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Contents of an Early Byzantine Amphora from Kruglaya Bay, the Black Sea

A fragment of an amphora found in the Kruglaya Bay near Sevastopol was filled with an unknown brown substance with a strong smell of tar. On the vessel's neck, there is a round stamp ~30 mm in diameter, depicting the bust of an emperor encircled by an inscription. It resembles stamps on amphorae made in Alexandria and the Geronisos Island. The inscription reads, "✠επί Πτολεμαίου επάρχου". The gas chromatography–mass spectrometry analysis revealed dehydroabietic acid, methyl dehydroabietate, norabietatrienes, retene, and other phenanthrene derivatives, suggesting that the substance resulted from dry distillation of wood of the Pinaceae family. The headspace analysis yielded components of turpentine oil such as α-pinene, camphene, limonene, cymenes, and others terpenes. To establish the sample's origin, the amphora's content was compared with modern pinewood tar obtained by the traditional method. Given nearly identical chromatogram profiles of the amphora's contents and of tar in areas relating to resin acids, similar values of peak areas of biomarker components, and the presence of turpentine oil components in the sample, it is highly probable that the amphora indeed contained tar.

Keywords: *Late Roman amphorae, Black Sea, tar, pitch, gas chromatography, mass spectrometry.*

Introduction

The routes of active maritime trade have long passed through the Black Sea. The remains of numerous shipwrecks provide a valuable source of information for analyzing economic interactions between coastal regions across various historical periods (Zelenko, 2008; Okorokov, 2016). The depths of the sea preserve archaeological evidence undisturbed, but its detailed study is very complicated. In 2006 and 2008, the remains of two ships were found off the coast of Crimea. One sank in the 9th–11th century near Sevastopol; the other one, in the 13th century near the village of Foros on the southern coast of Crimea (Vakhoneev, 2015). When examining the sites of these shipwrecks, no remains of contents were found in the amphorae. In 2015, an accumulation of amphorae (Günsenin, type IIb) from the 11th–12th centuries and fragments of wooden structures

of a ship that transported wine were discovered in the Black Sea near Balaklava (Sevastopol area), at a depth of 85.6 m (Ginkut, Lebedinsky, 2018).

Although shipwreck sites are more accessible for examination in the shallow coastal zone (Zelenko et al., 2016), these have been subjected to heavy hydrophysical and anthropogenic impact. Underwater finds are associated with eroded cultural layers in the flooded area or with the functioning of ports, harbors, and anchorages. The problems of using the bays of the Heracles Peninsula as harbors of Chersonesus, as well as quantitative assessment of the area of that ancient city and its agricultural surroundings absorbed by the sea, still remain controversial. In this regard, underwater archaeological evidence is of special importance, since it makes it possible to determine the dynamics of the sea's advance, and the intensity of the use of bays in different historical periods. Underwater finds from Kruglaya Bay include a large number of complete amphorae and tableware typical for anchorages and harbors of the Hellenistic period and the Middle Ages. Numerous fragments of amphorae of the 8th–9th centuries recovered from the bottom of the bay were similar to some finds from the Phanagoria harbor (Bukatov, Arzhanov, 2021), which suggests that a significant part of the water area of Kruglaya Bay was used as the Chersonesus harbor starting from the 4th century BC. Archaeological evidence from the bay area includes large fragments and archaeologically intact pieces of pottery (amphora containers) from the Hellenistic period and the Middle Ages, dated back to the time from the 4th century BC (Kadeev, 1964). Such finds usually come from ancient harbors and anchorages, where cargo damaged during transportation was thrown overboard (Bukatov, Bondarev, Dyuzhenko, 2020).

In addition to the types and contents of amphorae, ceramics (Morozova, Waksman, Zelenko, 2021) also serve as a source of information, and analysis of pottery indicates the centers of vessel production. Under favorable conditions, remains of amphora contents and traces of organic compounds on the vessel's surface can be well preserved in shallow water, which provides valuable information about the cargo transported. One of the most informative and sensitive methods is gas chromatography-mass spectrometry (GC/MS) (Bonaduce et al., 2016; Oudemans, Boon, 1991; Colombini, Modugno, 2009; Reber, 2018; Charrié-Duhaut et al., 2009; Pollard et al., 2007). This method was used for studying archaeological samples of organic origin from Kruglaya Bay.

This article presents the data about a fragment of a vessel discovered during underwater archaeological research in Kruglaya Bay, and the results of studying components of its contents.

Materials and methods

The contents of an amphora, a part of which was discovered in Kruglaya Bay in 2020 by the underwater expedition from the Tauric Chersonese Museum-Reserve directed by A.A. Bukatov, were the subject of research.

For identifying components of amphora contents, the following substances were used: natural pinewood tar (100 %) (OgneBioZashchita Company, Russia) produced by traditional dry distillation of wood where tar is collected continuously at furnace temperature of 155–450 °C; chloroform (99.8 %) (Sigma-Aldrich, USA), pyridine (99.5 %) (Supelco, USA), toluene (99.5 %) (Supelco), N,O-bis(trimethylsilyl)trifluoroacetamide or BSTFA (99.0 %) (Sigma-Aldrich), trimethylchlorosilane or TMCS (99.0 %) (Sigma-Aldrich), helium (99.9995 %), and nylon filter, i.d. 0.45 μm (Sartorius, Germany).

For gas chromatography-mass spectrometry (GC/MS) analysis, a Clarus 600 TMS chromatography-mass spectrometer (PerkinElmer, USA) with quadrupole mass analyzer and electron ionization (EI) mode was used. Chromatographic separation was carried out using an Rtx 5MS column (30 m × 0.25 mm, 0.25 df) (Restek, USA). Turbomass 5.4.2 software (PerkinElmer, USA) and the NIST library (2017) were used to control the unit, collect, and process data.

Samples for research were prepared in the following way:

using the *GC/MS method*, the contents of the amphora dissolved in chloroform were concentrated to 2 mg/ml;

using the *GC/MS TMS method (analysis of trimethylsilyl derivatives)*, about 10 mg of the sample was placed in a 2 ml vial, dissolved in 300 μl of pyridine; 300 μl of BSTFA and 30 μl of TMCS were added. The vial was kept at 60 °C for an hour, after which 400 μl of toluene was added and the contents were analyzed;

using the *GC/MS method (headspace analysis)*, about 1 g of the sample was placed into a 20 ml vial for headspace analysis. The vial was thermostated at 120 °C for 60 minutes.

The sample was analyzed by the *GC/MS method* under the following conditions: GC – initial temperature 60 °C, holding for 1 min, heating to 280 °C at a rate of 5 °C/min, holding for 5 min at 280 °C. Carrier gas (helium) flow was 1 ml/min. Injector temperature was 280 °C. The split ratio was 10 ml/min. Sample volume was 0.5 μl. MS electron ionization (70 eV, interface and ion source temperatures are 280 and 240 °C, respectively) scanning mode was total ion current (TIC) in the range of m/z 45–450. The NIST 2017 library was used to identify the mass spectra obtained.

Trimethylsilyl derivatives were analyzed by the *GC/MS TMS method* under the same GC conditions as

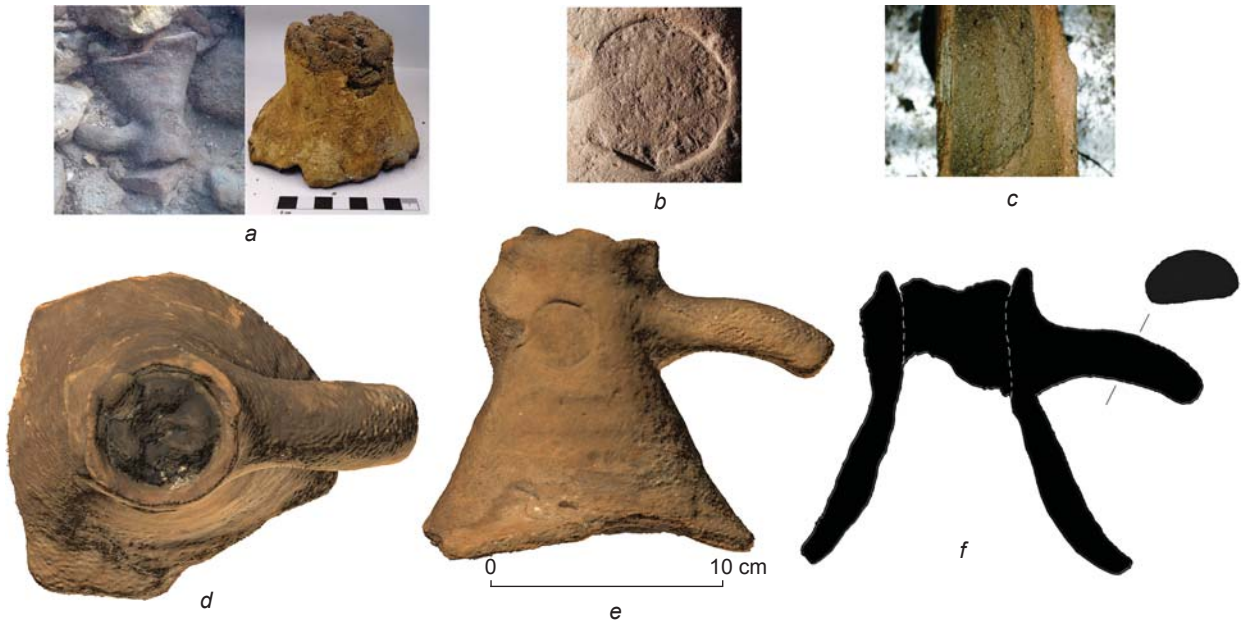


Fig. 1. Fragment of the upper part of the amphora *in situ* and its contents (*a*), stamp (*b*), fracture of the wall (*c*), top view (*d*), side view (*e*), cross-sectional view (*f*).

those used to analyze by the GC/MS. The split ratio was 50 ml/min, and m/z range was 45–550.

Headspace analysis by the *GC/MS method* was carried out under the same GC conditions as those used to analyze by GC/MS. Headspace injection volume was 250 µl, and m/z range was 45–400.

Discussion

A fragment of the upper part of an amphora filled with hard brown substance was discovered in the area of a rocky shoal during underwater research in Kruglaya Bay. The fragment lay with its neck down in a layer of bottom soil (Fig. 1, *a*). The surface of the amphora's contents, which weighed 340 g, was lumpy at the point of contact with water and had streaks. A round stamp about 30 mm in diameter, showing a full-face image of emperor's head with an inscription around, was on the neck of the vessel (Fig. 1, *b*). This imprint is one of 12 stamps* on amphorae (Opait, Diamanti, 2014) from excavations in Constantinople, Athens, on the Geronisos Island (off the northwestern coast of Cyprus), Alexandria, Selia, and Tokra. The stamp on the fragment of the amphora in question has been largely erased. Small details have not survived, and only the outlines of the emperor's image and some letters are visible. This stamp was identified immediately upon discovery of the amphora owing to specific marine conditions (the find lay in the bottom sediments in a water area protected from waves) and to the absence of biological growth on the surface of the shard. Based on the design of the letters and a number of distinctive features (location of the stamp, image details), this stamp was similar to stamps on the artifacts from Alexandria and the Geronisos Island (Ibid.). The inscription reads as follows: ✞*επί Πτολεμαίου επάρχου* ("✞under Ptolemy the Eparch"). The stamp was made by the office of *kommerkiarios*. On similar stamps, the Emperor is shown holding a scepter surmounted by a cross in his left hand and probably a *mappa* in his right hand. On the imprint on a vessel fragment from Kruglaya Bay, these elements of the image are almost illegible. Only the end of the cross on the scepter can be barely discerned. Most of the amphorae branded in this way belong to the LRA2/LRA13 type. Such vessels were made mainly in the areas adjacent to the Aegean Sea. The color of the clay in the shard (Fig. 1, *c*) varies from light red-brown and pink to red-orange (5YR 6/4, 6-7/4,6). Considering the stratigraphic position and archaeological context, two similar stamps on the amphorae, which were made and found in Alasarna on the Kos Island (Greece), were attributed to the last quarter of the 6th–first quarter of the 7th century (Ibid.).

The contents extracted from the amphora fragment were carefully analyzed to establish their chemical composition. The homogenized sample was a brown, solid, resinous substance with a distinctive smell of wood tar. The mass fraction of insoluble sediment after

*Such stamps on items are rare, which can be explained by their poor preservation due to the low relief of the image and weak imprint of the stamp.

dissolving the contents of the amphora in chloroform was 6.54 %. The ash content after burning the sample in a crucible was 5.37 %, which indicated that the contents of the amphora were organic and the dissolved sample was highly representative. The inorganic composition of the sample was not studied, because the contents of the amphora had been in contact with sea water.

After analyzing the sample by GC/MS, chromatograms 2–4 were obtained. A fragment of a TIC chromatogram of the sample dissolved in chloroform with concentration of ca 2 mg/ml indicated a low intensity (Fig. 2, *a*) of the peaks belonging to the components with a retention time up to 28 min, which made their reliable identification problematic. The results of identifying the main peaks in the range of 28–40 min are shown in Table 1 in accordance with an increase in their retention time (t_R). The broadened peak in Fig. 2, *a* with a retention time of 38.16 min was identified (with the probability of 65–75 %) as abietic acid (AA). Broadening of the peak resulted from low volatility of the analyte and/or presence of other related compounds that were not separated from this component under the given chromatographic conditions. Moreover, the sample could have contained other high-boiling components.

For increasing volatility of high-boiling components, TMS derivatives were prepared using BSTFA with the addition of 10 % TMCS. Fig. 2, *b* shows a fragment of the TIC chromatogram from 28.0 to 40.5 min of analysis after silylation of the test sample. The results of identifying the main peaks, shown in the order of their appearance on the chromatogram on Fig. 2, *b*, are provided in Table 1. The peaks of the TMS derivatives of dehydroabietic and abietic acids, as well as peaks of other tricyclic diterpenoid compounds, demonstrated the highest intensity in the chromatograms. Acids with abietane and pimaran skeletons are the main components of resins obtained from the coniferous plants. A large

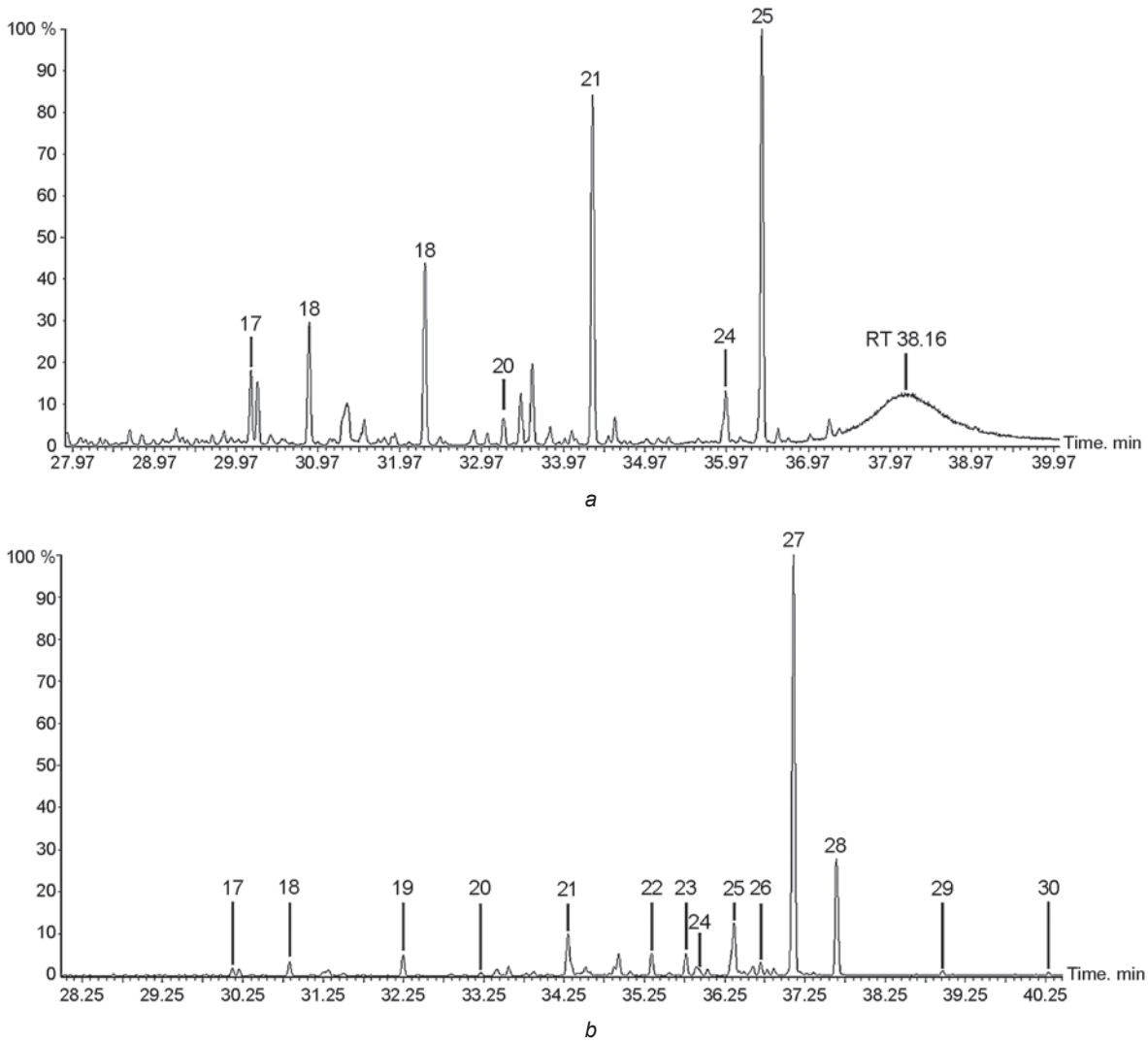
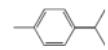
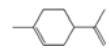
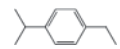
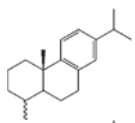
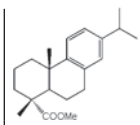
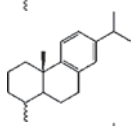
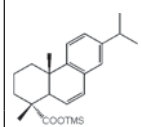
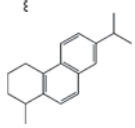
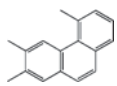
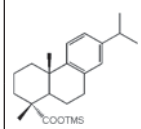
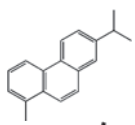
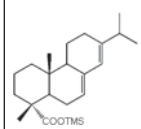
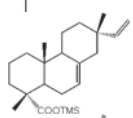
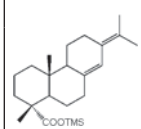
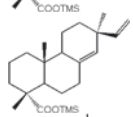
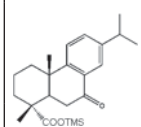
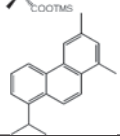


Fig. 2. Fragment of the TIC chromatogram of amphora contents (*a*) and amphora contents with BSTFA derivatization (*b*).

Table 1. **Results of identification of the main peaks**

Peak	t_R, min	Compound	Chemical structure	Matching degree	Peak	t_R, min	Compound	Chemical structure	Matching degree
Headspace analysis of amphora's contents by the GC/MS method									
1	2.57	2, 4-Heptadiene		931	10	5.69	Camphene		961
2	2.72	Toluene		918					
3	3.04	n-Octane		936	11	7.29	o/m-Cymene		962
4	3.40	1, 3-Dimethyl-1-cyclohexene		959	12	7.41	p-Cymene		953
5	4.09	m/p-Xylene		962	13	7.55	Limonene		947
6	4.49	o-Xylene		971	14	9.39	p-Ethylcumene		938
7	4.59	Nonane		942	15	9.90	Fenchol		854
8	5.11	Tricyclene		945	16	11.34	Borneol		879
9	5.33	α-Pinene		977					
Analysis of amphora's contents with and without derivatization by the GC/MS method									
17	30.15	18/19-Norabieta-8, 11, 13-triene*		859	25	36.40	Methyl dehydro-abietate		928
18	30.86	18/19-Norabieta-8, 11, 13-triene*		842	26	36.70	Didehydroabietic acid, TMS		(Colombini, Modugno, Ribechini, 2005; Otto, Simoneit, 2001)
19	32.28	10, 18-Bisnorabieta-5, 7, 9 (10), 11, 13-pentaene (1, 2, 3, 4-tetrahydroretene)		852					
20	33.25	2, 3, 5-Trimethylphenanthrene		809	27	37.11	Dehydroabietic acid, TMS		910
21	34.33	Retene		948	28	37.65	Abietic acid, TMS		896
22	35.34	Isopimaric acid, TMS		852	29	38.96	Neoabietic acid, TMS		(Max Planck Institute, (s.a.))
23	35.77	Pimaric acid, TMS		825	30	40.28	7-Oxo-dehydro abietic acid, TMS		805
24	35.96	8-Isopropyl-1,3-dimethylphenanthrene		872					

*Stereoisomeric compounds. Different procedures for data output of isomers on the column with (5% phenyl)-methylpolysiloxane are proposed in the studies by (Hamm, Bleton, Tchapla, 2004; Dimitrakoudi et al., 2011; Preusz et al., 2019; Stacey et al., 2010).

amount of dehydrobietic acid, and the presence of markers such as methyl ester of dehydroabietic acid, tetrahydrorethene, norabietatrienes, retene, and other phenanthrene derivatives in the sample, indicate that the contents of the amphora were a product of dry distillation of Pinaceae wood (Colombini, Modugno, Ribechini, 2005; Carpy, Marchand-Geneste, 2003; Izzo et al., 2013; Pollard, Heron, 1996; Mills, White, 1999; Hjulström, Isaksson, Hennius, 2006). The extremely low content of 7-oxo-dehydroabietic acid in the sample (the ratio of the peak areas of TMS derivatives of dehydroabietic acid (TMS-DA) and 7-oxo-dehydroabietic acid were ~140 : 1) and absence of 15-hydroxy-7-oxo-dehydroabietic acid, 15-hydroxy-dehydroabietic acid, and other oxidation products of dehydroabietic acid indicate a low degree of oxidation (Colombini, Modugno, 2009; Colombini, Modugno, Ribechini, 2005; Mezzatesta et al., 2021; Guo et al., 2021) and good preservation of the amphora's contents.

The general profile of the chromatogram in the area of resin acids (Fig. 2) was close to those of some archaeological samples (see, e.g., (Colombini, Modugno, Ribechini, 2005; Izzo et al., 2013)), but showed the greatest similarity with those of the modern samples of pine tar produced in classical furnaces (Egenberg et al., 2002).

Notably, products of dry distillation of wood are most often referred to as pitch or tar in archaeological literature. However, owing to their antiquity, poor preservation of samples, and many other reasons, they cannot be identified more accurately in most cases. In this article, just as in the study (Egenberg et al., 2002), the word "tar" denotes a sample in a liquid state at room temperature, and the word "pitch" denotes an almost solid sample at the same temperature.

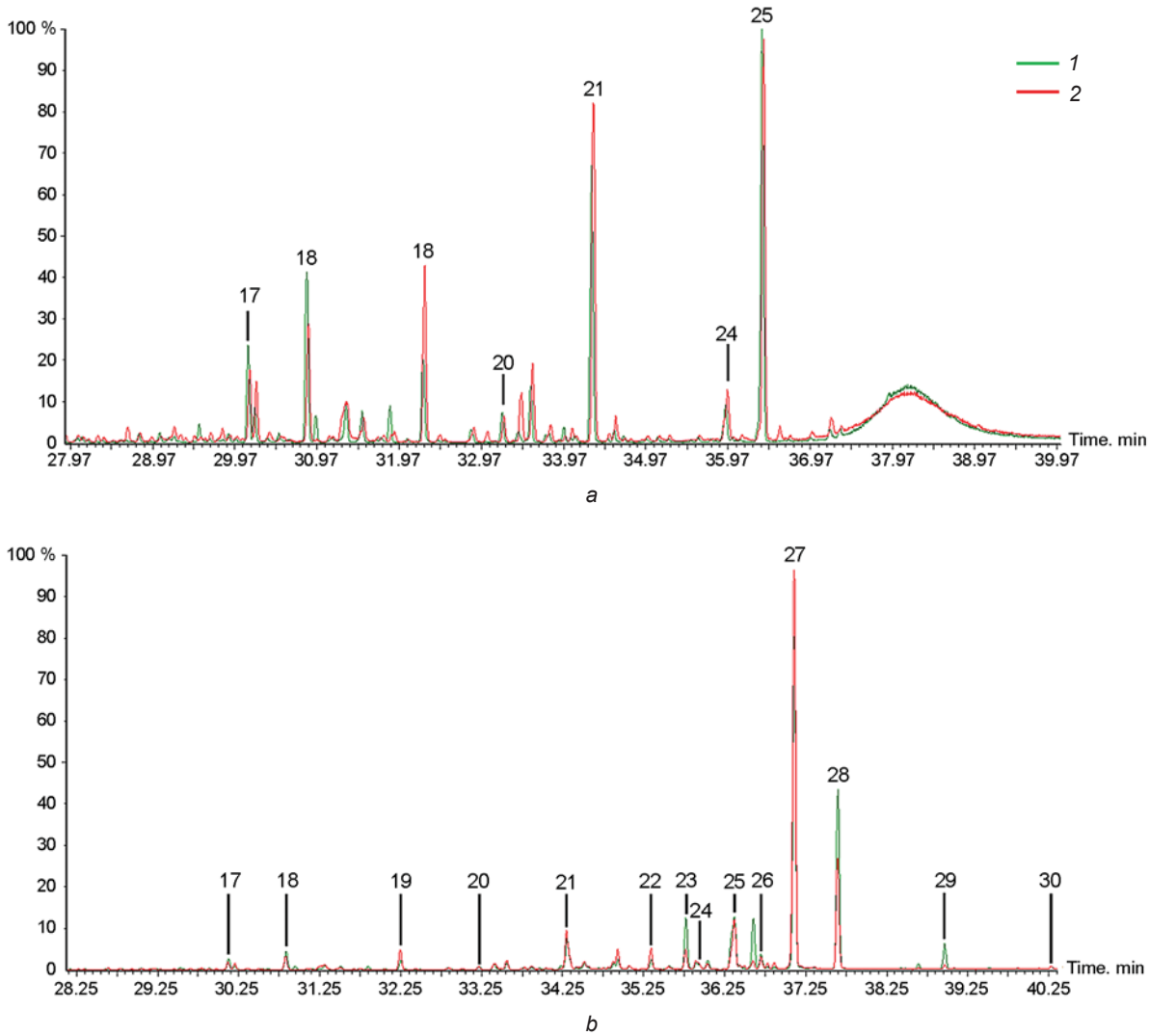


Fig. 3. Overlay of fragments of TIC chromatograms.
a – amphora contents (*1*) and modern wood tar (*2*) (sample concentration 2 mg/ml^{-1}); *b* – amphora contents with BSTFA derivatization (*1*) and modern wood tar with BSTFA derivatization (*2*) (sample concentration 10 mg/ml^{-1}).

Table 2. **Average values of peak areas, RSD, %**

Indicator	Amphora's contents	Modern wood tar	Areas ratio
Without derivatization, 2 mg/ml^{-1}			
Retene m/z 219	695,749 (2.99)	595,727 (3.2)	1.17
MDA m/z 239	1,116,129 (2.58)	1,207,031 (2.05)	0.92
With derivatization, 10 mg/ml^{-1}			
TMS-DA m/z 239	5,783,640 (5.14)	4,870,708 (2.44)	1.19
TMS-AA m/z 256	683,350 (5.94)	1,091,874 (2.29)	0.63

Note. Relative standard deviation is indicated in parenthesis, %.

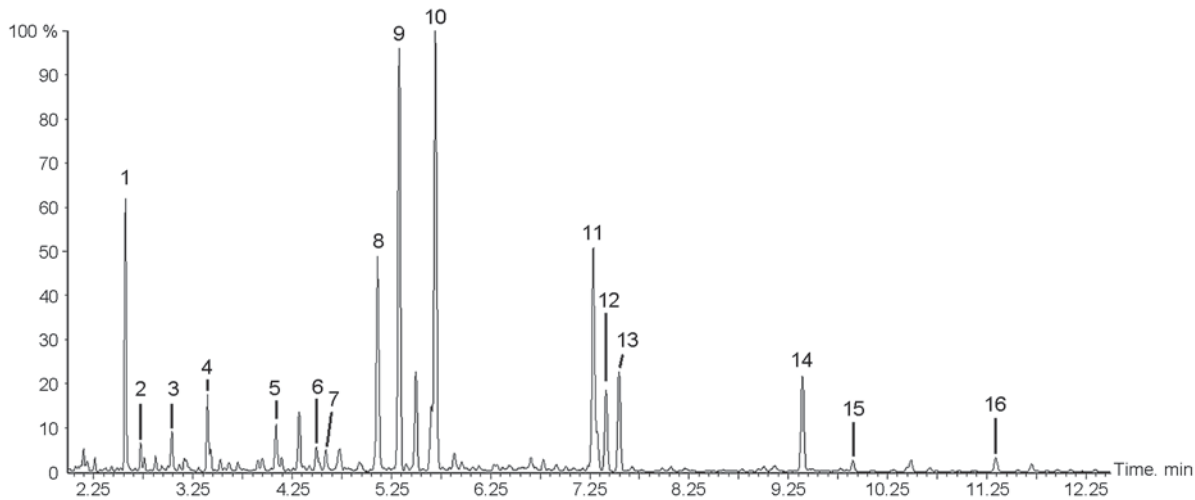


Fig. 4. Fragment of the TIC chromatogram obtained from headspace analysis of amphora contents using the GC/MS method.

To identify the nature of the sample in more detail, modern pine-tar obtained in the traditional way was compared with the contents of the amphora. Superposition of chromatograms obtained from solutions of the same concentration of amphora contents and modern tar without (Fig. 3, *a*) and with derivatization (Fig. 3, *b*) revealed identical general profiles. Table 2 shows a comparison of average peak areas of main ions belonging to key markers in the contents of the amphora and modern wood tar with and without derivatization. Average values (n=3) of peak areas for the main ions in retene, dehydroabietic acid methyl ester (MDA), and TMS derivatives of dehydroabietic acid (TMS-DA) and abietic acid (TMS-AA) were obtained by analyzing solutions of samples taken from the contents of the amphora and modern wood tar of the same concentration. Similar peak areas of retene, dehydroabietic acid methyl ester, and the TMS derivative of dehydroabietic acid in the contents of the amphora and modern tar suggest similar conditions for their production.

As was mentioned above, the peaks of highly volatile components (up to 28 min) had low intensity. For their reliable identification, headspace analysis, increasing the sensitivity of the method, was carried out under the same chromatographic conditions (column, carrier-gas flow, and thermostat temperature program) as analysis of the liquid phase by direct injection (of the dissolved samples). The fragment of the chromatogram (from 3 to 12.5 min) of headspace analysis of the amphora's contents suggests the presence of volatile components α-pinene, camphor, limonene, cymene, etc., which are components of turpentine oil, in the sample (Fig. 4) (Evans W.C., Evans D., 2009). This also serves as additional evidence of the good preservation of the amphora's contents. The modern wood tar sample also contained most of the volatile components provided in Table 1. However, from our point of view, it did not make sense to compare chromatogram profiles in the area of highly volatile components, owing to old age of the amphora's contents and their contact with water.

Conclusions

The almost identical profiles of chromatograms showing the contents of the amphora and modern wood tar in the area of resin acids, similar peak areas of components that serve as biomarkers, and the presence of turpentine oil components in the sample suggest, with a high degree of probability, that the amphora contained wood tar rather than pitch. Wood tar was widely used by ancient sailors for treating ropes and elements of wooden ship structures. Amphorae stamped in this way might have been intended for transporting olive oil or wine. Judging by its contents, the vessel under study had been reused. The examined stamped Late Roman amphora with remains of wood tar is the only one with such content among those discovered in the Northern Black Sea region. Until now, no traces of contents have been identified in containers of this type, owing to their significant fragmentation. Information on the place where the amphora fragment was discovered is important for reconstructing the outlines of the shores of the ancient bay. Considering the occurrence of the find under discussion, it can be assumed that the amphora with wood tar belonged to a ship that visited one of the harbors of Chersonesus, located in the present-day Kruglaya Bay in the last quarter of the 6th–first quarter of the 7th century.

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