
METHODS OF NATURAL SCIENCES IN THE STUDY
OF CULTURAL HERITAGE OBJECTS

Study of the Composition of Organic Residues on Ceramics from the Bottom of the Kerch Bay

V. M. Pojidaev^{a,*}, S. V. Olkhovsky^b, E. Yu. Tereshchenko^{a,c,d}, and E. B. Yatsishina^{a,c}

^a National Research Center “Kurchatov Institute,” Moscow, Russia

^b Physical Institute, Russian Academy of Sciences, Moscow, Russia

^c Institute of Chemical Reagents and High Purity Chemical Substances, National Research Center “Kurchatov Institute,”
Moscow, Russia

^d Shubnikov Institute of Crystallography, Federal Research Center “Crystallography and Photonics,”
Russian Academy of Sciences, Moscow, Russia

*e-mail: pojidaev2006@yandex.ru

Received July 12, 2022; revised July 12, 2022; accepted July 15, 2022

Abstract—The research presents the results of studying a series of samples of organic materials preserved on the inner surface of ancient ceramic vessels which were found at the bottom of the Kerch Bay during underwater archaeological excavations. Using the method of gas chromatography-mass spectrometry, the composition of organic compounds was determined and the contents of the vessels were identified: traces of olive oil were found in five, traces of fish products in nine, traces of wine in 32 (17 from red grape varieties, 15 from white grape varieties), and one contained traces of turpentine oil. In six vessels, traces of both wine and fatty acids were found, which can probably be considered a sign of reuse of the container. The obtained results are a valuable source of data on the range and geography of commodity supplies in antiquity.

DOI: 10.1134/S2635167622050147

INTRODUCTION

In 2014, during a survey of the projected route for the Crimean bridge at the bottom of the Kerch Bay near Cape Ak-Burun, a large accumulation of fragments of pottery, dating mainly from the VI century BC—V century AD was found. As a result of underwater excavations in 2015–2017, carried out by the expedition of the Institute of Archeology of the Russian Academy of Sciences, about 70000 archaeological objects were recovered from the sea: mainly container, kitchen, table and building ceramics, lamps, lutheria, and terracotta [1]. It was found that these objects belonging to the cultural layer of the port of Panticapaeum, had originally deposited at the bottom of the Genoese harbor of Kerch and had been moved to Cape Ak-Burun during dredging. This cultural layer was damaged and mixed by displacement, but has retained its scientific significance, as it contains many highly preserved items, showing a wide range of pottery imports from Panticapaeum throughout its history. Due to the long stay of these objects in the conservation layer of bottom sediments, many of them retained the remains of organic substances, probably the products contained in them or waterproofing coatings.

By now detailed typologies have been developed for most forms of amphora containers, areas and peri-

ods of production have been determined, but it is rarely possible to convincingly establish the type of products contained in them: after being in the ground for a long time, organic remains usually do not remain. Often it is not even possible to establish whether a vessel has been subjected to resin to increase its waterproofing properties.

The discovery of a large series of amphora containers of different times and different types with the remains of the products contained in it, brought to Panticapaeum from a number of manufacturing centers of the Mediterranean and Asia Minor, allows to obtain unique data on the composition of Bosphoran imports.

Container ceramics in the Mediterranean and Black Sea regions were mainly used for the transportation of wine, vegetable oils, fish sauces, oil and products of its processing [2–6]. Thermally treated resins [7–14], usually pine resins (Pinaceae), were used as a waterproofing coating on the inner surface of the container, which has been proven by the presence of their biomarkers: dehydroabiatic, 7-hydroxy-dehydroabiatic, and 7-oxodehydroabiatic acids [9, 10].

Undoubtedly, in the Mediterranean and the Black Sea region, wine was one of the main items of trade. The oldest traces of wine in amphoras date back to 5400–5000 BC [15]. Numerous researches on the

determination of biomarkers of wine residues have shown that they include tartaric, hydroxybenzoic, syringic, and succinic acids [14–16]. Syringic acid is proposed to be considered a biomarker for red wines [17–19].

No less important goods for the region were vegetable (mainly olive) oil and fish sauce (garum) [25]. To identify fatty or oily organic residues, the ratios of saturated fatty acids in triacylglycerides are used [21–25], usually the ratio of the content of palmitic and stearic acids (P : S) [25–27].

Thus, the contents of amphora containers can be identified due to characteristic biomarkers.

The purpose of this study is to determine the composition of organic residues preserved on vessels from the bottom of the Kerch Bay, and to identify the types of products that were stored in them.

EXPERIMENTAL

Objects. From a large array of fragmented ceramic vessels with traces of organic residues, a series of 53 samples was taken, mainly from the inner surface of the bottoms. A description of the samples is given in Table 1.

For the sequential testing of various hypotheses, specialized sample preparation was performed for each type of residue. All used solvents and reagents were chemically pure (CP) or for high-efficiency liquid chromatography (HPLC).

Determination of the presence of petroleum oil and wax hydrocarbons. 0.5 mL *n*-hexane was added to a weighed portion of ~200 mg of a powdered sample. Extraction was carried out in an ultrasonic bath for 60 min at 60°C. The resulting suspension was centrifuged (4000 rpm, 10 min). The liquid above the precipitate was separated, the solvent was removed with a flow of nitrogen to a dry residue and dissolved in 200 μ L of hexane.

Determination of residues of other organic substances. After extraction with hexane, 0.5 mL of a 2% solution of sulfuric acid in methanol was added to the solution and heated under reflux for 3 h. After heating was completed, the reaction mixture was cooled to room temperature, 5 mL of diethyl ether and 3 mL of water were added and shaken for 5 min. The layers were separated, the upper ethereal layer was separated. The ether was removed with a nitrogen flow to dryness and dissolved in 200 μ L of methyl tert-butyl ether.

Analysis was carried out using the gas chromatography–mass spectrometry method (GC/MS) on an HP-6890 chromatograph equipped with an Agilent Technologies MSD 5975 mass-spectrometry detector. Chromatography conditions: an HP-5ms capillary column of 30 m long and 0.25 mm in inner diameter and a stationary-phase film thickness of 0.25 μ m. The initial temperature of the column is 80°C (exposure 5 min); temperature programming was carried out

from 80 to 280°C at a rate of 5°C/min. Exposure occurred at the final temperature for 10 min. The carrier gas was helium, at 1 mL/min, with a split ratio of 1 : 10. The evaporator temperature was 280°C and the detector interface temperature was 280°C. The sample volume was 1 μ L. Detection was performed using the electron-impact-ionization method in the scanning mode for a total ion current in the range of 50–900 *m/z*. The scanning rate was 1.76 scans/s, the ionization energy was 70 eV, and the temperatures of the quadrupole and ion source were 150 and 230°C.

Compounds were identified using mass spectra from the NIST/EPA/NIH mass spectral library 2014 database.

RESULTS AND DISCUSSION

In the hexane extracts of the entire series of studied samples, no alkane hydrocarbons were found; therefore, these vessels did not contain petroleum oil and waxes.

The results of identification of other identified compounds are given in Tables 2–5.

All studied samples contained dehydroabietic and 7-oxodehydroabietic resin acids (pine-resin biomarkers), as well as alkyl-substituted phenanthrenes, mainly retene, i.e., products of its thermal degradation [9, 10].

In one sample (RA-114), in contrast to the rest of the series, in addition to biomarkers of pine resin, there have been trace amounts of (about 0.15% in total): α - and β -pinene, 3-carene, camphene, myrcene, limonene, cymene terpineol, borneol and sesquiterpene, which are the main components of turpentine oil obtained by the distillation of coniferous resin. We note that in ancient times, turpentine oil was used in medicine and as a solvent.

In 38 samples (Tables 2–4) tartaric, hydroxybenzoic, syringic, and succinic acids have been found, which are characteristic wine markers. These compounds are absent in pine resin, vegetable oils and animal fats, which allows us to conclude that these vessels were used to store wine.

In 23 samples of the studied series, syringic acid was identified, the content of which reaches 0.5% (Tables 2, 4). In 15 other samples (Table 3) syringic acid is not detected, or its content does not exceed 0.07%. Since syringic acid is considered a biomarker of red wine, it can be assumed that in 23 amphoras (Tables 2, 4), red wine was stored, and in 15, white (Table 3).

In addition to biomarkers of wine, saturated fatty acids were found in the studied samples: tetradecanoic (myristic), hexadecanoic (palmitic), octadecanoic (stearic), and dicarboxylic nonadiic (azelaic). The total amount of fatty acids in different samples varies. Fatty acids in the composition of esters of glycerol (acylglycerides) are present in almost all animal

Table 1. Description of the samples. Samples were taken mainly from the inner surface of the bottoms of vessels

Sample	Sample code	Region of production and dating
1	PRA-1	Sinope, IV–V centuries AD
2	PRA-22	Crete, second quarter of the VI–first half of the VII centuries AD
3	PRA-28	Pontus, second quarter of the VI–VII centuries AD
4	KS-7	Sinope, 350–340 BC
5	KS-17	Mende, IV century BC
6–7	KS-21, 22	Kos, IV–II centuries BC
8	KS-30	undefined center and date
9	KS-37	presumably Kos, IV–II centuries BC
10	KS-41	Kos, IV century BC
11	KS-15	Sinope, last quarter of the IV century BC
12	KS-5	Heraclea, mid-IV century BC
13	KS-13	Heraclea, end of the IV–first quarter of the III centuries BC
14	KS-33	Sinope, circa 362 BC
15	KS-34	Heraclea, II century AD
16	KS-40	Rhodes, II century BC
17	KS-6	Heraclea, mid-IV century BC
18	RA-11	Aegean, II–IV centuries AD
19–21	RA-14, 26, 27	Heraclea, second half of I century BC–first third of the II century AD
22	RA-28	Heraclea, I–II centuries AD
23	RA-47	Heraclea, I century BC–II century AD
24	RA-49	Heraclea, mid-I century BC–first third of the II century AD
25–30	RA-52, 67, 89, 90, 94, 130	Bosporus, II–III centuries AD
31	RA-53	Aegean, II–IV centuries AD
32–37	RA-63, 70, 71, 73, 95, 96	Colchis, I century BC–II century AD
38–39	RA-65, 74	Sinope, I century BC–II century AD
40	RA-85	Heraclea, III century AD
41	RA-86	Heraclea, I century BC–II century AD
42–43	RA-88, 104	Aegean, I–III centuries AD
44	RA-97	Heraclea, I century BC–II century AD
45	RA-99	Heraclea, I century BC–first third of the II century AD
46	RA-113	Heraclea, second half of I century BC–first third of the II century AD
47	RA-114	Heraclea, I century BC–II century AD
48	RA-116	Pontus, II–III centuries AD
49	RA-117	Heraclea, III century AD
50–51	RA-118	Aegean, II–IV centuries AD
52	RA-132	Heraclea, I–II centuries AD
53	RA-139	Heraclea, 2nd quarter of the I–III centuries AD

Table 2. Composition of the main compounds in samples with identified wine markers from red grape varieties

Sample	Compound	Sample code																
		RA-65	RA-71	RA-86	RA-89	RA-94	RA-95	RA-96	RA-97	RA-99	RA-113	RA-117	RA-14	RA-27	RA-28	RA-49	RA-67	RA-139
1	Succinic acid			0.01	0.02	0.01		0.01				0.04			0.02			
2	Tartaric acid	0.88	0.05	0.00	0.02	0.01	0.02	0.08	0.08	0.15	0.09	0.07	0.13	0.06	0.12	0.07	0.04	0.12
3	4-Hydroxybenzoic acid	0.63	0.02	0.02	0.02	0.01	0.02	0.10	0.06	0.10	0.23	0.15	0.05	0.05	0.07	0.08	0.04	0.12
4	Azelaic acid			0.02	0.02			0.07	0.15	0.14		0.07	0.22	0.08	0.16	0.06	0.06	
5	Syringic acid	0.20	0.38	0.45	0.21	0.15	0.18	0.16	0.21	0.40	0.15	0.12	0.32	0.13	0.12	0.11	0.14	0.14
6	Myristic acid	–	0.03	0.01	0.04	0.04	0.04	0.05	0.04	0.04	0.07	0.10	0.03	0.02	0.02	0.03	0.05	0.02
7	Palmitic acid	0.6	1.5	0.2	0.5	0.5	0.3	0.4	0.9	4.1	0.6	0.4	4.8	2.3	1.6	0.4	1.1	2.2
8	3,6-Dimethyl-phenanthrene	0.9	1.9	2.1	2.1	2.1	3.0	2.7	2.4	1.5	3.5	2.3	1.4	1.9	1.4	0.5	1.6	2.3
9	10,18-Bisnor-abieta-pentaene	5.4	3.8	1.3	4.5	6.2	4.8	2.5	2.0	7.9	3.5	2.6	5.3	6.6	3.7	2.4	5.6	6.7
10	Stearic acid	0.5	0.5	0.3	0.2	0.3	0.11	0.1	0.3	1.4	0.3	0.4	1.9	0.8	0.6	0.1	0.3	1.0
11	2,3,5-Trimethyl-phenanthrene	0.8	1.0	0.5	0.4	2.7	1.3	0.5	0.6	0.9	0.5	0.5	1.2	1.7	0.7	0.5	0.4	0.8
12	Retene	5.8	15.7	11.1	5.7	21.2	16.2	14.4	5.8	19.7	19.4	8.1	16.0	15.1	6.8	11.1	12.4	16.6
13	8-Isopropyl, 1,3-dimethyl-phenanthrene	13.1	5.3	1.2	4.8	5.3	2.7	2.8	1.7	5.2	13.2	2.5	4.60	2.91	4.44	1.23	2.7	10.5
14	1-Phenanthrene-carboxylic acid	11.3	8.1	4.3	3.1	6.9	8.1	9.1	6.7	4.2	7.2	7.4	3.8	13.2	10.4	4.3	6.1	6.6
15	Dehydroabietic acid	17.2	30.4	7.9	12.8	29.4	38.6	22.7	24.4	7.8	10.0	13.9	12.6	23.1	27.4	7.9	31.2	15.5
16	7-Oxodehydroabietic acid	2.4	4.8	1.3	2.5	1.2	4.3	8.7	4.1	2.3	5.2	6.7	2.8	10.3	6.1	1.3	2.0	3.7
	Amount of fatty acids	1.1	2.0	0.5	0.7	0.9	0.5	0.6	1.4	5.6	1.0	0.9	7.0	0.6	2.4	0.5	1.6	3.3

and/or vegetable products, including wines and resins of coniferous trees. At the same time, their content varies significantly: in vegetable oils it is up to 100%, in animal fats, about 80%, and in the resins of coniferous trees and wines, it is no more than a few percent.

Analyzing the results of determining the total content of “fat” residues, we can come to the following conclusions.

The samples containing wine biomarkers and a low percentage of fatty acids (0.25–1.7%), apparently, belong to vessels in which grape wine was stored.

Samples in which no wine markers were found and the amount of fatty acids reaches 47% (6.3–47.1%) belong to vessels in which products with a high content of acylglycerides (animal fats, vegetable oils) were stored.

Samples with a high content of fatty acids (Table 5) according to the ratio of palmitic and stearic acids (P : S) can be divided into two groups:

– group I (five samples: KS-7, KS-15, KS-21, KS-40, RA-130) with a P : S ratio of 4.8–5.1;

– group II (nine samples: RA-11, RA-53, RA-73, RA-74, RA-88, RA-90, RA-104, RA-116, RA-120) with a P : S ratio of 2.6–3.1.

The fatty-acid compositions of various animal fats and vegetable oils are given in Table 6 [28, 29]. It follows from this that the ratio of the content of palmitic and stearic acids (P : S) in animal products is 1–2, in fish products, 2.5–3.5, and in vegetable oils, 3–6. Myristic acid (14 : 0) is found only in products of animal origin, in vegetable oils it is present in small quantities (less than 0.1%).

In samples of group I, the content of myristic acid does not exceed 0.02%, and the P : S values are in the range of 4.8–5.1 (Table 5). Comparing these results with the data from Table 6, we can conclude that olive oil was stored in the vessels of this group.

Table 3. Composition of the main compounds in samples with identified wine markers from white grape varieties

Sample	Compound	Sample code														
		KS-5	KS-6	KS-33	KS-37	PRA-1	PRA-22	PRA-28	RA-26	RA-47	RA-52	RA-53	RA-63	RA-70	RA-118	RA-132
1	Succinic acid				0.05	0.02	0.11	1.64	0.02	0.02			0.03			0.01
2	Tartaric acid	0.13	0.01	0.01	0.03	0.01	0.03	0.39	0.07	0.10	0.02	0.02	0.03	0.02	0.05	0.01
3	4-Hydroxybenzoic acid	0.19	0.14	0.02	0.04	0.02	0.03	0.19	0.09	0.12	0.01	0.01	0.06	0.06	0.06	0.01
4	Azelaic acid	0.08	0.07	0.02	0.05	0.00	0.00	0.00	0.08	0.08		0.6	0.03	0.01		
5	Syringic acid	0.02	0.02	0.02	0.02	0.01	0.05	0.02		0.03	0.05		0.02	0.02	0.04	0.07
6	Myristic acid	0.02	0.02	0.02	0.06	0.02	0.01	0.02	0.07	0.10	0.05	2.65	0.02	0.06	0.06	0.05
7	Palmitic acid	0.10	0.08	0.09	0.38	0.10	0.71	0.75	0.39	0.63	0.80	10.47	0.28	0.09	0.98	0.35
8	3,6-Dimethylphenanthrene	0.6	0.6	0.5	1.5	1.3	1.2	2.2	1.2	1.3	1.4	1.1	1.7	1.5	2.0	2.1
9	10,18-Bisnor-abietapentaene	2.2	2.3	1.9	8.4	2.5	2.0	5.3	2.2	2.8	7.6	3.3	3.7	3.2	5.6	5.4
10	Stearic acid	0.5	0.3	0.1	0.5	0.3	0.7	0.9	0.5	0.6	0.7	3.9	0.2	0.7	0.3	0.7
11	2,3,5-trimethyl-phenanthrene	0.6	0.2	0.4	1.2	0.3	1.1	1.5	0.7	0.7	0.9	2.9	1.1	0.8	0.8	0.9
12	Retene	20.1	12.3	6.5	27.4	13.1	22.5	13.1	12.6	15.1	12.7	6.9	20.3	14.5	11.9	14.9
13	8-Isopropyl, 1,3-dimethylphenanthrene	0.9	1.6	0.9	7.7	4.5	3.5	10.8	3.0	3.1	3.3	1.7	2.8	3.3	2.4	3.7
14	1-Phenanthrenecarboxylic acid	19.0	18.8	20.4	6.8	11.7	6.6	8.4	10.4	4.8	4.9	8.3	2.7	4.3	8.4	4.4
15	Dehydroabietic acid	38.1	46.8	47.5	22.0	54.4	47.3	28.9	19.3	12.0	24.7	17.5	8.2	6.0	26.6	30.8
16	7-Oxodehydro-abietic acid	21.5	19.8	11.6	6.6	5.9	7.1	1.6	7.7	4.7	1.5	6.0	2.0	0.7	5.2	2.3
	Amount of fatty acids	0.71	0.4	0.2	1.0	0.39	1.6	1.7	1.0	1.4	1.6	15.0	0.5	0.8	1.4	1.1

Table 4. Composition of the main compounds in the samples with the revealed presence of traces of wine and fish products (presumably reused vessels)

Sample	Compound	Sample code					
		RA-14	RA-27	RA-28	RA-71	RA-99	RA-139
1	Succinic acid						
2	Tartaric acid	0.13	0.06	0.12	0.05	0.15	0.23
3	4-Hydroxybenzoic acid	0.05	0.05	0.07	0.02	0.10	0.05
4	Azelaic acid	0.22	0.08	0.16		0.14	
5	Syringic acid	0.32	0.13	0.12	0.38	0.40	0.14
6	Myristic acid	0.03	0.02	0.02	0.03	0.04	0.02
7	Palmitic acid	4.8	2.3	1.6	1.5	4.1	2.2
8	3,6-Dimethylphenanthrene	1.4	1.9	2.8	2.6	2.9	2.3
9	10,18-Bisnor-abietapentaene	5.3	6.6	3.7	3.8	7.9	6.7
10	Stearic acid	1.9	0.8	0.6	0.5	1.4	1.0
11	2,3,5-Trimethyl-phenanthrene	0.9	1.7	0.8	1.0	0.9	0.8
12	Retene	16.0	15.7	6.8	15.7	19.7	16.6
13	8-Isopropyl, 1,3-dimethylphenanthrene	4.6	7.5	4.4	5.3	5.2	10.5
14	1-Phenanthrenecarboxylic acid	3.8	5.1	10.4	8.1	4.2	6.6
15	Dehydroabietic acid	12.6	12.8	27.4	30.4	7.8	15.5
16	7-Oxodehydro-abietic acid	2.8	3.1	6.1	4.8	3.7	3.7
	Amount of fatty acids	7.0	3.2	2.4	2.0	5.6	3.3
	P : S	2.5	2.9	2.7	3.0	2.9	2.2

Table 5. Composition of major compounds in samples with identified vegetable oil/fish sauce markers

Sample	Compound	Sample code													
		KS-7	KS-15	KS-21	KS-40	RA-11	RA-53	RA-73	RA-74	RA-88	RA-90	RA-104	RA-116	RA-120	RA-130
1	Succinic acid														
2	Tartaric acid														
3	4-Hydroxybenzoic acid														
4	Azelaic acid	2.4	3.6	1.3	2.4		0.6					0.4	2.2		0.4
5	Syringic acid														
6	Myristic acid	0.02	0.02	0.02	0.02	2.5	2.6	0.3	0.5	1.8	0.7	0.5	1.2	0.5	0.02
7	Palmitic acid	9.3	4.9	4.2	12.9	32.2	10.5	1.8	3.1	13.8	1.4	6.3	10.7	5.6	4.9
8	3,6-Dimethylphenanthrene			2.2		1.2									2.6
9	10,18-Bisnorabieta-pentayen		6.8	4.0	8.7	5.5	3.3	2.9	7.6	5.5	8.2	3.9	6.2	1.9	6.7
10	Stearic acid	1.8	1.1	0.9	2.5	12.4	3.9	0.7	1.0	4.5	0.5	2.3	4.2	1.9	1.0
11	Trimethylphenanthrene		0.7	1.7				7.3			1.2				1.6
12	Retene	11.0	16.3	12.9	20.7	5.4	6.9	7.27	11.5	2.9	2.1	6.9	3.0	2.2	15.1
13	Isopropyl, dimethylphenanthrene	6.7	6.2	3.8	7.4	1.1			2.1		3.1	1.2			8.9
14	1-Phenanthrenecarboxylic acid	14.6	13.6	6.9	7.3	2.7	8.3	6.3	7.9	4.8	7.9	6.9	3.9	1.8	6.5
15	Dehydroabietic acid	32.5	23.1	42.1	24.2	6.7	17.5	16.9	16.7	12.2	33.7	20.0	8.4	5.6	2.3
16	7-Oxodehydroabietic acid	16.8	12.1	7.3	8.2	1.6	6.0	4.6	8.4	3.6	3.4	6.6	3.0	1.7	3.7
Amount of fatty acids		8.9	10.1	7.0	18.0	47.1	15.0	2.5	4.4	20.1	2.6	9.2	18.3	8.0	6.4
P : S		5.1	4.5	4.8	5.1	2.6	2.7	2.7	3.0	3.1	2.9	2.7	2.6	2.9	5.0

Table 6. Fatty-acid compositions of modern animal fats and vegetable oils

Animal and plant products	Composition of fatty acids*, %					
	A : N (A is the number of carbon atoms; N is the number of unsaturated bonds)					
	14 : 0	16 : 0	18 : 0	18 : 1	18 : 2	P : S
Beef	3.0 ± 0.9	27 ± 5	24 ± 6	38 ± 10	3.7 ± 2.0	1.1 ± 0.2
Mutton	2.9 ± 1.1	27 ± 11	26 ± 6	36 ± 13	4.8 ± 2.5	1.0 ± 0.3
Pork	1.4 ± 0.7	27 ± 3	16 ± 5	43 ± 10	7.5 ± 3.2	1.9 ± 0.3
Fish	3.0 ± 1.0	12 ± 4	2.0 ± 1.0	31 ± 4	37 ± 6	3.0 ± 0.5
Sunflower oil	0.02 ± 0.01	8.2 ± 1.8	2.9 ± 0.8	34 ± 9	57 ± 11	2.9 ± 0.2
Olive oil	0.01 ± 0.01	11.5 ± 1.8	2.5 ± 1.0	80 ± 15	8.2 ± 4.1	5.1 ± 1.3
Corn oil	0.03 ± 0.01	12.0 ± 1.1	1.7 ± 1.2	31 ± 3	54 ± 5	5.5 ± 1.6
Peanut butter	0.1 ± 0.1	9.5 ± 0.9	2.3 ± 0.7	45 ± 6	31 ± 6	4.1 ± 0.6

* 14 : 0 is myristic acid; 16 : 0 is palmitic acid; 18 : 0 is stearic acid, 18 : 1 is oleic acid; 18 : 2 linoleic acid; P : S is the ratio of palmitic and stearic acids.

The fatty residues of group-II specimens contain more pronounced amounts of myristic acid (0.48–2.65%). Since the P/S values are in the range of 2.6–3.1 (Table 5), these samples refer to vessels containing products of animal origin (probably garum fish sauce).

The presence in the composition of the six studied samples of both “wine” markers and a significant amount of fatty acid (2.0–7.0%, Table 4) can be explained by the practice of reusing vessels for storing

a different type of product, for example, oil or fish sauce could be stored in wine amphoras.

CONCLUSIONS

As a result of studying a series of 53 samples of organic compounds by GC/MS, the types of products that were contained in the corresponding vessels were established:

- in one vessel there are traces of turpentine oil;
- in five vessels there are traces of olive oil;
- nine vessels contain traces of fish products (probably sauce);
- in 38 vessels there are traces of wine (in 23, from red grape varieties and in 15, from white grape varieties);
- in six vessels, traces of reuse were found; probably, fish sauce was placed in amphoras for wine.

Evidence-based identification of product types and their comparison with a well-developed classification of areas and periods of production of amphora containers provides researchers with new opportunities to study the composition of Bosphorus imports from a number of cities of the Mediterranean and the Southern Black Sea region.

ACKNOWLEDGMENTS

We are grateful to A.V. Smokotina (Vernadsky Crimean Federal University, Simferopol) for the identification of the ceramic vessels and M.A. Nikitin (Institute of Archaeology of the Russian Academy of Sciences, Moscow) for taking the series of samples.

REFERENCES

1. S. V. Ol'khovskii, *Tavrish. Studii*, No. 12, 118 (2017).
2. G. A. Lomtadze, V. M. Pozhidaev, and V. P. Tolstikov, *Drevn. Bospora* **21**, 1 (2017).
3. V. M. Pojidaev, Ya. E. Sergeeva, V. M. Retivov, S. K. Belus', E. B. Yatsishina, and P. K. Kashkarov, *J. Anal. Chem.* **73**, 929 (2018).
<https://doi.org/10.1134/S1061934818090125>
4. I. I. Lyapushkin, *Slavic-Russian Settlements of the 9th–12th Centuries on the Don and Taman* (MIA, Moscow, 1941), p. 6 [in Russian].
5. S. A. Pletneva, *Ceramics and Glass of Ancient Tmutarakan* (BAM, Moscow, 1963), p. 52 [in Russian].
6. K. V. Kostrin, *Sov. Arkheol.*, No. 1, 285 (1967).
7. R. Stacey, C. Cartwright, and S. Tanimoto, *Brit. Museum Tech. Res. Bull.* **4**, 19 (2010).
8. M. P. Colombini, G. Giachi, F. Modugno, et al., *Geoarchaeol. Bioarchaeol. Stud.* **3**, 157 (2002).
9. I. Pastorova, K. J. van der Berg, J. J. Boon, et al., *J. Anal. Appl. Pyrol.* **43**, 41 (1997).
10. M. P. Colombini, G. Giachi, F. Modugno, et al., *Archaeometry* **45**, 649 (2003).
11. R. P. Evershed, *Archaeometry* **50**, 895 (2008).
12. C. W. Beck, C. J. Smart, and D. J. Ossenkop, in *Archaeological Chemistry IV*, Ed. by R. O. Allen (Am. Chem. Soc., 2004), p. 369.
13. F. Formenti, A. Hensard, and A. Tchernia, *Archaeonautica* **2**, 95 (1978).
14. F. Formenti and J. M. Duthel, in *The Origins and Ancient History of Wine*, Ed. by P. E. McGovern (Gordon and Breach, Langhorne, 1996), p. 79.
15. P. McGovern, *Ancient Wine: The Search for the Origins of Viniculture* (Princeton Univ. Press, Oxford, 2003).
16. R. H. Michel, P. E. McGovern, and V. R. Badler, *Anal. Chem.* **65**, 408A (1993).
17. M. R. Guasch-Jané, M. Ibero Gómez, C. Andrés-Lacueva, et al., *Anal. Chem.* **76**, 1672 (2004).
18. M. R. Guasch-Jané, M. Ibero Gómez, C. Andrés-Lacueva, et al., *J. Archaeol. Sci.* **33**, 1075 (2006).
19. H. Barnard, A. N. Dooley, G. Areshian, et al., *J. Archaeol. Sci.* **38**, 977 (2011).
20. J. Condamin, F. Formenti, M. O. Metais, et al., *Archaeometry*, No. 18, 195 (1976).
21. R. P. Evershed, S. N. Dudd, M. J. Lockhean, et al., in *Handbook of Archaeological Sciences* (2001), p. 331.
22. R. P. Evershed, H. R. Mottram, S. N. Dudd, et al., *Naturwissenschaften* **82**, 402 (1997).
23. R. P. Evershed, C. Heron, S. Charters, et al., *Proc. Brit. Acad.* **77**, 187 (1992).
24. M. Patrick, A. J. Dekoning, and A. B. Smith, *Archaeometry* **27**, 231 (1985).
25. R. P. Evershed, S. N. Dudd, M. S. Copley, et al., *Acc. Chem. Res.* **35**, 660 (2002).
26. M. P. Colombini, F. Modugno, and E. Ribechini, in *Organic Mass Spectrometry in Art and Archaeology*, Ed. by M. P. Colombini and F. Modugno (Wiley, Chichester, 2009), p. 191.
27. I. Bonaduce and A. Andreotti, in *Organic Mass Spectrometry in Art and Archaeology*, Ed. by M. P. Colombini and F. Modugno (Wiley, Chichester, 2009), p. 310.
28. V. M. Pozhidaev, Ya. E. Sergeeva, E. N. Ofitserov, et al., *Butler. Soobshch.* **56** (11), 47 (2018).
29. M. I. Goryaev and N. A. Evdakova, *Handbook of Organic Acid Chromatography* (Nauka, Alma-Ata, 1977) [in Russian].