	**Sr 221-2**	**Sr 221-3**	**Sr 221-4**	**Sr 221-5**	**Sr 221-6**	**Sr 221-7**	**Sr 332**	**Sr 334-1**	**Sr 334-2**	**Sr 334-3**
Wavenumber [cm^{-1}]	3166	3116	3190	3065	3051	3048	3325	3355	3371	3384	3349
	2923	2924	2922	2916	2916		2915	2926	2928	2926	2928
	2853	2848	2845	2845	2848	2876	2864	2867	2869	2856	2868
						2815					
	1703		1700				1691	1703	1709	1709	1709
	1657	1654	1653	1653		1653		1657		1657	1657
	1643	1635					1635			1632	1632
	1599	1599							1609		
				1576	1576	1576					
	1439	1431	1437	1457	1435	1436	1437	1460	1436	1461	1460
											1442
	1402	1378	1395	1384	1374	1383	1381	1383	1376	1383	1382
					1271	1221			1241		
		1161	1150			1139			1144		
	1084	1085	1095	1094	1085	1090	1076	1084	1102	1102	1096
									1060		
	1026	1034	1037	1032	1032	1032	1037	1036		1036	1036
					873	873					
	787						798	797	799		798
	769	774					778	774			
	745		755	757	747	755			745	745	
	694		695	697	688		695	697			
	668	668	668	668	668	668	668	672	672	672	664
	603	602	604		602	602		605	600	604	604
	556	555	559	558	557	558	551	557			563
	486	480	491	492	491	491	468	479	473	475	473

Only the main peaks were shown in the above table.

Cycle of cultural systems of the Carpathian Basin

Eastern Linear Pottery culture

Table 71

Infrared spectrophotometry results of archaeological samples representing *the Cycle of cultural systems of the Carpathian Basin (Eastern Linear Pottery culture)*

Sample code	**Sr 10**	**Sr 438**
Wavenumber [cm^{-1}]	3409	3402
	2926	2923
	2853	2853
	1734	
	1709	
		1653
	1608	
	1507	1507
	1457	1457
	1419	
	1375	1384
	1244	
	1122	1103
	1034	1027
		911
	883	
	799	795
		776
	727	
		691
	662	665
	603	596
	468	467

Bükk culture

Table 72

Infrared spectrophotometry results of archaeological samples representing *Cycle of cultural systems of the Carpathian Basin (Bükk culture)*

Sample code	**Sr 151**
Wavenumber [cm^{-1}]	3351
	2924
	2852
	1730
	1709
	1603
	1510
	1453
	1412
	1385
	1234
	1155
	1063
	1033
	879
	781
	725
	664
	596
	468

Only the main peaks were shown in the above.table

Birch tar sample

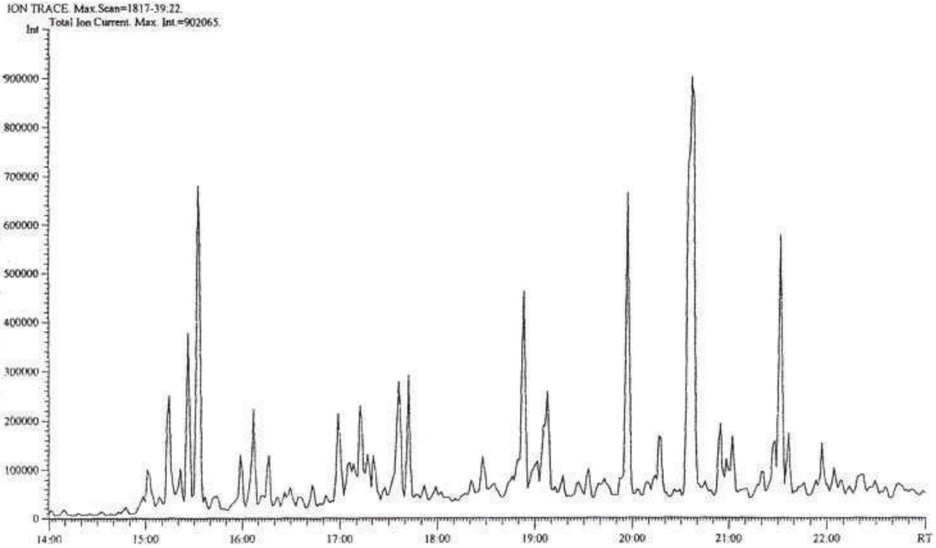


Fig. 22. Chromotogram GC of partially separated fraction extracted from a sample of birch tar obtained in modern times according to past technology in a two-chamber production set

Pine tar sample

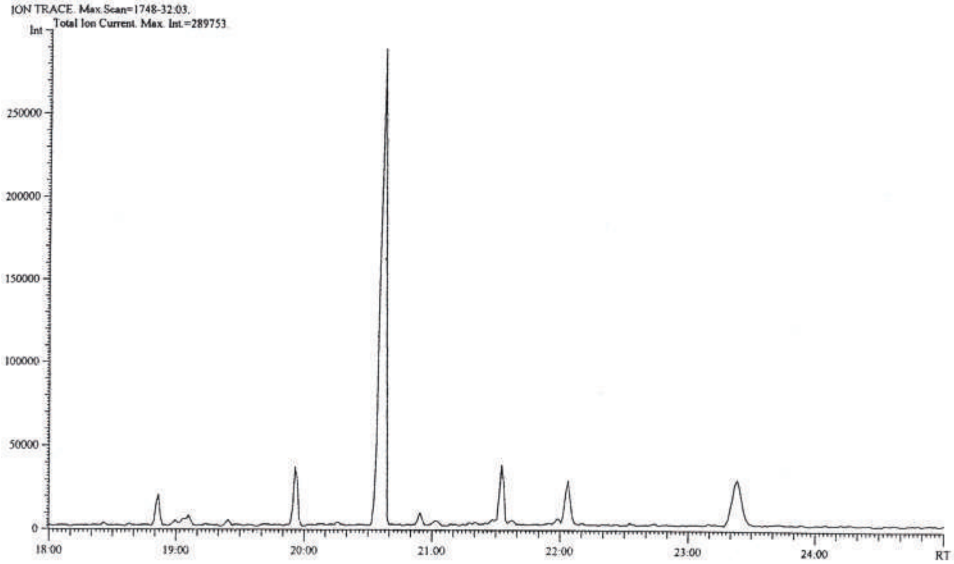


Fig. 23. Chromotogram GC of partially separated fraction extracted from a sample of pine tar obtained in modern times according to past technology in a two-chamber production set

Cycle of cultural systems of the Baltic drainage basin

Lusatian culture

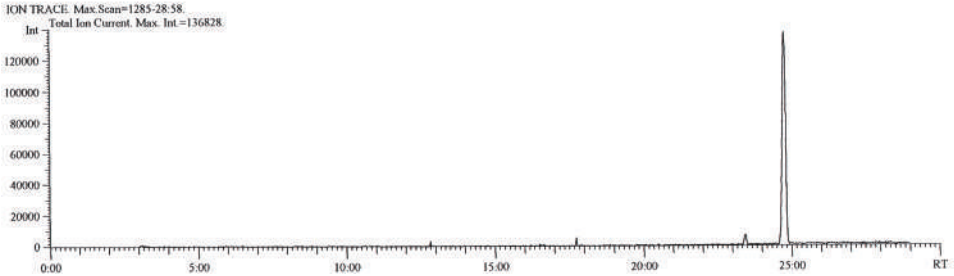


Fig. 24. Chromatogram GC of a partially separated fraction extracted from an archaeological preparation (Sr 71w) representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Birch tar sample

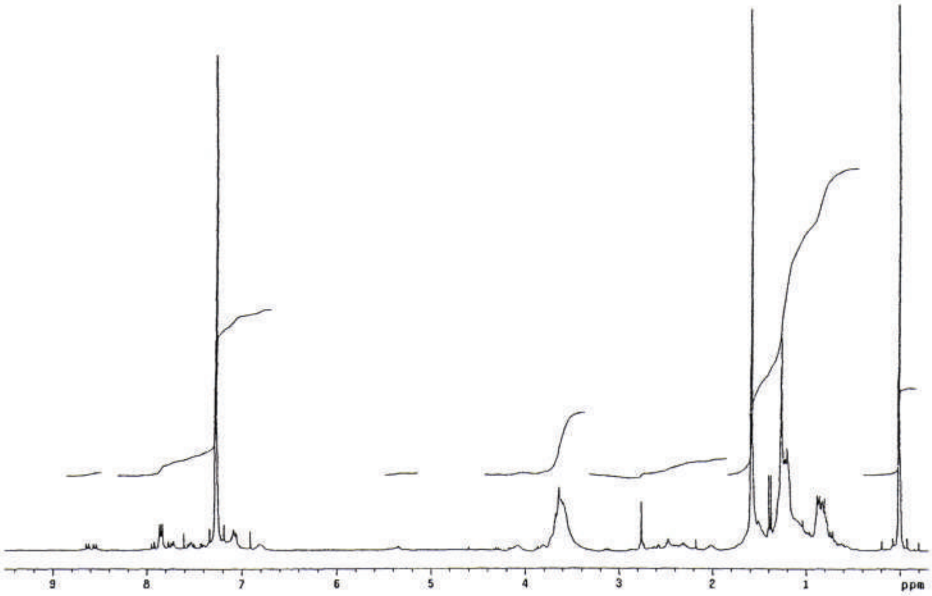


Fig. 25. The spectrum ^{1}H–NMR, partially separated fraction extracted from a sample of birch tar obtained in modern times according to past technology in a two-chamber production set

- group of signals in the range 6,8 – 8,8 δ (8H) corresponds to the structure of an aromatic compound
- occurrence of complicated signals at 3,6 δ is caused by the presence of double bonds
- presence of the CH_3–**CH**–CH_3 group is confirmed by the signal at 3,1 δ, J = 7 Hz
- the CH_3 groups joined to the aromatic rings emit a single signal at 2,8 δ
- the complex signal at 2,5 δ should be noted as bearing the structure of –CH2–CH2–Ar
- the confirmation of cyclohexane by a signal at 1,6 δ
- doublet 1,4 δ, J = 7 Hz is the result of interaction in the CH_3–**CH**–CH_3 group
- the complex group of peaks in the range 0,8 – 1,2 δ is a confirmation of numerous CH_3 groups.

Pine tar sample

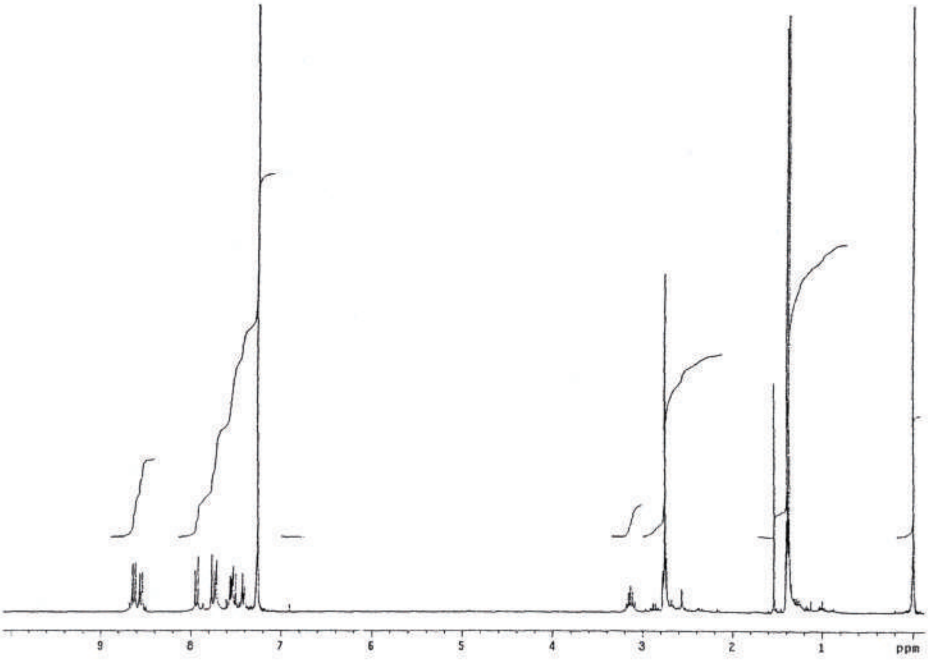


Fig. 26. The spectrum ^{1}H–NMR, partially separated fraction extracted from a sample of pine tar obtained in modern times according to past technology in a two-chamber production set

- group of signals in the range 6,8 – 8,8 δ (8H) corresponds to the structure of an aromatic compound
- seven signals at 3,1 δ, J = 7 Hz, (1H), correspond to the structure CH_3–C**H**–CH_3
- signal appearing at 2,8 δ, (3H), is the result of the presence of the group CH_3, joined to the aromatic ring
- the six-proton doublet 1,35 δ, J = 7 Hz corresponds to the group CH_3–C**H**–CH_3
- the number of peaks in the range 0,8 – 1,2 δ should be ascribed to the CH_3 groups.

Cycle of cultural systems of the Baltic drainage basin

Lusatian culture

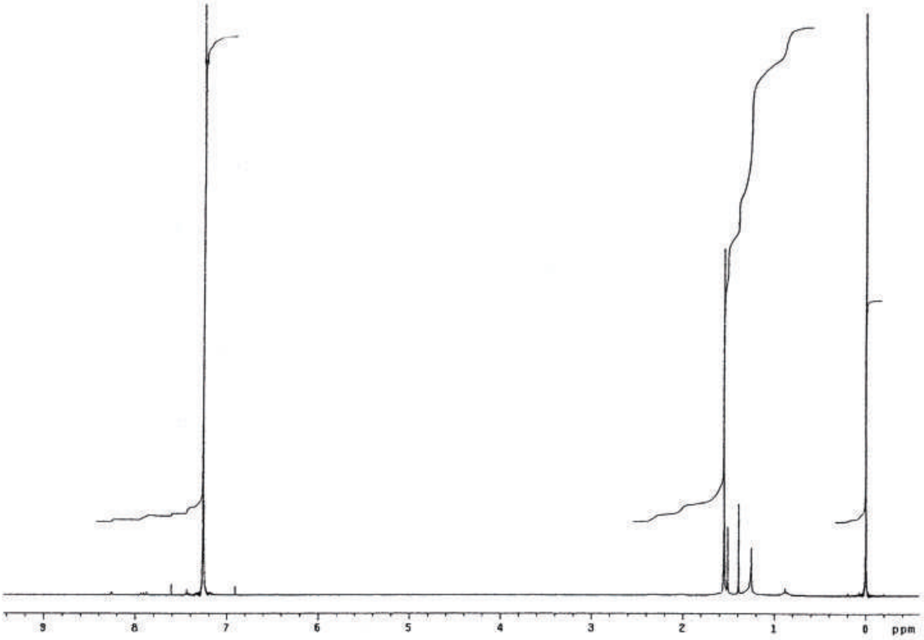


Fig. 27. The spectrum ^{1}H–NMR, partially separated fraction extracted from an archaeological preparation (Sr 71w) representing *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

- group of signals in the range 6,8 – 8,2 δ (6H) corresponds to the structure of an aromatic compound
- the structure of cyclohexane is confirmed by the presence of a strong peak at 1,6 δ
- in the range 1,2 – 1,6 δ, signals are found that correspond to the CH_3 groups joined to the aromatic ring, as in similar fashion to signals in the range 0,8 – 1,0 δ.

The ^{1}H–NMR spectrum clearly points therefore to the presence of aromatic compounds with an asymmetrically placed benzene ring, as in the particles of glyco-vanillic aldehide and betulin: at 7,4 – 8,3 δ and a multiplicity of signals, also continually measured compression (J_{orto} = 9,07 Hz, J_{meta} = 2,47 Hz i J_{para} = 0,55 Hz) correspond well to these structures.

Wood tar samples

Table 73

EPR spectrum characteristics of organic radical signals occurring in wood tar samples: birch (Db), pine (Ds), oak (Dd), beech (Dbu), spruce (Dśw), alder (Do), hornbeam (Dg), ash (Dj) obtained in modern times according to past technology in a two-chamber production set

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Birch tar (Db)	2,0030	0,65
Pine tar (Ds)	2,0030	0,69
Oak tar (Dd)	2,0031	0,59
Beech tar (Dbu)	2,0030	0,69
Spruce tar (Dśw)	2,0031	0,66
Alder tar (Do)	2,0030	0,66
Hornbeam tar (Dg)	2,0027	0,68
Ash tar (Dj)	2,0030	0,71

Cycle of cultural systems of the Baltic drainage basin

Linea Pottery culture

Table 74

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
1	2	3
Sr 162	2,0036	0,44
Sr 167	2,0035	0,44
Sr 72	2,0031	0,43
Sr 73	2,0030	0,41
Sr 74	2,0034	0,44
Sr 77	2,0039	0,54
Sr 79	2,0030	0,56
Sr 80	2,0033	0,44
Sr 81	2,0031	0,42
Sr 82	2,0034	0,5

1	2	3
Sr 83	2,0031	0,51
Sr 87	2,0029	0,38
Sr 88-1	2,0027	0,46
Sr 88-2	2,0029	0,47
Sr 89	2,0034	0,45
Sr 95	2,0029	0,5
Sr 96	2,0029	0,5
Sr 98	2,0035	0,5
Sr 90	2,0031	0,4
Sr 91	2,0032	0,46
Sr 92	2,0033	0,45
Sr 93	2,0027	0,59
Sr 94	2,0032	0,49
Sr 97	2,0029	0,57

Table 75

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Linear Pottery culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 162	2,0102	126,66
Sr 167	2,1268	90,16
Sr 72	2,0074	64,99
Sr 73	2,1823	83,45
Sr 74	2,1736	115,99
Sr 77	2,2460	86,60
Sr 79	2,3809	180,49
Sr 80	2,0557	72,69
Sr 81	2,0521	86,99
Sr 82	2,1061	112,94
Sr 83	1,8150	98,45
Sr 87	2,0758	76,93
Sr 88-1	2,1618	83,55
Sr 88-2	2,0104	27,06

1	2	3
Sr 89	2,2059	116,30
Sr 95	2,2046	124,11
Sr 96	2,0959	64,42
Sr 98	2,1417	108,90
Sr 90	2,3456	66,79
Sr 91	2,1587	84,62
Sr 92	2,0677	56,02
Sr 93	2,1134	65,78
Sr 94	2,1899	140,42
Sr 97	2,1274	53,84

Late Band Pottery culture

Table 76

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Late Band Pottery culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 174	2,0033	0,45
Sr 99	2,0030	0,44
Sr 100	2,0029	0,52

Table 77

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Late Band Pottery culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 174	2,0025	69,95
Sr 99	2,1643	54,39
Sr 100	2,2429	26,26
	1,9892	32,97

Funnel beaker culture

Table 78a

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 140	2,0027	0,49
Sr 16	2,0029	0,48
Sr 128	2,0029	0,46
Sr 41	2,0028	0,47
Sr 40	2,0030	0,46
Sr 9	2,0031	0,5
Sr 66	2,0025	0,56
Sr 137	2,0029	0,48
Sr 33	2,0030	0,46
Sr 34	2,0030	0,4
Sr 35	2,0031	0,51
Sr 327	2,0029	0,46
Sr 212	2,0030	0,49
Sr 215	2,0039	0,55
Sr 211	2,0029	0,53
Sr 213	2,0034	0,5
Sr 214	2,0030	0,48
Sr 325-1	2,0029	0,5
Sr 325-2	2,0030	0,46
Sr 325-3	2,0025	0,48
Sr 175w	2,0030	0,51
Sr 175z	2,0028	0,48
Sr 193	2,0030	0,47
Sr 1	2,0027	0,45
Sr 42	2,0029	0,45
Sr 43	2,0032	0,46
Sr 55	2,0026	0,46
Sr 56	2,0030	0,45
Sr 28	2,0028	0,54

1	2	3
Sr 30	2,0029	0,48
Sr 31	2,0030	0,43
Sr 252	2,0029	0,48

Table 78b

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 198w	2,0031	0,5
Sr 198z	2,0029	0,48
Sr 263	2,0028	0,48
Sr 264	2,0029	0,47
Sr 32-1	2,0030	0,49
Sr 32-2	2,0030	0,49
Sr 328	2,0030	0,48
Sr 329w	2,0030	0,5
Sr 329z	2,0029	0,46
Sr 46	2,0028	0,56
Sr 321	2,0022	0,92
Sr 464	2,0031	0,57
Sr 465	2,0030	0,56
Sr 466	2,0030	0,53
Sr 467	2,0030	0,59
Sr 468	2,0030	0,54
Sr 469-1	2,0033	0,61
Sr 469-2	2,0032	0,56
Sr 177-1	2,0033	0,5
Sr 177-2	2,0034	0,48
Sr 177-3w	2,0034	0,47
Sr 177-3z	2,0031	0,46
Sr 37	2,0030	0,49
Sr 192	2,0041	0,84
Sr 57	2,0028	0,48

1	2	3
Sr 189	2,0029	0,46
Sr 249	2,0018	1,59
Sr 253	2,0028	0,48
Sr 254	2,0029	0,48

Table 78c

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 3w	2,0031	0,46
Sr 3z	2,0030	0,47
Sr 36	2,0030	0,51
Sr 12	2,0023	0,46
Sr 5	2,0026	0,45
Sr 284	2,0024	0,54
Sr 324	2,0026	0,59
Sr 8	2,0022	0,52
Sr 219	2,0030	0,48
Sr 13	2,0023	0,53
Sr 23	2,0030	0,46
Sr 24	2,0033	0,51
Sr 58w	2,0029	0,46
Sr 58z	2,0029	0,47
Sr 59	2,0028	0,46
Sr 68w	2,0033	0,41
Sr 68z	2,0031	0,42
Sr 14	2,0024	0,5
Sr 25	2,0025	0,47
Sr 26	2,0027	0,46
Sr 243	2,0027	0,45
Sr 67w	2,0033	0,43
Sr 67z	2,0030	0,42

Table 79a

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 140	1,8952	56,16
Sr 16	1,9548	58,62
Sr 128	1,9701	59,5
Sr 41	1,9850	54,57
Sr 40	2,0544	43,62
Sr 9	2,0356	46,27
Sr 66	2,1917	96,90
Sr 137	2,1217	74,11
Sr 33	2,0439	51,63
Sr 34	2,0124	54,39
Sr 35	2,0367	45,51
Sr 327	2,0044	50,64
Sr 212	2,0653	47,57
Sr 215	2,3221	86,92
Sr 211	2,1456	93,84
Sr 213	1,9564	58,73
Sr 214	2,1484	44,88
Sr 325-1	2,0371	45,41
Sr 325-2	2,0601	46,4
Sr 325-3	2,1130	66,54
Sr 175w	2,1944	83,59
Sr 175z	2,0568	64,51
Sr 193	2,0840	80,02
Sr 1	2,1873	84,36
Sr 42	2,0433	49,34
Sr 43	2,0677	59,47
Sr 55	2,2187	99,00
Sr 56	2,0089	91,49
Sr 28	2,3211	167,33
Sr 30	2,3087	120,49
Sr 31	2,0059	109,34
Sr 252	2,1388	112,13

Table 79b

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 198w	2,0572	64,83
Sr 198z	2,0801	72,23
Sr 263	1,9182	118,17
Sr 264	2,0659	62,44
Sr 32-1	1,9405	45,48
Sr 32-2	1,9470	37,90
Sr 328	2,1918	36,42
Sr 329w	2,4847	84,38
Sr 329z	2,3413	53,1
Sr 46	2,2207	100,75
Sr 321	2,1541	92,41
Sr 464	2,2102	90,90
Sr 465	2,1987	113,04
Sr 466	2,1578	104,04
Sr 467	2,2072	98,53
Sr 468	2,2134	104,46
Sr 469-1	2,1079	79,15
Sr 469-2	2,1321	99,79
Sr 177-1	2,1131	63,09
Sr 177-2	2,0092	55,00
Sr 177-3w	2,2367	116,13
Sr 177-3z	2,3164	98,78
Sr 37	2,1425	92,21
Sr 192	1,9658	84,97
Sr 57	2,0049	94,03
Sr 189	2,0682	62,66
Sr 249	2,0723	50,13
Sr 253	2,1447	107,5
Sr 254	2,2045	130,7

Table 79c

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Funnel beaker culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 3w	2,0369	43,27
Sr 3z	2,0582	39,89
Sr 36	1,9518	68,80
Sr 12	2,1177	65,86
Sr 5	2,2431	68,35
Sr 284	2,1213	72,37
Sr 324	2,2281	87,37
Sr 8	2,3233	130,13
Sr 219	2,2392	105,9
Sr 13	2,2274	57,83
Sr 23	2,0899	58,65
Sr 24	2,0366	62,39
Sr 58w	2,1081	66,45
Sr 58z	2,0785	51,64
Sr 59	2,0487	64,52
Sr 68w	2,0501	42,26
Sr 68z	1,9394	62,72
Sr 14	2,1657	82,52
Sr 25	2,1306	57,34
Sr 26	2,2340	62,38
Sr 243	2,9804	50,2
Sr 67w	2,0256	56,27
Sr 67z	2,0372	58,74

Globular Amphora culture

Table 80

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 517	2,0029	0,49
Sr 18	2,0027	0,51
Sr 19	2,0025	0,72
Sr 141	2,0024	0,85

Table 81

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Globular Amphora culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 517	2,2582	66,29
Sr 18	2,1688	83,99
Sr 19	2,1493	75,40
Sr 141	2,1656	89,55

Mierzanowice culture

Table 82

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 229	2,0035	0,46
Sr 166	2,0029	0,47
Sr 227	2,0033	0,49
Sr 326	2,0031	0,46

Table 83

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Mierzanowice culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 229	2,2188	103,35
Sr 166	2,0734	86,45
Sr 227	2,3783	103,35
Sr 326	2,0384	68,71

Trzciniec Circle culture

Table 84

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Circle culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
1	2	3
Sr 268	2,0042	0,72
Sr 271	2,0040	0,64
Sr 272-1	2,0041	1,97
Sr 272-2	2,0048	1,57
Sr 459	2,0029	0,46
Sr 460	2,0039	0,6
Sr 461	2,0031	0,54
Sr 462	2,0031	0,53
Sr 463	2,0030	0,45
Sr 449	2,0030	0,57
Sr 450	2,0031	0,49
Sr 447	2,0031	0,55
Sr 448	2,0030	0,45
Sr 451	2,0031	0,47
Sr 452	2,0033	0,58
Sr 453	2,0031	0,53
Sr 454	2,0030	0,57
Sr 455	2,0033	0,59
Sr 456	2,0030	0,46
Sr 457	2,0030	0,58
Sr 220	2,0033	0,66

1	2	3
Sr 223	2,0032	0,67
Sr 224	2,0044	0,77
Sr 258	2,0032	0,48
Sr 225	2,0037	0,65
Sr 257	2,0030	0,49
Sr 439w	2,0031	0,57
Sr 439z	2,0030	0,58
Sr 440	2,0034	0,6
Sr 228	2,0031	0,46

Table 85

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Trzciniec Circle culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 268	2,2437	152,67
Sr 271	1,9803	91,65
Sr 272-1	2,2668	90,62
Sr 272-2	2,3618	64,27
Sr 459	2,2920	110,32
Sr 460	2,3061	115,91
Sr 461	2,3770	110,88
Sr 462	2,0926	57,41
Sr 463	2,1083	73,41
Sr 449	2,2590	114,21
Sr 450	2,3026	115,35
Sr 447	2,4111	117,72
Sr 448	2,3779	130,87
Sr 451	2,2188	85,38
Sr 452	2,3276	118,77
Sr 453	2,0054	53,73
Sr 454	2,1092	79,07
Sr 455	2,2655	105,24
Sr 456	2,0796	79,75

1	2	3
Sr 457	2,1751	101,53
Sr 220	2,3853	104,87
Sr 223	2,4516	100,17
Sr 224	2,4760	104,06
Sr 258	2,1444	116,16
Sr 225	2,3747	93,28
Sr 257	2,4648	102,34
Sr 439w	2,2728	108,77
Sr 439z	2,1218	69,07
Sr 440	2,2557	107,79
Sr 228	2,1	50,9

Tumulus culture

Table 86

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Tumulus culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 171	2,0029	0,61
Sr 172	2,0020	0,72

Table 87

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Tumulus culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 171	2,4918	89,07
Sr 172	2,2568	98,42

Lusatian culture

Table 88

EPR spectrum characteristics of organic radical signals occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 441	2,0030	0,49
Sr 443	2,0029	0,5

1	2	3
Sr 444-1	2,0030	0,55
Sr 444-2	2,0030	0,53
Sr 71w	2,0035	0,51
Sr 71z	2,0035	0,5
Sr 256w	2,0029	0,5
Sr 256z	2,0031	0,48
Sr 267	2,0024	0,42
Sr 270	2,0027	0,64
Sr 374w	2,0032	0,59
Sr 374z	2,0031	0,66
Sr 129w	2,0034	0,58
Sr 129z	2,0030	0,63
Sr 130	2,0029	0,54
Sr 131	2,0030	0,51
Sr 132w	2,0042	0,6
Sr 132z	2,0031	0,59
Sr 133w	2,0031	0,56
Sr 133z	2,0037	0,6

Table 89

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the Baltic drainage basin (Lusatian culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 441	2,3028	133,94
Sr 443	2,2685	98,27
Sr 444-1	2,6535	187,45
Sr 444-2	2,2694	122,76
Sr 71w	2,8605	52,92
Sr 71z	2,0479	71,78
Sr 256w	2,1786	123,72
Sr 256z	2,3347	132,79
Sr 267	2,1795	164,90
Sr 270	2,1669	82,04

1	2	3
Sr 374w	2,1649	60,58
Sr 374z	2,0345	20,54
Sr 129w	2,1480	74,88
Sr 129z	2,0350	39,44
Sr 130	2,0136	47,69
Sr 131	1,9842	57,47
Sr 132w	2,1662	77,10
Sr 132z	2,1512	75,02
Sr 133w	2,1231	68,51
Sr 133z	2,1254	67,84

Cycle of cultural systems of the steppe and forest steppe in Eastern Europe

Tripolye culture

Table 90

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 47	2,0035	0,43
Sr 184	2,0030	0,53

Table 91

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 47	1,9889	51,90
Sr 184	2,0158	57,63

Pre-Yamnaya culture

Table 92

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Pre-Yamnaya culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 38	2,0031	0,42
Sr 39	2,0033	0,42

Table 93

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Pre-Yamnaya culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 38	1,9429	55,76
Sr 39	1,9097	45,59

Catacomb culture

Table 94

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 51	2,0030	0,48
Sr 52	2,0031	0,42
Sr 53	2,0030	0,46
Sr 54	2,0029	0,47

Table 95

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of cultural systems of the steppe and forest steppe in Eastern Europe (Tripolye culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 51	2,2038	142,89
Sr 52	1,8587	85,52
Sr 53	1,8485	87,00
Sr 54	1,9505	53,80

Dnieper-Donets culture

Table 96

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Dnieper-Donets culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
1	2	3
Sr 315w	2,0032	0,56
Sr 315z	2,0030	0,52

1	2	3
Sr 317	2,0027	0,47
Sr 319	2,0027	0,38
Sr 318	2,0027	0,49

Table 97

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Dnieper-Donets culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 315w	2,1360	149,30
Sr 315z	2,2173	136,97
Sr 317	2,2364	117,12
Sr 319	2,2360	111,10
Sr 318	2,2108	99,35

Zedmar culture

Table 98

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe Zedmar culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 230	2,0033	0,55
Sr 232w	2,0033	0,52
Sr 232z	2,0031	0,49
Sr 233	2,0032	0,52
Sr 234	2,0033	0,44
Sr 235	2,0031	0,53

Table 99

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Zedmar culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
1	2	3
Sr 230	2,0013	63,06
Sr 232w	2,0127	57,88
Sr 232z	2,1285	76,92
Sr 233	1,9068	79,54

1	2	3
Sr 234	1,9193	80,76
Sr 235	1,9587	87,42

Comb culture

Table 100

EPR spectrum characteristics of organic radicals occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Comb culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 231	2,0031	0,51

Table 101

Spectrum characteristics of EPR mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe Comb culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 231	2,2515	30,15

Neman culture

Table 102

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Neman culture)*

Sample code	**Spectroscopic coefficient g of separation**	**Extent of gradient [mT]**
Sr 255-1	2,0031	0,67
Sr 255-2	2,0031	0,62
Sr 188	2,0031	0,49
Sr 520	2,0025	0,82
Sr 320	2,0028	0,5
Sr 356	2,0030	0,53
Sr 355	2,0027	0,48
Sr 236	2,0032	0,51
Sr 237	2,0032	0,53
Sr 238	2,0032	0,51

Table 103

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Neman culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 255-1	2,1279	74,33
Sr 255-2	2,1981	90,72
Sr 188	2,0587	46,48
Sr 520	2,2630	108,95
Sr 320	2,1476	96,37
Sr 356	2,2592	83,46
Sr 355	2,1355	64,29
Sr 236	1,9936	55,71
Sr 237	2,1409	100,38
Sr 238	2,3481	54,64

Trzciniec Circle culture – eastern branch

Table 104

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Trzciniec Circle culture – eastern branch)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 330	2,0030	0,46
Sr 331	2,0032	0,48
Sr 333	2,0031	0,48

Table 105

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (Trzciniec Circle culture – eastern branch)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 330	2,4892	76,10
Sr 331	2,0413	36,52
Sr 333	2,5624	103,34
	1,9903	27,44

North Belarus culture

Table 106

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (North Belarus culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 221-1	2,0041	0,51
Sr 221-2	2,0033	0,54
Sr 221-3	2,0036	0,57
Sr 221-4	2,0034	0,53
Sr 221-5	2,0033	0,52
Sr 221-6	2,0031	0,48
Sr 221-7	2,0037	0,53
Sr 332	2,0033	0,55
Sr 334-1	2,0031	0,53
Sr 334-2	2,0032	0,58
Sr 334-3	2,0033	0,58

Table 107

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of forest zone culture systems in Eastern Europe (North Belarus culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 221-1	2,1446	67,40
Sr 221-2	2,1165	60,13
Sr 221-3	2,0938	67,93
Sr 221-4	2,1563	43,79
Sr 221-5	2,1063	54,76
Sr 221-6	2,1063	63,91
Sr 221-7	2,2105	97,01
Sr 332	2,4579	79,96
	1,9563	39,29
Sr 334-1	1,9439	41,06
Sr 334-2	1,9790	28,23
Sr 334-3	1,8919	54,19

Cycle of cultural systems of the Carpathian Basin

Eastern Linear Pottery culture

Table 108

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of Carpathian Basin cultural systems (Eastern Linear Pottery culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 10	2,0029	0,51
Sr 438	2,0020	0,59

Table 109

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of Carpathian Basin cultural systems (Eastern Linear Pottery culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 10	2,0893	42,63
Sr 438	2,2357	95,84

Bükk culture

Table 110

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of Carpathian Basin cultural systems (Bükk culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 151	2,0030	0,46

Table 111

EPR spectrum characteristics of mineral components occurring in representative samples of *the Cycle of Carpathian Basin cultural systems (Bükk culture)*

Sample code	Spectroscopic coefficient g of separation	Extent of gradient [mT]
Sr 151	2,0086	58,50

CONCLUSIONS

The attempt at a reconstruction of transformations that took place in respect to the application and manufacture of wood tar among prehistoric communities in the interfluvial region of the Dnieper and Łaba presented in this study has focused on several vital issues in this cultural context.

Apart from a brief presentation of chemical constituents present in wood and bark (Chapter II.1), as well as wood tar materials, the development of the method of processing was briefly outlined (Chapter II.2), as well as the preparation of wood tar (Chapter II.4). The next issue was that of research aiming at establishing a basis for distinguishing sources for the processing of wood tars (macroscopic identification and verification during field research), as well as the identification of the most frequently occurring groups of finds. Finally, one of the most vital issues in archaeological field work, was the establishment of recording methods for wood tar materials in respect to their differentiation from externally similar organic remains (Chapter II.5 and IV).

Equally important, proved to be the possibility of identification with the aid of physico-chemical research (Chapter V), features of intended wood tar work of prehistoric peoples in the context of no visible distinguishing elements of processing of wood tar applications (Chapter IV). In addition, a taxonomy was successfully completed on the physico-chemical basis of all the materials analysed, in terms of the six main technological (Chapter IV.1) and four functional groups (Chapter IV.2).

Taking into account the research aims set out in the introduction, this study by no means exhausts, however, all the relevant issues in respect to the processing and application of wood tar substances in the Stone and Bronze Ages in the interfluvial region of the Dnieper and Łaba rivers. It is envisaged, however, rather that it will be possible to establish the potential opportunities for research in respect to wood tar substances from field research, most often overlooked in studies of source materials.

The present study constitutes therefore an introduction to further interdisciplinary archaeometric research, which should be directed towards the realisation of comprehensive studies aiming initially at a broadening of the source base of wood tar materials, as well as their subsequent archaeometric research in line with the proposed methodology in Chapters III, IV and V.

The most urgent task facing archaeometric research of wood tar substances in the prehistory of Europe thus is the establishment of a representative collection of source materials from all the respective cycles of cultural systems, in particular – those of comparative regions: *the Cycle of cultural systems of the steppe and forest steppe in eastern Europe, the Cycle of cultural systems of the forest zone in eastern Europe and the Cycle of cultural systems of the Carpathian Basin*. This in turn will allow in the future for a precise observation of trends in respect to the technology of processing and use of wood tar among the communities of pre-historic Europe.

The application of relevant research methods and their corresponding results during analysis of the manufacture of wood tar in the communities of prehistoric Europe, should provide a basis for further interdisciplinary research programmes. At the first stage, fieldwork, the separation of organic materials according to the criteria proposed in Chapter II.5 should constitute standard practice, subsequently the ability for appropriate selection (equally archaeological and physico-chemical) of samples (in-house research) for specialist archaeometric studies (Chapter II.6). The above should be complemented subsequently by comprehensive analysis with the aid of possibly varied and far-reaching research methods; equally archaeological and archaeometric. At this stage of research it would seem that it is essential that there be a close collaboration between archaeologists and relevant scholars from the natural sciences.

In conclusion is necessary to maintain that the basic research aim that should also be realised in future is on the one hand, the inclusion of wood tar processing issues in the context of standard fieldwork practice on the part of archaeologists, and on the other, the undertaking of the broadest possible base of source materials in terms of specialist archaeometric research.

Thus it would appear that the study has sufficiently demonstrated the research value of the wood tar substances under analysis, as a new but often insufficiently recognised category of source materials that would allow for broad ranging observations of prehistoric cultures.

Further, this study it would seem, also presents an innovate proposition for a multi-aspectual research programme plan aiming at the integration of scholarly work in the humanities with that of life sciences, which takes into consideration European-wide experience, as well as English (so-called *Archaeological Sciences*, to take the example of programme structure at the University of Oxford).

In this respect the direction of archaeometric research, in this particular case that of wood tar substances preserved in a form that often prevents their macroscopic identification, allows to better understand their special position in the light of ‘the archaeology of organic substances”. At the same time one needs to emphasise that despite the need for the application of knowledge from natural sciences (physics and chemistry) in respect to archaeology, it is possible however, to draw conclusions purely from the humanities – which it is hoped, this study at least in part succeeded in.

CATALOGUE OF FINDS

The catalogue of finds has taken into account all the samples of wood tar subject to physico-chemical analysis in the archaeometry laboratory, Physico-chemical Materials and Nanotechnology Section at the Faculty of Chemistry, Adam Mickiewicz University, Śrem. These are samples of wood tar registered foremost at archaeological excavation research sites, as well as those discovered by means of survey (Polish Archaeological Photographic Documentation).

The collection of samples presented here and identified as wood tar substances (218 samples), then subsequently classified in groups into the Cycle of Cultural Systems, respectively for the Baltic drainage basin, steppe and forest steppe of Eastern Europe, forest zone of Eastern Europe and the Carpathian Valley, have their genesis in 80 respective archaeological sites found in the interfluvial region of the Dnieper and Łaba river.

In the documentation of samples a coherent system of catalogue recording was applied, embracing only the most essential information expressed in the form of tabular abbreviations. All the samples found in the catalogue were systematized chronologically in respect to corresponding taxonomic units relevant to a given Cycle of Cultural Systems and enscribed with a call number from the archaeometry laboratory in Śrem. The fundamental criterium of source material presentation was chronological and cultural, which despite further sample call numbers, determined the relevant sequence.

In the catalogue, apart from the number or site number, information was placed relating to the origin of a given location for a defined unit of government administration such as commune, county and province, while in the case of sites now found beyond present borders of Poland, the relevant country has also been given. Further catalogue information in relation to particular samples contains the following: research unit (inventory no., excavation and feature), functional and technological groups of wood tar materials whose profile is presented in the first part of the study (Chapter V).

Information relating to chronology and culture of presented samples was given in the form of taxonomic units and accepted dating (in a BC calibrated scale). For some samples or archaeological sites from whose surface wood tar samples were gained, C14 analysis was conducted. The radiocarbon dating results were presented in the form of non-calibrated BP dates, as well as in reference to the material under chronological analysis (wood tar, wood coal, bones etc.). The dates gained were then subjected to calibration with the aid of the OxCal v 3.9 programme and the results gained were presented only as BC datings true to 68,2%.

Colour photographs or drawings of all the samples, except for lost materials or those destroyed, were recorded on a CD in the monograph ‘Application and Technology of Wood Tar Manufacture Among societies of the Dnieper and Łaba Interfluvial Region, 6000 – 2000 BC’ [in:] Archaeologia Bimaris Monographies, Vol. 4, Poznań 2010.

Sample number	Place, site number	Administrative unit	Catalogue no., excavation, relic/feature	Functional group	Technological group	Cultural and chronological profile
1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 162	Site 7, Miechowice	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 9306	post-production residue	III	Linear Pottery culture, phase I / II, (14 C: GrN-10774: 6205 ± 50 BP – Wood charcoal chronology; 5260 – 5060 BC)
Sr 167	Site 7, Miechowice	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 9353	post-production residue	IV	Linear Pottery culture, phase I / II, (14 C: GrN-10774: 6205 ± 50 BP – Wood charcoal chronology; 5260 – 5060 BC)
Sr 72	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 21, Trench A 1b, ML I, Feature A 5	post-production residue	IV	Linear Pottery culture, phase II
Sr 73	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 50, Trench A 1a, thill part NW, Feature A 71	post-production residue	IV	Linear Pottery culture, phase II
Sr 74	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 54, Trench A 3b, ML III (40 – 60 inches), Feature A 13	vessel sealing	IV	Linear Pottery culture, phase II
Sr 77	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. E 9, Trench E 1, below ML IV, Feature E 5 part S	post-production residue	IV	Linear Pottery culture, phase II
Sr 79	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. E 25, Trench E 1, ML II, Feature E 5 part N	post-production residue	II	Linear Pottery culture, phase II
Sr 80	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 16, Trench F 6, Feature F 102a part E	vessel sealing	IV	Linear Pottery culture, phase II

1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 81	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 23, Trench F 3, Feature F 16b part E	vessel sealing	IV	Linear Pottery culture, phase II
Sr 82	Site 29, Radojewice, (GAZ / 403)	Dąbrowa Biskupia Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. B 10, Trench B 3a, ML IV	post-production residue	IV	Linear Pottery culture, phase II
Sr 83	Site 2, Rożniaty, (GAZ / 388)	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. E 35, Trench E 10a, NL I	vessel sealing	VI (composite)	Linear Pottery culture, phase II
Sr 87	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. S 5, Feature S 125	post-production residue	III	Linear Pottery culture, phase II
Sr 88-1	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. S 7, Trench S 4a, Feature S 16	colorant	IV	Linear Pottery culture, phase II
Sr 88-2	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. S 7, Trench S 4a, Feature S 16	vessel sealing	VI (composite)	Linear Pottery culture, phase II
Sr 89	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. S 67, Trench S 4b / a, Feature S 84	vessel sealing	III	Linear Pottery culture, phase II
Sr 95	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. P 8, Trench P 8 / 9a, Feature P 11 (20 – 40 inches)	vessel sealing	VI (composite)	Linear Pottery culture, phase III (early)

1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 96	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. P 10, Trench P 9a, ML III, Feature P 11	vessel sealing	VI (composite)	Linear Pottery culture, phase III (early)
Sr 98	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. P 16, Trench P 8a / 9a, ML IV, Feature P 11	post-production residue	III	Linear Pottery culture, phase III (early)
Sr 90	Site 18, Żegotki, (GAZ / 380)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 17, Trench A 7e, Feature A 42 part S	post-production residue	III	Linear Pottery culture, phase III
Sr 91	Site 18, Żegotki, (GAZ / 380)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 20, Trench 5a / 5b, Feature A 10 part S	post-production residue	IV	Linear Pottery culture, phase III
Sr 92	Site 18, Żegotki, (GAZ / 380)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 47, Trench A 7e, ML III – thill, Feature A 13 part S	post-production residue	IV	Linear Pottery culture, phase III
Sr 93	Site 5, Kuczkowo, (GAZ / 109)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. J 498	post-production residue	III	Linear Pottery culture, phase III
Sr 94	Site 5, Kuczkowo, (GAZ / 109)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. B 432, Trench B 2a, ML III, Feature B 228	post-production residue	III	Linear Pottery culture, phase III
Sr 97	Site 1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. P 16, Feature P 1	post-production residue	IV	Linear Pottery culture, derivate deposit
Sr 174	Site 1, Kozielice, (GAZ / 119)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. K / 1 / 6 / 96, Feature 6	post-production residue	I / II	Late Band Pottery culture, phase III

1	2	3	4	5	6	7
Sr 99	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 38, Feature F 38	post-production residue	IV	Late Band Pottery culture
Sr 100	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 57, Trench F 1, NL I, Feature F 4,	post-production residue	IV	Late Band Pottery culture, (14 C: Ki-6225: 4980 ± 40 BP – bone chronology; 3890 – 3700 BC)
Sr 140	Site 29A, Dęby	Dobre Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 12314 / 9	post-production residue	I	Funnel Beaker culture, phase III A, (14C: Gd-6919: 5020 ± 80 BP; Gd-6918: 5130 ± 100 BP – fossil chronology; 3970 – 3710 BC)
Sr 16	Site 17, Jezuicka Struga	Rojewo Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 2060, Trench VII, działka α, Feature 1, ML IV- thill	colorant	VI (composite)	Funnel Beaker culture, phase III A, (14C: Ki-5876: 5060 ± 70 BP – bone chronology, Feature 1 – Cat. No. 2098; 3960 – 3790 BC)
Sr 128	Site 95, Lembarg	Jabłonowo Pomorskie Commune, Brodnica County, Kujawy-Pomorze Province, Poland	Cat. No. 95 / 34, Feature 34	post-production residue	I	Funnel Beaker culture, phase III A, (14C: Ki-5889: 5020 ± 40 BP – nagar chronology; 3940 – 3710 BC)
Sr 41	Site 35, Łojewo	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 10549, Feature 9	post-production residue	I	Funnel Beaker culture, phase III A, (14C: Gd-6256: 5080 ± 90 BP – wood tar chronology; 3940 – 3700 BC)
Sr 40	Site 6A, Łącko	Pakość Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 21673	post-production residue	I	Funnel Beaker culture, phase III A, (14C: GifA–95488: 5010 ± 70 BP – wood tar chronology; 3940 – 3700 BC)
Sr 9	Site 17, Jezuicka Struga	Rojewo Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 2096, Trench X, NL II, ML I	binder	II	Funnel Beaker culture, phase III A, (14C: Ki-5878: 4890 ± 50 BP – wood tar chronology; 3710 – 3635 BC)
Sr 66	Site 2, Rożniaty, (GAZ / 388)	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. F 25, Trench F3b	binder	I	Funnel Beaker culture, phase III A, 4000 – 3650 BC
Sr 137	Site 9, Smogorzewiec	Obrowo Commune, Toruń County, Kujawy-Pomorze Province, Poland	Cat. No. 1923, concentration 5	binder	I	Funnel Beaker culture, phase III A – III B, (14C: Ki-8897: 4860 ± 200 BP – wood tar chronology; 3950 – 3350 BC)

1	2	3	4	5	6	7
Sr 33	Site 21, Dąbrowa Biskupia	Dąbrowa Biskupia Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 2973, Feature 81 / 90	post-production residue	I	Funnel Beaker culture, phase III B, (14C: Gd-2638: 4870 ± 80 BP – wood tar chronology; 3770 – 3530 BC)
Sr 34	Site 21, Dąbrowa Biskupia	Dąbrowa Biskupia Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 2982, Feature 81 / 90	post-production residue	I	Funnel Beaker culture, phase III B, (14C: Gd-2638: 4870 ± 80 BP – wood tar chronology – sample Sr 33; 3770 – 3530 BC)
Sr 35	Site 21, Dąbrowa Biskupia	Dąbrowa Biskupia Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	nr inw. 2965, Ob. 81 / 90	post-production residue	I / II	Funnel Beaker culture, phase III B, (14C: Gd-2638: 4870 ± 80 BP – wood tar chronology – sample Sr 33; 3770 – 3530 BC)
Sr 327	Site G, Słonowice	Kazimierza Wielka Commune, Kazimierza Wielka County, Świętokrzyskie Province, Poland	Trench XXIV, Feature 14 (grave)	binder (cataplasm)	I	Funnel Beaker culture, phase BR I – BR III, 3900 – 3100 BC
Sr 212	Site 1, Bronocice	Działoszyce Commune, Pińczów County, Świętokrzyskie Province, Poland	Cat. No. 693 / 74, Feature 110 / S, region A-1	colorant	VI (composite)	Funnel Beaker culture, phase BR II, 3650 – 3400 BC
Sr 215	Site 1, Bronocice	Działoszyce Commune, Pińczów County, Świętokrzyskie Province, Poland	Cat. No. 713 / 74, Feature 73 / N, region A-1	post-production residue	IV	Funnel Beaker culture, phase BR II, 3650 – 3400 BC
Sr 211	Site 3, Donosy	Kazimierza Wielka Commune, Kazimierza Wielka County, Świętokrzyskie Province, Poland	Cat. No. 77 / 95	post-production residue	I	Funnel Beaker culture, phase BR II – BR III, 3650 – 3100 BC
Sr 213	Site 1, Bronocice	Działoszyce Commune, Pińczów County, Świętokrzyskie Province, Poland	Cat. No. 950 / 74, Feature 99 / SW, region A-1	post-production residue	III	Funnel Beaker culture, phase BR III, 3400 – 3100 BC
Sr 214	Site 1, Bronocice	Działoszyce Commune, Pińczów County, Świętokrzyskie Province, Poland	Cat. No. 576 / 74, Feature 95 / N, region A-1	colorant	VI (composite)	Funnel Beaker culture, phase BR III, 3400 – 3100 BC

1	2	3	4	5	6	7
Sr 325-1	Wrocław, Czekoladowa Street	Wrocław Commune, Wrocław County, Dolny Śląsk Province, Poland	nr inw. CZ / 6 / 03, ob. 14, warstwa 2, wykop III	post-production residue	I / II	Funnel Beaker culture, phase II, 3600 BC
Sr 325-2	Wrocław, Czekoladowa Street	Wrocław Commune, Wrocław County, Dolny Śląsk Province, Poland	nr inw. CZ / 6 / 03, ob. 14, warstwa 2, wykop III	post-production residue	I / II	Funnel Beaker culture, phase II, 3600 BC
Sr 325-3	Wrocław, Czekoladowa Street	Wrocław Commune, Wrocław County, Dolny Śląsk Province, Poland	Cat. No. CZ / 6 / 03, Feature 14, layer 2, Trench III	post-production residue	I / II	Funnel Beaker culture, phase II, 3600 BC
Sr 175w	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 14	post-production residue	I	Funnel Beaker culture, phase III B, 3600 – 3300 BC
Sr 175z	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 14	post-production residue	I / II	Funnel Beaker culture, phase III B, 3600 – 3300 BC
Sr 193	Site 1, Piecki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. GMW 31 / 51	post-production residue	I	Funnel Beaker culture, phase III B, 3700 – 3200 BC
Sr 1	Site 33, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 4753 / 198, F 114 / 33	colorant	VI (composite)	Funnel Beaker culture, phase III B, (14C: Poz-9835: 4590 ± 50 BP – wood tar chronology; 3500 – 3120 BC)
Sr 42	Site 7, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 413	post-production residue	I	Funnel Beaker culture, phase III B, 3700 – 3200 BC
Sr 43	Site 34, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 411	post-production residue	I	Funnel Beaker culture, phase III B, 3700 – 3200 BC

1	2	3	4	5	6	7
Sr 55	Site 4, Bachorce	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. GMW 34 / 1	post-production residue	I / II	Funnel Beaker culture, phase III B, 3700 – 3200 BC
Sr 56	Site 4, Bachorce	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	nr inw. GMW 34 / 60, Ob. 63	post-production residue	I	Funnel Beaker culture, phase III B, 3700 – 3200 BC
Sr 28	Site 1, Żuławka Mała	Wyrzysk Commune, Piła County, Kujawy-Pomorze Province, Poland	?	post-production residue	I	Funnel Beaker culture, phase III B, 3700 – 3200 BC
Sr 30	Site 4, Poganice	Potęgowo Commune, Słupsk County, Pomorze Province, Poland	Cat. No. 498 / 73, ML IV	post-production residue	I	Funnel Beaker culture, Łupawa Group, phase III B, 3700 – 3200 BC
Sr 31	Site 4, Poganice	Potęgowo Commune, Słupsk County, Pomorze Province, Poland	Cat. No. 2 / 123 / 87, Feature 608	post-production residue	IV	Funnel Beaker culture, Łupawa Group, phase III B, 3700 – 3200 BC
Sr 252	Site 42, Komorniki	Luboń Commune, Poznań County, Wielkopolska Province, Poland	Cat. No. 38, Ar 15, Trench b, Feature 12 quarter D, ML V (40 – 50 inches deep)	binder	I / II	Funnel Beaker culture, phase III B, (14C: Poz-888: 4840 ± 35 BP – wood tar chronology; 3670 – 3530 BC)
Sr 198w	Site 1, Zabrzezie	Rząśnia Commune, Pajęczno County, Łódź Province, Poland	Cat. No. K 155, Trench K57b i K67a, Feature K56, section K, No KWB 105	binder	I / II	Funnel Beaker culture, phase III B – III B / III C, (14C: Ki-11601: 4740 ± 80 BP – ceramic ware chronology; 3640 – 3370 BC)
Sr 198z	Site 1, Zabrzezie	Rząśnia Commune, Pajęczno County, Łódź Province, Poland	Cat. No. K 155, Trench K57b i K67a, Feature K56, section K, No KWB 105	binder	I / II	Funnel Beaker culture, phase III B – III B / III C, (14C: Ki-11601: 4740 ± 80 BP – ceramic ware chronology; 3640 – 3370 BC)
Sr 263	Site 42, Komorniki	Luboń Commune, Poznań County, Wielkopolska Province, Poland	Cat. No. 22, Ar 16, Trench b, Feature 12 quarter C, ML V (40 – 50 inches deep)	post-production residue	I	Funnel Beaker culture, phase III B / IIIC – IIIC, (14C: Poz-889: 4330 ± 35 BP – bone chronology; 3020 – 2890 BC)

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Sr 264	Site 42, Komorniki	Luboń Commune, Poznań County, Wielkopolska Province, Poland	Cat. No. 19, Ar 16, Trench b, Feature 12 quarter C, ML IV (30 – 40 inches deep)	post-production residue	I	Funnel Beaker culture, faza III B / IIIC – IIIC, (14C: Poz-925: 4400 ± 35 BP – wood charcoal chronology; 3020 – 2890 BC)
Sr 32-1	Site 13, Żuławka	Wyrzysk Commune, Piła County, Wielkopolska Province, Poland	Cat. No. Ż. 13. 603-96	binder	I	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 32-2	Site 13, Żuławka	Wyrzysk Commune, Piła County, Wielkopolska Province, Poland	Cat. No. Ż. 13. 603-96	binder	I	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 328	Site 13, Żuławka	Wyrzysk Commune, Piła County, Wielkopolska Province, Poland	Cat. No. Ż. 13. 656-98	post-production residue	I / II	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 329w	Site 13, Żuławka	Wyrzysk Commune, Piła County, Wielkopolska Province, Poland	Cat. No. Ż. 13. 756-98	binder	I	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 329z	Site 13, Żuławka	Wyrzysk Commune, Piła County, Wielkopolska Province, Poland	Cat. No. Ż. 13. 756-98	binder	I	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 46	Site 1, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 11239 / 2	binder	I	Funnel Beaker culture, phase III B – III C, 3700 – 2950 / 2900 BC
Sr 321	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 32, Trench A 13, NL II, ML I	post-production residue	IV	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)

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Sr 464	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 27, Trench A 12, NL II, ML III	post-production residue	III	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 465	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 6, Trench A 14, NL II, ML III	vessel sealing	I	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 466	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 28, Trench A 14, ML V	post-production residue	I	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 467	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 5, Trench A 13, ML V	vessel sealing	VI (composite)	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)

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Sr 468	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. C 53, Trench C 31, concentration A, NL II, ML III-IV	post-production residue	I	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 469-1	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. C 39, Trench C 31, NL I	colorant	I	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 469-2	Site 5, Krągola, (AUT / 373)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. C 39, Trench C 31, NL I	binder	VI (composite)	Funnel Beaker culture, phase III B – III C, (14C: Ki-11482: 4705 ± 80 BP – ceramic ware chronology; Ki-10779: 4680 ± 70 BP – bone chronology; Ki-11355: 4650 ± 120 BP – ceramic ware chronology; Ki-10780: 4645 ± 70 BP – bone chronology; Ki-10778: 4605 ± 70 BP – wood charcoal chronology; Ki-11356: 4590 ± 80 BP – bone chronology; 3630 – 3140 BC)
Sr 177-1	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 10	post-production residue	I	Funnel Beaker culture, phase III B – IIIC, (14C: Ki-11251: 4580 ± 160 BP – wood tar chronology – sample Sr 177-2; Ki-11248: 4540 ± 70 BP – ceramic ware chronology attesting to wood tar – sample Sr 177-2; 3500 – 3040 BC)

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Sr 177-2	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 10	post-production residue	I	Funnel Beaker culture, phase III B – IIIC, (14C: Ki-11251: 4580 ± 160 BP – wood tar chronology – sample Sr 177-2; Ki-11248: 4540 ± 70 BP – ceramic ware chronology attesting to wood tar – sample Sr 177-2; 3500 – 3040 BC)
Sr 177-3w	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 10	post-production residue	I	Funnel Beaker culture, phase III B – IIIC, (14C: Ki-11251: 4580 ± 160 BP – wood tar chronology – sample Sr 177-2; Ki-11248: 4540 ± 70 BP – ceramic ware chronology attesting to wood tar – sample Sr 177-2; 3500 – 3040 BC)
Sr 177-3z	Site 1, Annopol	Szczawin Kościelny Commune, Gostynin County, Mazowsze Province, Poland	section 10	post-production residue	I / II	Funnel Beaker culture, phase III B – IIIC, (14C: Ki-11251: 4580 ± 160 BP – wood tar chronology – sample Sr 177-2; Ki-11248: 4540 ± 70 BP – ceramic ware chronology attesting to wood tar – sample Sr 177-2; 3500 – 3040 BC)
Sr 37	Site 3, Łagiewniki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Feature 40	binder	VI (composite)	Funnel Beaker culture, phase III B – III B / III C, (14C: Gd-813: 4500 ± 110 BP – wood tar chronology; 3360 – 3020 BC)
Sr 192	Site 1, Piecki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. GMW 31 / 52, Feature 32	post-production residue	III	Funnel Beaker culture, phase III B – III B / III C, (14C: Ki-9938: 4480 ± 55 BP – bone chronology; 3340 – 3040 BC)
Sr 57	Site 1, Piecki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. GMW 31 / 112, Feature 105	post-production residue	I	Funnel Beaker culture, phase III B – III B / III C, (14C: Ki-9941: 4450 ± 55 BP – bone chronology; 3330 – 3010 BC)
Sr 189	Site 1, Piecki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. GMW 31 / 112, Feature 105	colorant	VI (composite)	Funnel Beaker culture, phase III B – IIIB / III C, (14C: Ki-9941: 4450 ± 55 BP – bone chronology; 3330 – 3010 BC)
Sr 249	Site 1, Piecki	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 31 / 111, Feature 104	colorant	VI (composite)	Funnel Beaker culture, phase III B – III B / IIIC, (14C: Ki-9940:4420 ± 55 BP – bone chronology; 3330 – 3010 BC)

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Sr 253	Site 42, Komorniki	Luboń Commune, Poznań County, Wielkopolska Province, Poland	Cat. No. 40, Ar 15, Trench b, Feature 12 A	vessel sealing	VI (composite)	Funnel Beaker culture, phase III B / IIIC – IIIC, (14C: Poz-925: 4400 ± 35 BP – wood charcoal chronology; 3090 – 2920 BC)
Sr 254	Site 42, Komorniki	Luboń Commune, Poznań County, Wielkopolska Province, Poland	Cat. No. 32, Ar 15, Trench b, Feature 12 A	vessel sealing	VI (composite)	Funnel Beaker culture, phase III B / IIIC – IIIC, (14C: Poz-925: 4400 ± 35 BP – wood charcoal chronology; 3090 – 2920 BC)
Sr 3w	Site 5, Inowrocław – Mątwy	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 3233	vessel sealing	I	Funnel Beaker culture, Mątwy Group, phase III C, (14C: Bln-2186: 4470 ± 60 BP – wood tar chronology – sample Sr 36; 3340 – 3020BC)
Sr 3z	Site 5, Inowrocław – Mątwy	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 3233	colorant	VI (composite)	Funnel Beaker culture, Mątwy Group, phase III C, (14C: Bln-2186: 4470 ± 60 BP – wood tar chronology – sample Sr 36; 3340 – 3020BC)
Sr 36	Site 5, Inowrocław – Mątwy	Inowrocław Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 3320, Feature 4	binder	I	Funnel Beaker culture, Mątwy Group, phase III C, (14C: Bln-2186: 4470 ± 60 BP – wood tar chronology; 3340 – 3020BC)
Sr 12	Site 42, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Cat. No. 8270 / 33	colorant	VI (composite)	Funnel Beaker culture, phase IV A / IV B, (14C: Gd-2764: 4460 ± 80 BP – wood charcoal chronology; 3340 – 3020 BC)
Sr 5	Site 6B, Papros	Kruszwica Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. 5556	colorant	I	Funnel Beaker culture, phase IV B, 3200 – 3000 BC
Sr 284	Site 5, Szczuczyn	Szamotuły Commune, Szamotuły County, Wielkopolska Province, Poland	Cat. No. 109, Trench III, NL II, ML VI	colorant	VI (composite)	Funnel Beaker culture, Mrowino Group, phase IV A / V A, 3475 / 3450 – 3150 BC
Sr 324	Site 5, Szczuczyn	Szamotuły Commune, Szamotuły County, Wielkopolska Province, Poland	Cat. No. KPW 37, Trench II A, NL II, ML V	colorant	VI (composite)	Funnel Beaker culture, Mrowino Group, phase IV A / V A, 3475 / 3450 – 3150 BC

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Sr 8	Site 3, Bąkowo	Dąbrowa Biskupia Commune, Inowrocław County, Kujawy-Pomorze Province, Poland	Cat. No. B / 31 5523	colorant	II	Funnel Beaker culture, phase IV / V, 3475 / 3450 – 3150 BC
Sr 219	Site 96, Jeziora Wielkie	Jeziora Wielkie Commune, Mogilno County, Kujawy-Pomorze Province, Poland	AZP 50 – 40 No 306, PSOZ 5932	colorant	VI (composite)	Funnel Beaker culture, phase IV / V, 3475 / 3450 – 3150 BC
Sr 13	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 32, Trench A2a, Feature A 108	colorant	VI (composite)	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 23	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 45, Trench A7a, Feature A 38,	colorant	VI (composite)	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 24	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 113, Trench A8a, Feature A 38	colorant	VI (composite)	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 58w	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 114, Trench A8a, Feature A 136,	binder	I	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 58z	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 114, Trench A8a, Feature A 136,	binder	I	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 59	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. C 39, Trench C5a, Feature C9	binder	I	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC

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Sr 68w	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 191, Trench A8a, ML V, Feature A 136	post-production residue	III	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 68z	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 191, Trench A8a, ML V, Feature A 136	post-production residue	III	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 14	Site 5, Kuczkowo, (GAZ / 109)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. 109 / B 1, Trench B1a	colorant	V	Funnel Beaker culture, phase V A, (14C: Ki-6500: 4630 ± 35 BP; 3500 – 3350 BC)
Sr 25	Site 2, Żegotki, (GAZ / 378)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. 378 / B 207, Trench B1b	colorant	VI (composite)	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 B
Sr 26	Site 2, Żegotki, (GAZ / 378)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. 378 / B 125	colorant	VI (composite)	Funnel Beaker culture, phase V A, 3475 / 3450 – 3150 BC
Sr 243	Site 2, Kichary Nowe	Dwikozy Commune, Sandomierz County, Świętokrzyskie Province, Poland	Cat. No. KN – 225 / 96, grave 25, J24 – 40	binder	I	Funnel Beaker culture, phase V B, 3020 – 2780 BC
Sr 67w	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 1, Trench F1a	post-production residue	IV	Funnel Beaker culture, phase V B, 2900 – 2750 BC
Sr 67z	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. F 1, Trench F1a	post-production residue	IV	Funnel Beaker culture, phase V B, 2900 – 2750 BC
Sr 517	Site 1, Żuławka Mała	Wyrzysk Commune, Piła County, Kujawy-Pomorze Province, Poland	layer XVI, (150 – 160 inches deep)	binder	I	Globular Amphora culture, phase I, (14C: GifA-95490: 5190 ± 90 BP – wood tar chronology; 4220 – 3800 BC)

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Sr 18	Site 22, Bożejewice, (GAZ / 381)	Strzelno Commune, Mogilno County, Kujawy-Pomorze Province, Poland	Cat. No. A 75, Trench A2a, Feature A 10	colorant	VI (composite)	Globular Amphora culture, phase II b, 3250 / 3100 – 2800 / 2700 BC
Sr 19	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 106, Trench A8a, Feature A 136	colorant	VI (composite)	Globular Amphora culture, phase II b, (14 C: Ki-6917: 4415 ± 45 BP; Ki-6926: 4370 ± 50 BP; Ki-6927: 4420 ± 55 BP; Ki-6928: 4385 ± 45 BP; Ki-6929: 4400 ± 50 BP – bone chronology; Feature A136, Cat. No. A236; 3070 – 2920 BC)
Sr 141	Site 1, Żuławka Mała	Wyrzysk Commune, Piła County, Kujawy-Pomorze Province, Poland	?	binder	II	Globular Amphora culture, phase II b, 3250 / 3100 – 2800 / 2700 BC
Sr 229	Site 3, Średnia	Krzywcza Commune, Przemyśl County, Podkarpacie Province, Poland	kurhan 2, Feature 2 (grave)	post-production residue	III	Mierzanowice culture, Proto-Mierzanowice phase, Period A1 Bronze Age, 2400 – 2200 BC
Sr 166	Site 2, Kichary Nowe	Dwikozy Commune, Sandomierz County, Świętokrzyskie Province, Poland	Cat. No. 28 / 1989, Area I, kw. D – 30, layer j.s. [37], grave 10, (0,08 – (- 0,17 inches deep), (I D – 30 – 20)	binder	I	Mierzanowice culture, Proto-Mierzanowice phase, Period A1 Bronze Age, 2400 – 2140 BC
Sr 227	Site 65, Kraków – Nowa Huta – Cło, (Wanda Mound)	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature 112 (ceiling approx. 60 inches deep)	post-production residue	IV	Mierzanowice culture, classical phase – late phase, Period A1 / A2 – A2 Bronze Age, 2000 – 1600 BC
Sr 326	Site 14, Szarbia	Koniusza Commune, Proszowice County, Małopolska Province, Poland	Trench I / 200, Feature 9 (grave)	binder (cataplasm)	I	Mierzanowice culture, late phase, Period A2 Bronze Age, 1750 – 1600 BC
Sr 268	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A13, Trench A21, ML I	post-production residue	IV	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC

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Sr 271	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. D1, Trench B95, ML I	vessel sealing	IV	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 272-1	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A15, Trench A48, ML I	vessel sealing	VI (composite)	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 272-2	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A15, Trench A48, ML I	vessel sealing	VI (composite)	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 459	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. F 12, Trench F 10, ML III	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 460	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. F 2, Trench F 10, ML I	vessel sealing	III	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 461	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A 9, Trench A 17, NL I	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 462	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. F 9, Trench F 15, ML II	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 463	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. D 6, Trench D 98, ML I	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC

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Sr 449	Site 27, Krągola, (AUT / 383)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. C 2, Trench C 90, NL I	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 450	Site 27, Krągola, (AUT / 383)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. B 4, Trench B 43, NL I	post-production residue	III	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 447	Site 7 / 8, Janowice, (AUT / 385)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 53, Trench A 95a, Feature A 37	post-production residue	IV	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 448	Site 7 / 8, Janowice, (AUT / 385)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 3, Trench A 96a, ML I	post-production residue	IV	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 451	Site 7 / 8, Janowice, (AUT / 385)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. B 31, Trench B 7b, Feature B 19	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 452	Site 7 / 8, Janowice, (AUT / 385)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. B 30, Trench B 7b, ML I	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 453	Site 7 / 8, Janowice, (AUT / 385)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 85, Trench A 83b, Feature A 58	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 454	Site 6, Krągola, (AUT / 378)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. E 117, Trench E 56a, Feature E 86	vessel sealing	VI (composite)	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 455	Site 3, Rożniatów, (AUT / 466)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A 29, Trench A 43, Feature A 80, ML I – calec	post-production residue	I	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC
Sr 456	Site 6, Babia, (AUT / 354)	Rzgów Commune, Konin County, Wielkopolska Province, Poland	Cat. No. A 5, Trench A 90, ML I	post-production residue	II	Trzciniec Cultural circle, classical phase, Period A2 – C Bronze Age, 1750 / 1700 – 1400 BC

1	2	3	4	5	6	7
Sr 220	Site 1, Gabułtów	Kazimierza Wielka Commune, Kazimierza Wielka County, Świętokrzyskie Province, Poland	grave 5	vessel sealing	VI (composite)	Trzciniec Cultural circle, classical phase, Period B1 Bronze Age, 1600 – 1500 BC
Sr 223	Site 55B, Kraków Nowa Huta – Mogiła	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature B 131, (150 – 160 inches deep)	vessel sealing	VI (composite)	Trzciniec Cultural circle, classical phase, Period B1-B2 Bronze Age, 1600 – 1400 BC
Sr 224	Site 55, Kraków Nowa Huta – Mogiła, (Wanda Mound)	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature 68, (90 – 100 inches deep)	vessel sealing	VI (composite)	Trzciniec Cultural circle, late period classical phase, Period B2 / C Bronze Age, 1500 – 1350 BC
Sr 258	Site 55, Kraków Nowa Huta – Mogiła, (Wanda Mound)	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature 111, (90 – 100 inches deep)	vessel sealing	VI (composite)	Trzciniec Cultural circle, post-classical phase, Period C Bronze Age, 1400 – 1350 BC
Sr 225	Site 55B, Kraków Nowa Huta – Mogiła	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature B 49f, (120 – 130 inches deep)	vessel sealing	VI (composite)	Trzciniec Cultural circle, late phase, Period D Bronze Age, 1350 – 1200 BC
Sr 257	Site 55, Kraków Nowa Huta – Mogiła, (Wanda Mound)	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature 141, (80 – 90 inches deep)	post-production residue	II	Trzciniec Cultural circle, late phase, Period D Bronze Age, 1350 – 1200 BC
Sr 439w	Site 1, Podlodów	Łaszczów Commune, Tomaszów Lubelski County, Lublin Province, Poland	Cat. No. 562 / 2000, piece of land 3C, layer V (70-80 inches deep)	post-production residue	I	Trzciniec Cultural circle, late phase, Period D Bronze Age – Period A1 Hallstatt, 1300 – 1100 BC
Sr 439z	Site 1, Podlodów	Łaszczów Commune, Tomaszów Lubelski County, Lublin Province, Poland	Cat. No. 562 / 2000, piece of land 3C, layer V (70-80 inches deep)	post-production residue	I	Trzciniec Cultural circle, late phase, Period D Bronze Age – Period A1 Hallstatt, 1300 – 1100 BC

1	2	3	4	5	6	7
Sr 440	Site 1, Podlodów	Łaszczów Commune, Tomaszów Lubelski County, Lublin Province, Poland	Cat. No. 800 / 2003, piece of land 22B, layer III (50-60 inches deep)	colorant	I	Trzciniec Cultural circle, late phase, Period D Bronze Age – Period A1 Hallstatt, 1300 – 1100 BC
Sr 228	Site 55, Kraków Nowa Huta – Mogiła, (Wanda Mound)	Kraków Commune, Kraków County, Małopolska Province, Poland	Feature 145 (170 – 190 inches deep)	post-production residue	I	Trzciniec Cultural circle / Lusatian culture, Period A2 Bronze Age – Period A1 Hallstatt, 1700 – 1100 BC
Sr 171	Site 18, Szczepidło	Krzymów Commune, Konin County, Wielkopolska Province, Poland	Cat. No. 13908, Trench IX, ML II, NL II	post-production residue	IV	Trzciniec culture, (14C: Ki-5591: 3260 ± 50 BP – bone chronology, Feature 5; Ki-5592: 3180 ± 70 BP – bone chronology, Ob. 12; Period B1 – B2 Bronze Age, 1610 – 1410 BC)
Sr 172	Site 18, Szczepidło	Krzymów Commune, Konin County, Wielkopolska Province, Poland	Cat. No. 13909, Trench IX, ML III, NL II	colorant	IV	Trzciniec culture, (14C: Ki-5591: 3260 ± 50 BP – bone chronology, Feature 5; Ki-5592: 3180 ± 70 BP – bone chronology, Ob. 12; Period B1 – B2 Bronze Age, 1610 – 1410 BC)
Sr 441	Site 25, Krągola, (AUT / 381)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. B 73, Trench B 11b, Feature B 52	post-production residue	I	Lusatian culture, Period C – D Bronze Age, 1450 – 1300 BC
Sr 443	Site 25, Krągola, (AUT / 381)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. B 164, Trench B 56b, Feature B 131	colorant	VI (composite)	Lusatian culture, Period C – D Bronze Age, 1450 – 1300 BC
Sr 444-1	Site 25, Krągola, (AUT / 381)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. D 3, Trench D 30a, ML I, NL I	post-production residue	III	Lusatian culture, Period C – D Bronze Age, 1450 – 1300 BC
Sr 444-2	Site 25, Krągola, (AUT / 381)	Stare Miasto Commune, Konin County, Wielkopolska Province, Poland	Cat. No. D 3, Trench D 30a, ML I, NL I	post-production residue	III	Lusatian culture, Period C – D Bronze Age, 1450 – 1300 BC

1	2	3	4	5	6	7
Sr 71w	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 37, Trench A 26 / a	post-production residue	I	Lusatian culture, Period D Bronze Age, 1360 – 1220 BC
Sr 71z	Site 1, Kuczkowo, (GAZ / 108)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	Cat. No. A 37, Trench A 26 / a	post-production residue	I	Lusatian culture, Period D Bronze Age, 1360 – 1220 BC
Sr 256w	Site1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	?	post-production residue	I	Lusatian culture, Period D Bronze Age, 1360 – 1220 BC
Sr 256z	Site1, Siniarzewo, (GAZ / 79-80)	Zakrzewo Commune, Aleksandrów Kujawski County, Kujawy-Pomorze Province, Poland	?	post-production residue	II	Lusatian culture, Period D Bronze Age, 1360 – 1220 BC
Sr 267	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. A14, Trench A76, ML I	vessel sealing	IV	Lusatian culture, Period IV / V Bronze Age, 1100 – 820 BC
Sr 270	Site 5, Rożniatów Kolonia, (AUT / 450)	Uniejów Commune, Poddębice County, Łódź Province, Poland	Cat. No. B13, Trench B32, ML III	vessel sealing	VI (composite)	Lusatian culture, Period IV / V Bronze Age, 1100 – 820 BC
Sr 374w	Site 53, Wełtyń	Gryfino Commune, Gryfino County, West Pomorze Province, Poland	Cat. No. A / 20033 / MNS, kw / 6N, quarter D, Feature 27	vessel sealing	VI (composite)	Lusatian culture, Period IV / V Bronze Age, 1100 – 820 BC
Sr 374z	Site 53, Wełtyń	Gryfino Commune, Gryfino County, West Pomorze Province, Poland	Cat. No. A / 20033 / MNS, kw / 6N, quarter D, Feature 27	post-production residue	I / II	Lusatian culture, Period IV / V Bronze Age, 1100 – 820 BC
Sr 129w	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 52 / 70, Ar I, Fire-hearth 3	vessel sealing	VI (composite)	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC

1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 129z	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 52 / 70, Ar I, Fire-hearth 3	colorant	VI (composite)	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 130	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 52 / 70, Ar II, layer IV	colorant	III	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 131	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 52 / 70, Ar II, layer IV	binder	VI (composite)	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 132w	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 56a / 70, Ar II, layer IV	post-production residue	II	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 132z	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 56a / 70, Ar II, layer IV	post-production residue	III	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 133w	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 27 / 70, Ar I, Fire-hearth 3	vessel sealing	VI (composite)	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC
Sr 133z	Site 4, Szczecin – Niemierzyn	Szczecin Commune, Szczecin County, West Pomorze Province, Poland	Cat. No. A / 14530 / MNS, Field No. 27 / 70, Ar I, Fire-hearth 3	colorant	VI (composite)	Lusatian culture, Period IV – V Bronze Age / Halstatt C – Halstatt D, 1150 – 900 / 820 – 530 / 470 BC

Sample number	Place, site number	Administrative unit	Catalogue no., excavation, relic/feature	Functional group	Technological group	Cultural and chronological profile
1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 47	Talianki	District Czerkask, Region Umeń, Ukraine	?	binder	I	Trypolye culture, phase CII, 3300 – 2700 BC
Sr 184	Kosenivka	District Czerkask, Region Umeń, Ukraine	Feature 2	binder	I	Trypolye culture, phase CII, 2870 – 2690 BC
Sr 38	Obloj	District Chersonsk, Region Golajapristansk, Ukraine	kurhan 2, grave 16	binder	I	Pre-Yamnaya culture, 3575 – 3375 BC
Sr 39	Obloj	District Chersońsk, Region Golajapristansk, Ukraine	kurhan 2, grave 23	binder	I	Pre-Yamnaya culture, 3575 – 3375 BC
Sr 51	Telmana	District Lugansk, Region Lugansk, Ukraine	?	binder	I	Catacomb culture, 2800 BC
Sr 52	Site stan. 1 / 5a, Gonczarowka	District Lugansk, Region Svatowo, Ukraine	?	binder	I	Catacomb culture, 2800 BC
Sr 53	Site stan. 1 / 5b, Gonczarowka	District Lugansk, Region Svatowo, Ukraine	?	binder	I	Catacomb culture, 2800 BC
Sr 54	Site stan. 1 / 6, Gonczarowka	District Lugansk, Region Svatowo, Ukraine	?	binder	I	Catacomb culture, 2800 BC

Sample number	**Place, site number**	**Administrative unit**	**Catalogue no., excavation, relic/feature**	**Functional group**	**Technological group**	**Cultural and chronological profile**
1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 315w	Bolszije Bortnieje	upper Dnieper basin, Region Bobrujec, Belarus	kw. 13, Trench 1	vessel sealing	IV	Dnieper-Donets culture, stage III, 3800 – 3000 BC
Sr 315z	Bolszije Bortnieje	upper Dnieper basin, Region Bobrujec, Belarus	kw. 13, Trench 1	vessel sealing	IV	Dnieper-Donets culture, stage III, 3800 – 3000 BC
Sr 317	Site 2, Prorva	District Homel, Region Rogaczów, Belarus	kw. D-04, Trench 3, (30 – 40 inches deep)	post-production residue	IV	Dnieper-Donets culture, stage III, (14C: Ki-9280: 4520 ± 190 BP – wood tar chronology; 3600 – 2900 BC)
Sr 319	Site 2, Prorva	District Homel, Region Rogaczów, Belarus	kw. DD-14; GG-6, Trench 2, (20 – 30 inches deep)	post-production residue	IV	Dnieper-Donets culture, stage III / IV, (14C: Ki-9282: 4340 ± 190 BP – wood tar chronology; 3350 – 2650 BC)
Sr 318	Site 2, Prorva	District Homel, Region Rogaczów, Belarus	kw. GG-5, Trench 2, (40 – 50 inches deep)	post-production residue	IV	Dnieper-Donets culture, stage IV, (14C: Ki-9281: 4270 ± 180 BP – wood tar chronology; 3300 – 2550 BC)
Sr 230	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 418, No. 1219	post-production residue	III	Zedmar culture, 4445 / 4350 – 3600 BC
Sr 232w	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 408, No. 1274	post-production residue	III	Zedmar culture, 4445 / 4350 – 3600 BC
Sr 232z	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 408, No. 1274	post-production residue	III	Zedmar culture, 4445 / 4350 – 3600 BC
Sr 233	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 418	post-production residue	IV	Zedmar culture, 4445 / 4350 – 3600 BC
Sr 234	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 418, No. 1231	post-production residue	IV	Zedmar culture, 4445 / 4350 – 3600 BC

1	2	3	4	5	6	7
Sr 235	Site D, Zedmar	District Kaliningrad, Region Ozersk, Russia	Cat. No. MMA / 418, No. 1273	post-production residue	III	Zedmar culture, 4445 / 4350 – 3600 BC
Sr 231	Site ?, Barkweda	Dywiły Commune, Olsztyn County, Warmia-Mazury Province, Poland	Cat. No. MMA / 408	vessel sealing	III	Comb culture, phase II, 3400 / 3300 – 2600 BC
Sr 255-1	Site 35, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Feature 83	colorant	IV	Nemen culture, classical stage; (14C: Ki-5129: 4070 ± 40 BP – bone chronology; 2840 – 2490 BC)
Sr 255-2	Site 35, Opatowice	Radziejów Commune, Radziejów County, Kujawy-Pomorze Province, Poland	Feature 83	colorant	IV	Nemen culture, classical stage; (14C: Ki-5129: 4070 ± 40 BP – bone chronology; 2840 – 2490 BC)
Sr 188	Site ?, Szlachcin	Środa Wlkp. Commune, Środa Wlkp County, Wielkopolska Province, Poland	unrelated find	colorant	IV	Nemen culture, classical stage; (14C: Poz-1728: 4920 ± 40 BP – wood tar chronology; 3760 – 3640 BC)
Sr 520	Site VII, Pluski	Stawiguda Commune, Olsztyn County, Warmia-Mazury Province, Poland	Cat. No. P / VII / 256 / 04 / E	post-production residue	III	Nemen culture, classical stage; 2200 / 2150 – 1950 / 1800 BC
Sr 320	Site 1, Parchuty	District Grodno, Belarus	kw. B2, Trench 3	post-production residue	IV	Nemen culture, classical stage, Dobryj Bor Type; (14C: Ki-9285: 4700 ± 200 BP – wood tar chronology; 3700 – 3100 BC)
Sr 356	Site 4, Podgornaja	District Brześć, Region Baranowicze, Belarus	kw. H35, Trench 3	post-production residue	IV	Nemen culture, classical stage, Dobryj Bor Type; (14C: Poz-1731: 4270 ± 40 BP – wood tar chronology; 2920 – 2790 BC)
Sr 355	Site 4, Podgornaja	District Brześć, Region Baranowicze, Belarus	kw. K20, Trench 1	colorant	VI (composite)	Nemen culture, classical stage, Lysa Gora Type, 2590 – 1790 BC
Sr 236	Site 1, Chwalim	Kargowa Commune, Zielona Góra County, Lubuskie Province, Poland	Cat. No. Ch. 1 WKT II / 79 53	post-production residue	III	Nemen culture, Linin Horizon 2 (LH 2), (14C: Bln-1767: 3900 ± 50 BP – wood charcoal chronology; 2470 – 2300 BC)

1	2	3	4	5	6	7
Sr 237	Site 1, Chwalim	Kargowa Commune, Zielona Góra County, Lubuskie Province, Poland	Cat. No. Ch. 1 WKT I / 77 178	post-production residue	IV	Nemen culture, Linin Horizon 2 (LH 2), (14C: Bln-1767: 3900 ± 50 BP – wood charcoal chronology; 2470 – 2300 BC)
Sr 238	Site 1, Chwalim	Kargowa Commune, Zielona Góra County, Lubuskie Province, Poland	Cat. No. Ch. 1 WKT I / 77 126	colorant	VI (kompozyt)	Nemen culture, Linin Horizon 2 (LH 2), (14C: Bln-1767: 3900 ± 50 BP – wood charcoal chronology; 2470 – 2300 BC)
Sr 330	Site 5, Lipljany	Lower Uborta, District Homel, Region Lel'čickij, Belarus	Cat. No. 90	vessel sealing	VI (kompozyt)	Trzciniec Cultural circle – eastern branch, Turowo-Mozyr Group, 1700 / 1600 – 1200 BC
Sr 331	Site 1, Buchličkij Chutar	interfluvium Lower Horyn and Lower Stwigia, District Brześć, Region Stolin, Belarus	?	post-production residue	IV	Trzciniec Cultural circle – eastern branch, Turowo-Mozyr Group, 1700 / 1600 – 1200 BC
Sr 333	Site 1, Kuciec	right bank upper Nemen, District Minsk, Region Stawbcow, Belarus	?	post-production residue	III	Trzciniec Cultural circle – eastern branch, 1700 / 1600 – 1200 BC
Sr 221-1	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 221-2	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 221-3	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 221-4	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 221-5	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)

1	2	3	4	5	6	7
Sr 221-6	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	III	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 221-7	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	III	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 332	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	III	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 334-1	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 334-2	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)
Sr 334-3	Site III, Krywina	District Witebsk, Region Sennensk, Belarus	?	post-production residue	IV	North Belarus culture, (14C: Ki-9217: 4560 ± 100 BP; Ki-9322: 4390 ± 180 BP; Ki-9287: 4170 ± 170 BP; 3500 – 2650 BC)

Sample number	**Place, site number**	**Administrative unit**	**Catalogue no., excavation, relic/feature**	**Functional group**	**Technological group**	**Cultural and chronological profile**
1	**2**	**3**	**4**	**5**	**6**	**7**
Sr 10	Šarišské Michaĺany	District Prešov, Easrern Slovakia	Cat. No. 236, Feature 56 / 82	colorant	VI (composite)	Eastern Linear Pottery culture, Tiszadob Group
Sr 438	Site 42, Ryńsk	Wąbrzeźno Commune, Wąbrzeźno County, Kujawy-Pomorze Province, Poland	Feature 1	colorant	VI (composite)	Eastern Linear Pottery culture, Tiszadob-Kapušany Group,
Sr 151	Šarišské Michaĺany	District Prešov, Easrern Slovakia	Feature 114 / 83	colorant	II	Bükk culture

ABBREVIATIONS

AA - Acta Archaelogica. Copenhagen.
AC - Analytical Chemistry. Urbana.
ACS - Acta Chemica Scandinavica. Copenhagen.
AF - Ausgrabungen und Funde. Berlin.
AK - Archäologisches Korrespondenzblatt. Mainz.
AP - Archeologia Polski. Warszawa.
APA - Acta Praehistorica et Archaeologica. Rahden.
AR - Archaeologické Rozhledy. Praha.
CI - Chemistry and Industry. Chichester, West Sussex.
FJAC - Fresenius' Journal of Analytical Chemistry. Belaterra.
FPP - Folia Praehistorica Posnaniensias. Poznań.
JASC - Journal of Archaeological Science, Elsevier. Amsterdam.
JC - Journal of Chromatography, Elsevier. Amsterdam.
PA - Przegląd Archeologiczny. Wrocław.
Proceedings … - Brzeziński W., Piotrowski W. (Ed). Proceedings of the First International Symposium on Wood Tar and Pitch, State Archaeological Museum. Warsaw.
SA - Spectrochimica Acta Part A, Elsevier. Amsterdam.
SAr - Sprawozdania Archeologiczne. Kraków.
TL - Tetrahedron Letters. London.
WA - World Archaeology. London.
WAr - Wiadomości Archeologiczne. Warszawa.

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