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АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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The determination of the origin of natural bitumen in mummifying resins of Ancient Egyptian mummies from the collection of the Pushkin Museum of Fine Arts

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This work presents the results of a study of the resins of seven Ancient Egyptian mummies from the collection of the Pushkin State Museum of Fine Arts using a complex of analytical methods: gas chromatography, atomic emission and mass spectrometry. Natural bitumen and beeswax were identified in the resins using the gas chromatography–mass spectrometry method. Based on the results of hydrocarbon distribution in the profiles of n-alkanes in the resin coatings of the mummies and naturally occurring bitumen, it was assumed that the Dead Sea bitumen was used. The gas chromatography–mass spectrometry studies of mummy resins in the selected ion mode (m/z 217 and 191) provided additional evidence of the bitumen's geographic origin. Atomic emission spectrometry with inductively coupled plasma was used as a means to determine the content of microelements. Vanadium, nickel and molybdenum were found in the tar of five mummies. The determined relative amounts of vanadium, nickel, and molybdenum in the resins of the studied mummies showed a good correlation with the available data on the content of these elements in the Dead Sea bitumen, as well as the Fayum mummy resin based on this bitumen. The advantages of using the method of identifying bitumen in mummy resins based on relative content of vanadium, nickel, and molybdenum were revealed.

Keywords: *Ancient Egyptian mummies, natural bitumen, gas chromatography, mass spectrometry, atomic emission spectrometry.*

Определение происхождения природного битума в мумифицирующих смолах древнеегипетских мумий из собрания ГМИИ им. А.С. Пушкина

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В работе представлены результаты исследования составов смол семи древнеегипетских мумий из коллекции Государственного музея изобразительных искусств имени А.С. Пушкина с применением комплекса аналитических методов: газовой хроматографии (ГХ), атомно-эмиссионной и масс-спектрометрии (МС). Методом ГХ–МС в них идентифицированы природный битум и пчелиный воск. По результатам распределений углеводородов в профилях н-алканов в смоляных покрытиях мумий и природных битумов высказано предположение об использовании битума Мертвого моря. Дополнительные доказательства географического происхождения битума получены ГХ–МС-исследованием смол мумий в режиме мониторинга заданных ионов (m/z 217 и 191). Методом атомно-эмиссионной спектрометрии с индуктивно связанной плазмой определено содержание микроэлементов и показано, что в смолах пяти мумий присутствуют ванадий, никель и молибден. Полученные результаты свидетельствуют об удовлетворительной корреляции их с литературными данными по содержанию указанных элементов в битуме Мертвого моря и смоле Фаюмской мумии на основе этого битума. Выявлены преимущества использования метода идентификации битума в смолах мумий по относительному содержанию ванадия, никеля и молибдена.

Ключевые слова: *древнеегипетские мумии, природный битум, газовая хроматография, масс-спектрометрия, атомно-эмиссионная спектрометрия.*

Introduction

Mummification is an integral part of Ancient Egyptian culture. The origin of the practice can be traced back to the early period of Ancient Egyptian history – the Neolithic era, 5000–4000 BC [1–7]. The first evidence of the artificial preservation of bodies relates to the archaeological culture of Badari (about 4500–4100 BC): at that time, some parts of the body were tightly wrapped in linen bandages saturated with resinous substances. Ancient Egyptian sources describing mummification have not been preserved. The first detailed descriptions were made by the ancient authors who visited Egypt, Herodotus (5th century BC) and Diodorus of Sicily (1st century BC) [1–3].

Currently, comprehensive studies of mummies are carried out by specialists in various fields of science. Abroad, systematic studies of Egyptian mummies by natural-scientific methods have been carried out since the 1990s, for which an interdisciplinary approach is widely used [1, 4–6]. In Russia, a comprehensive interdisciplinary study of Ancient Egyptian mummies was first conducted at the National Research Center "Kurchatov Institute" [7].

A large number of organic substances, including beeswax, natural bitumen, tar, resins of coniferous trees, animal fats, vegetable oils, as well as aromatic oils of some plants, were used for mummification in different periods in the history of Ancient Egypt [20]. Research of the resins for mummification was mainly related to the determination of the nature of the substances included in their composition. The quantitative composition of the components of the resins for mummification has not been extensively studied [9, 19, 20]. The most complete quantitative study of the composition of resins in eight Ancient Egyptian mummies from Mostageddah

(Badari culture, Upper Egypt) by a method of gas chromatography combined with mass spectrometry (GC–MS) was presented in a research by J. Jones et al. [19], where identified the following in the composition of the resins: vegetable oils and animal fat (34–95%), aromatic plant extracts (2.4–54%), pine resins (0.3–11%), bitumen (0.2–19%), vegetable and beeswax (0.2–7%).

One of the key points in the studying the resin coatings of Ancient Egyptian mummies is the development of methods for proving the use of bitumen in compositions for mummification and the determination of its geographical origin. The earliest occurrences of using the word "mummy" date around 1000 BC. According to the descriptions of Herodotus, Plutarch and Diodorus, natural bitumen was widely used in Egypt in preserving the bodies of the dead. Diodorus, Strabo, Pliny, Flavius, and Tacitus described the use of bitumen found in the Dead Sea [1–7] for these purposes.

A significant number of works in contemporary scientific literature has been devoted to the study of the use of bitumen in mummification. The primary areas of research are the reliable confirmation of the presence of bitumen in resin coatings of mummies and the determination of its origin. One of the first works on bitumen identification was the work of Benson et al. [21]: using gas chromatography, the authors studied the resin of the Egyptian mummy No. 1770 from the Historical Museum of Manchester. The profiles of *n*-alkanes in the mummy resin and bitumen from the Dead Sea were compared, and it was discovered that the Dead Sea bitumen has a characteristic alkane profile and is identical to the hydrocarbon profile of the mummy resin. Proefke and Rinehart conducted a study of an Egyptian mummy found in Fayoum oasis of Egypt [22] with the GC–MS method. *n*-Alkanes with a chain length of 19 to 33 carbon atoms were found in the mummy's resin. Distribution of saturated hydrocarbons in the resin coincided with the hydrocarbon profile of natural bitumen [23]. Normal paraffins with a chain length of 22 to 32 carbon atoms in the sample of mummy resin were discovered by Beck and Borromeo [24] and the bitumen was identified by their distribution. Hydrocarbon fractions of resins of four Egyptian mummies of a wide range of ages from the British Museum collection were studied by J. Rullkötter and A. Nissenbaum [25]: share of saturated alkanes in the hydrocarbon fractions of resins was at roughly 3%, close to the composition of the Dead Sea bitumen.

The GC analysis of the resins' hydrocarbon fraction of the Egyptian mummies dating to the 4th century BC from the Dakhleh oasis showed the presence of the long-chain *n*-alkanes with a predominance of hydrocarbons with an odd number of carbon atoms (C_{25}–C_{33}) [11], in addition to the Dead Sea bitumen. This, according to the authors, indicated the presence of terrestrial plant waxes. The distribution of *n*-alkanes, typical of the Dead Sea bitumen, was found only in one sample, while isoprenoid hydrocarbons, as well as marina and phytane, were completely absent.

Natural bitumen contains compounds known as "biomarkers", which have distinctive chemical structures closely related to their biological precursors: plants, bacteria and algae. Steranes and pentacyclic triterpenes (aromatic steroid hydrocarbons), which are widely used in organic geochemical correlation studies, are recognized as such biomarkers [26]. The distribution of these hydrocarbons varies across different deposits and is dependent on the geographical origin of bitumen [26–30]. Low chemical reactivity of the biomarkers and their resistance to photochemical and microbial degradation made it possible to use them to identify biodegraded crude oils [31–34], as well as naturally weathered bitumen [35, 36].

The distribution of steranes and triterpenes in the Dead Sea bitumen [37] was studied with the GC–MS method in the mode of monitoring specified characteristic ions (*m/z* 217 and 191). The presence of bitumen in the balms of 39 Egyptian mummies was analyzed with the same method and it was concluded [9, 14] that the black color of the mummy resin is not related to the content of bitumen, as was previously assumed. A number of mummies with an intense black resin coating did not contain bitumen; the black color of the resin was caused by the aging of animal or vegetable fats and beeswax esters. An additional confirmation of this conclusion was obtained via artificial replication of mummifying balms and their long-term heat treatment. Comparison of the distribution of steranes in the resins of the four mummies of the Roman period (4th century AD) from the Dakhleh oasis (Western Egypt) and the bitumen of the Dead Sea showed that they are close or practically coincided [11]. It should be noted, that the Dead Sea bitumen was identified in almost all studies of the compositions of mummifying resins in Ancient Egyptian mummies [11, 25, 31–33, 38, 39]. The bitumen of the Gebel El Zeit deposits was identified by studying the molecular distribution of steranes and terpenes by the GC–MS method in the bitumen of the Abu Durba and Gebel El Zeit deposits, (Gebel El Zeit, Suez Canal) and the scanning at *m/z* 191 and 217 in the resins of two Egyptian mummies [40, 41].

Thus, fossil hydrocarbons, such as profiles of *n*-alkanes (C_{19}–C_{35}), pristane, phytane, hopane derivatives and isomeric terpenes, may serve as the biomarkers of the presence and origin of bitumen in the embalming resins of Egyptian mummies.

Obstacles to the application of this identification method may be either the impossibility (in some cases) to detect pristane, phytane, hopanes and terpenes or their presence in trace amounts, that is, the lack of guarantees for their reliable identification in the mummifying compositions [12, 15]. At the same time, the presence of a well-defined profile of *n*-alkanes (C_{19}–C_{35}) makes it possible to reliably identify the presence of the products of oil origin in the mummies' resins [1, 12]. However, the lack of experimental data on the correspondence of the *n*-alkane profile to a specific field does not yet allow for determining the geographical origin of bitumen.

Most oils are characterized by the content of vanadium and nickel [42]. In the oils of some Volga-Ural deposits, the content of vanadium reaches 200–500 g/t. Approximately the same levels of vanadium and nickel are typical for the oils and bitumen in the West Canadian basin and the Orinoca basin in Venezuela [42–46]. The contents of vanadium and nickel are 4–6 and 0.3–0.5 kg/t respectively in the asphaltenes of carbonic oils of the Tatarstan Republic and Samara oblast. In the bitumen of oil fields in Syria, the share of these elements is 10–20 times lower [44–46]. These elements concentrate in bitumen and their ratio does not change in the course of oil refining or natural conversion processes. Therefore, the content and ratio of vanadium and nickel in natural bitumen can also serve as a biomarker of geographical origin.

Spielman was one of the first to detect the presence of vanadium, molybdenum, and nickel in the resins of Egyptian mummies [47]. He proved that the presence of these elements is a characteristic feature of the Dead Sea bitumen. Zaki and Iskander also identified vanadium, molybdenum and nickel [48] in the Persian mummy resin by spectrographic analysis and confirmed that the presence of these elements is an attribute of the Dead Sea bitumen. Also, 11.0 *ppm* vanadium and 93.8 *ppm* molybdenum[1] were detected in the resin of mummy No. 1770 by an atomic absorption spectroscopy [21]. The detection of 65 *ppm* vanadium, 33.4 *ppm* nickel and 17.4 *ppm* molybdenum [10] in the resin of the mummy from the Fayoum oasis confirmed Spielman's assumption [47] about the presence of the characteristic metals in the petroleum bitumen. Marshner and Wright [49] found Ni 10–200 *ppm* and V 30–300 *ppm* in several natural bitumen deposits of Mesopotamia.

Thus, the detection of vanadium, nickel and molybdenum in the resins of the mummies may be used to identify the presence of bitumen in mummification compositions. Furthermore, the quantitative ratios of these elements may be useful for determining the geographical origin of bitumen.

The purpose of this study is to identify and determine the origin of natural bitumen in the resins of seven Ancient Egyptian mummies from the Pushkin State Museum of Fine Arts collection using a set of analytical methods: gas chromatography, combined gas chromatography with mass spectrometry, and atomic emission spectroscopy.

Materials and Methods

Raw materials and reagents. The description of the exhibits from the Pushkin State Museum of Fine Arts collection submitted for the study is given in Table 1. The approximate dating of the mummies is 1000 years BC.

Table 1. The description of the studied exhibits from the Pushkin State Museum of Fine Arts collection

Mummy No.	Description, inventory No. of the Pushkin State Museum of Fine Arts
1	I – 1a 7150 Human mummy head in tarred shrouds. Length – 20 sm
2	I – 1a 6932 Mummy head. Height – 22 sm; girth – 53 sm
3	I – 1a 6505 Male mummy head. Height – 28 sm; girth – 54 sm
4	I – 1a 6506 Female mummy head. Height – 25 sm; girth – 53.5 sm
5	I – 1a 1241 Headless mummy, swaddled in a large number of bandages
6	I – 1a 5934 Female mummy head. Height – 24 sm, girth – 52 sm
7	I – 1a 1239 Mummy of Ipanha in a cardboard case

Test pieces of resinous substance were taken from the surface of the mummified bodies in the form of a naturally separated piece of resinous material of practically black color and odorless.

All solvents and reagents used in the work were qualified as "CP" (chemically pure) or "for HPLC" (for the high-performance liquid chromatography).

Sample preparation for the study and the identification of substances in the composition of the mummy resin. About 100 mg of the resin sample was ground, and 5 ml of *n*-hexane was added. Extraction was carried out in an ultrasonic bath for 60 min at 50 °C.

[1]For comparison: the Dead Sea natural bitumen contains V – 463 *ppm*, Ni – 251 *ppm*, Mo – 219 *ppm*.

The resulting suspension was centrifuged for 10 min at 5000 rpm. The supernatant was transferred to a mixing funnel, treated with an aqueous KOH solution (5%, 2×5 ml) and washed with water (2×5 ml). The organic layer was filtered through a paper filter with a small amount of anhydrous sodium sulfate, transferred to an evaporation cup, and the solvent was removed at room temperature. The residue was dissolved in 50 µl of hexane. Five milliliters of chloroform were added to the dry residue after extraction with hexane, and then extraction was carried out on an ultrasonic bath for 60 min at 50 °C, the resulting suspension was centrifuged (5000 rpm, 10 min). The supernatant was transferred to a mixing funnel, treated with an aqueous KOH solution (5%, 2×5 ml) and washed with water (2×5 ml). The organic layer was filtered through a paper filter with a small amount of anhydrous sodium sulfate and transferred to an evaporation cup. The solvent was removed at room temperature. The residue was dissolved in 50 µl of chloroform.

Fatty acid methyl esters (FAME) were obtained to confirm the presence of beeswax. For this purpose, the aqueous KOH solution after treatment with the hexane extract was acidified with a 20% aqueous solution of sulfuric acid and extracted with diethyl ether (2×5 ml). The ether layer was separated, filtered through a paper filter with a small amount of anhydrous sodium sulfate, transferred to an evaporation cup, after which the solvent was removed at room temperature. The residue was dissolved in 100 µl of chloroform and treated with methanol in presence of acetyl chloride according to the procedure described previously [50].

Hardware and auxiliary equipment

Chromatographic system 1. Gas chromatograph HP 6890 with mass spectrometric detector MSD 5975 (Agilent Technologies).

Chromatography conditions: the capillary column DB–5 ms, length is 30 m, inner diameter is 0.25 mm, stationary phase film thickness is 0.25 µm. The initial temperature of the column is 100 °C; temperature programming from 100 to 280 °C at a speed of 15 deg/min. Endurance at the final temperature is 10 min. The flow rate of the carrier gas (helium) is 1 ml/min; flow division 1:10. The temperature of the evaporator is 280 °C, the detector interface is 280 °C. The sample volume is 1 µl.

The analysis of the hexane extract was carried out in the scanning mode for the total ion current. Compounds were identified by mass spectra and retention indices of the NIST 14 2014/EPA/NIH database. The analysis of the chloroform extract was carried out in the mode of monitoring the specified ions (*m/z* 217 and 191).

Chromatographic system 2. Bruker 430 GC gas chromatograph with flame ionization detector.

Chromatography conditions: Capillary column Select™ Biodiselfor FAME, its length is 30 m, inner diameter is 0.32 mm, stationary phase film thickness is 0.25 µm. Temperature program of the column: initial temperature is 140 °C, held for 4 minutes. The temperature is risen to 260°C at the speed of 4 deg/min and held in isothermal mode for 10 minutes at 260 °C. Injector temperature is 260 °C, detector temperature is 260 °C. The flow rate of the carrier gas (nitrogen) is 2 ml/min, the division of the flow is 1:20. Sample volume is 2 µl.

Fatty acid methyl esters were identified using a FAME standard mixture (Supelco 37 Component $FAME_{Mix}$) and a comparison of the compounds retention parameters with the published data [12,13].

The determination of the micro-element content in mummy resins was carried out using inductively coupled plasma atomic emission spectroscopy (ICP) with iCAP 6300duo Thermo Scientific (USA) and the Thermo iTEVA (v. 2.5.0.84) software.

Standard 1 is the multielement calibration standard for ICP-spectroscopy ICP-MS-68B-100 Solution A (ICP-MS-68B-A-100) (5% HNO_3); standard 2 is the multielement calibration standard for ICP-spectroscopy ICP-MS-68B-100 Solution B (ICP-MS-68B-B-100) (5% HNO_3); standard 3 is the multielement calibration standard for ICP-spectroscopy MS-3 (5% HNO_3).

Sample preparation. About 10 mg of a sample of a mummy resin was weighed with an accuracy of up to 0.000001 g, then placed into an autoclave from PFA with a volume of 50 ml and dissolved in a mixture of nitric (4.5 ml) and hydrochloric acid (0.5 ml) in the unit for microwave decomposition of samples SINEO MDS10 (205 °C, 30 min). The solution was quantitatively transferred to an inert crucible, evaporated to a volume of 0.5 ml, transferred to a polymeric tube. The volume was adjusted to 10 ml with a 2% nitric acid solution.

Results and Discussion

In order to determine the composition of organic compounds present in the test resin taken from the surface of the body of the mummy, the sample was subjected to sequential extraction with various solvents. Identification of compounds in the extracts of embalming resins was carried out with GC–MS.

The chromatograms of the extracts of resins of two mummies in *n*-hexane are presented in Fig.1.

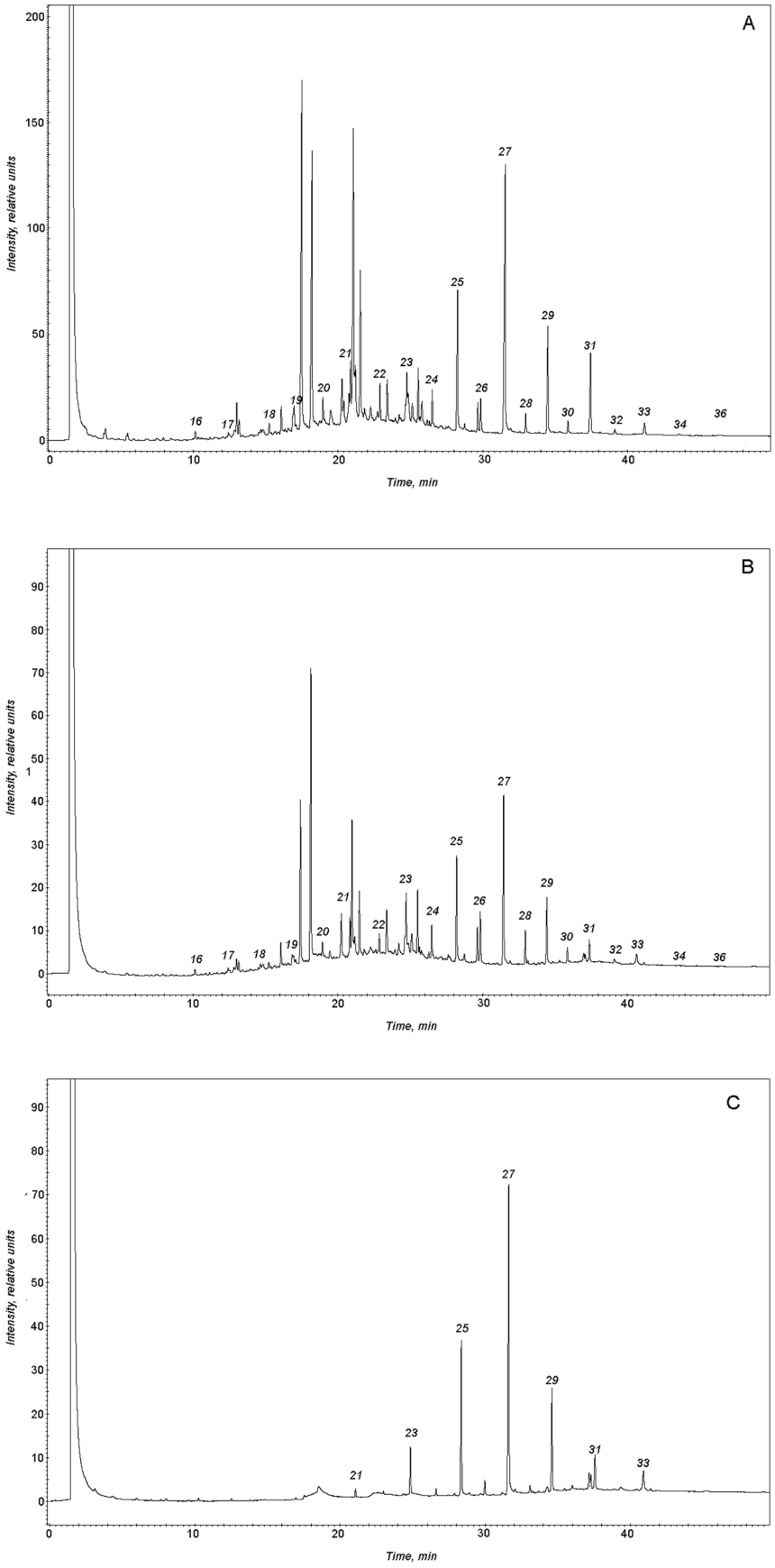

Fig. 1. Chromatograms of hydrocarbons in hexane extracts of the resins of two mummies (A, B) and beeswax (C).

The *n*-alkanes with a chain length of 16 to 35 carbon atoms were identified on the chromatograms of hexane extracts. There were three possible sources of normal saturated hydrocarbons (*n*-alkanes) with such a chain length: natural bitumen, bee and plant waxes in ancient Egypt. The predominance of *n*-alkanes C_{27}, C_{29}, C_{31} and C_{33} is typical for beeswax. A chromatogram of a solution of modern beeswax in *n*-hexane was recorded to identify wax in the resin.

The chromatogram of beeswax is also shown in Fig. 1. The predominance of C_{25}–C_{33} hydrocarbons in chromatograms of hexane resin extracts, typical for beeswax, leads to the assumption of its use in the embalming composition for the mummies.

To confirm the presence of beeswax fatty acids in the composition of mummies, alkaline solutions obtained after hexane extract treatment were studied. For what these solutions were acidified, extracted with diethyl ether, and then fatty acid methyl esters were obtained. Chromatographic separation was performed on a Select^{TM} Biodisel for FAME capillary column. The chromatograms of the FAME extract of one of the mummies resin and the beeswax are shown in Fig. 2.

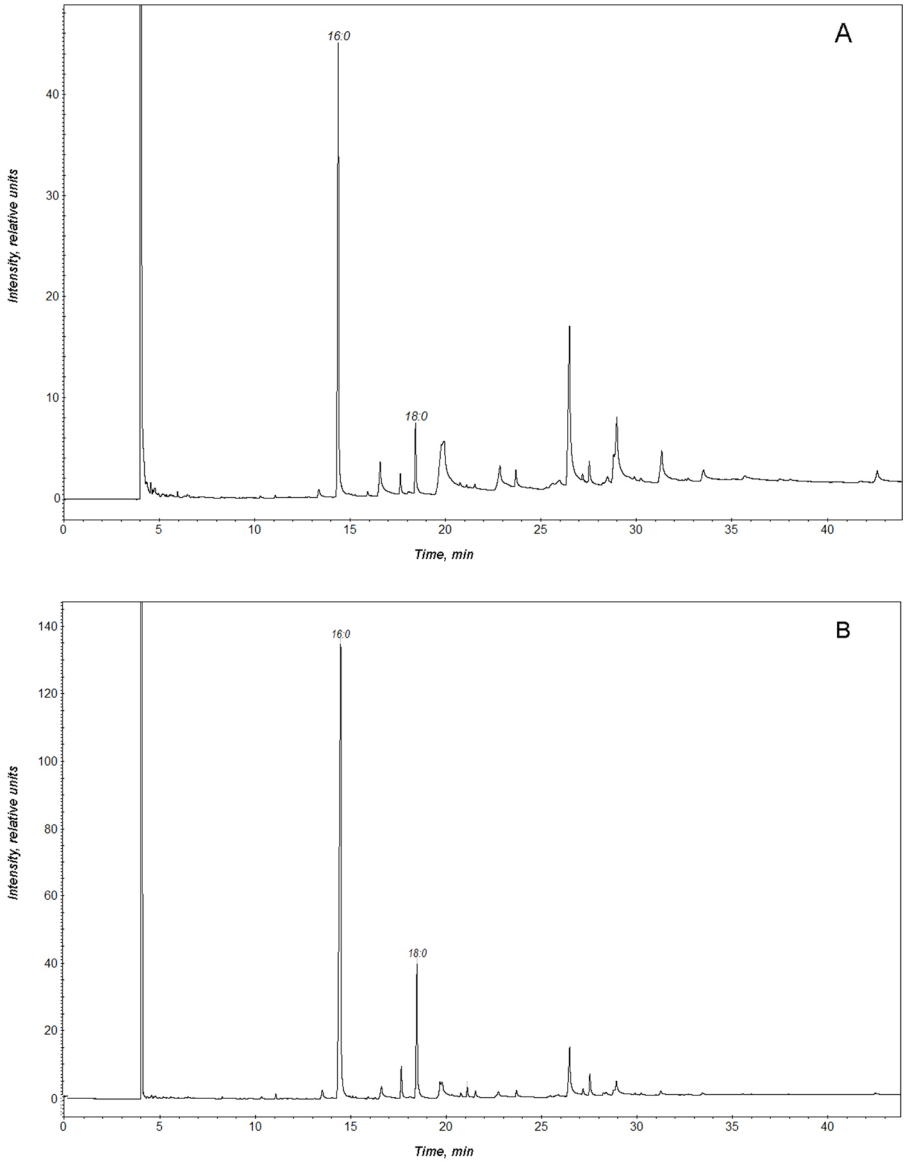

Fig. 2. Chromatograms of the FAME extract of one of the mummies (A) and the beeswax (B).

The chromatograms identified methyl esters of palmitic and stearic acids (Fig. 2). The relative content of these acids in resin samples of different mummies is 4.7–6.9 (for comparison: this ratio in the beeswax sample is about 5.2). A comparison of the obtained chromatograms confirms the beeswax using in the balsamic compositions of the studied mummies.

The *n*-alkanes with an even number of carbon atoms and a chain length of less than 23 atoms are absent at the beeswax chromatogram (Fig. 1B). These hydrocarbons were found in hexane extracts of resins of five mummies (Nos. 1, 3, 4, 6, 7), which allows

for the assumption of the presence of natural bitumen in the composition of the resins of these mummies. The examples of the presence of beeswax and natural bitumen in the resins of the mummies are described earlier [11, 19, 20, 51–53].

In order to establish the geographical origin of bitumen, histograms of the distribution of *n*-alkanes in the hydrocarbon profile of mummies were constructed. In order to exclude the influence of beeswax, the distribution profiles of *n*-alkanes were constructed by hydrocarbons with an even number of carbon atoms. The resulting histograms of hydrocarbon profiles are presented in Fig. 3. They show an approximately similar distribution of bitumen hydrocarbons in the resins of the studied mummies. The maximum hydrocarbon content is corresponded to the *n*-alkanes with the number of carbon atoms 22–26. The distribution of hydrocarbons in the resins of the mummies, in which bitumen from the Dead Sea basin was identified but beeswax was absent, was established in [19, 20]. The maximum distribution of hydrocarbons was observed in the region of 20–25 carbon atoms.

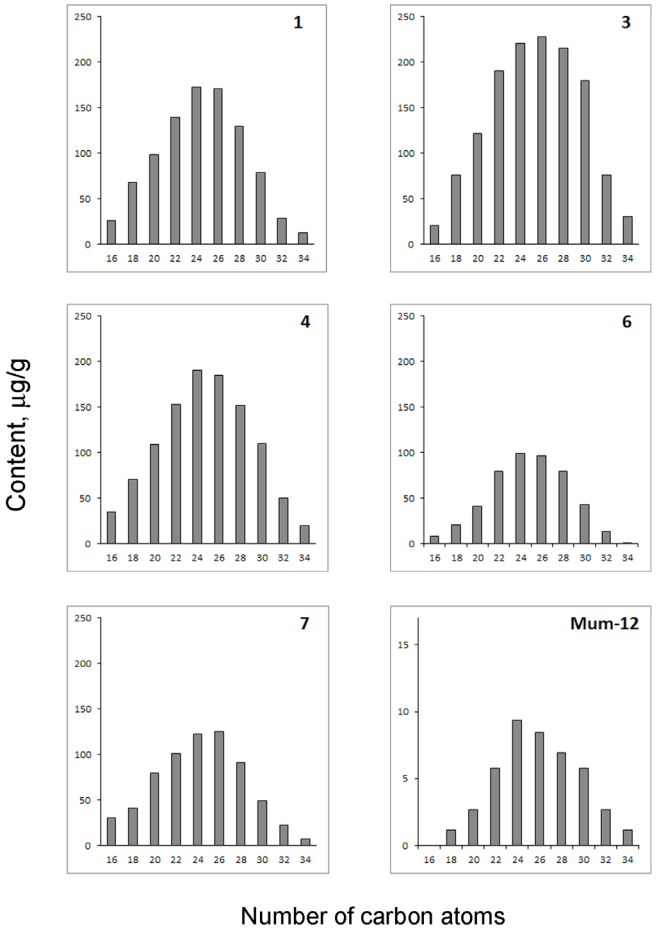

Fig. 3. Histograms of distribution of *n*-alkanes in the hydrocarbon profile of the resins of the studied mummies (Nos. 1, 3, 4, 6, 7) and the resin of Mum-12 mummy from Dakhleh oasis [8].

Based on the study of the distribution of *n*-alkanes in present-day bitumen from the Dead Sea and the resins of the Egyptian mummies from the Dakhleh oasis, it was shown [11] that the maximum in the Dead Sea bitumen profile was in the region of 19–22 carbon atoms. The maximum distribution of bitumen hydrocarbons in mummy resins (excluding beeswax hydrocarbons) was in the area of 20–26 carbon atoms. Despite a significant difference in the position of the maxima in the hydrocarbon profiles of bitumen resins of mummies and modern bitumen of the Dead Sea, the authors of [11] nevertheless made a conclusion about the use of bitumen from tar deposits of the Dead Sea basin in the composition of the mummy resins. It was confirmed by studies of the profiles of steranes in natural bitumen and mummies resins using the GC–MS method in the regime of monitoring the set ions (*m/z* 217).

The comparison of the distributions of hydrocarbons in resins that were obtained with the published data [11, 19, 20] allows for the assumption that the bitumen from the Dead Sea basin deposits was used in the resins of the studied mummies. We studied the chloroform extracts of mummy resins by GC–MS via scanning in the mode of monitoring the set ions (*m/z* 217 and 191) to confirm this assumption. The histograms of the content of some steranes in the extracts of mummy resins are presented in Figs. 4 and 5.

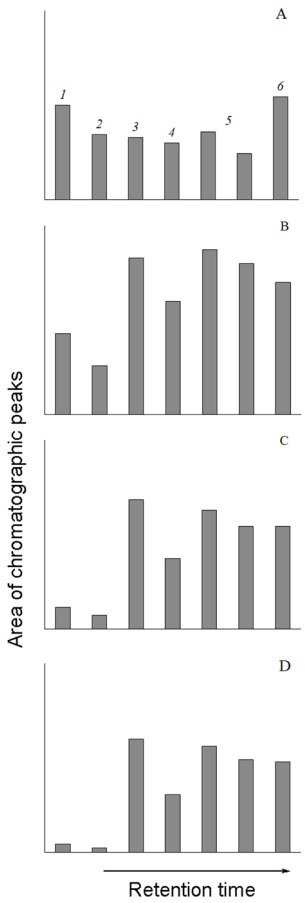

Fig. 4. Histograms of the content of steranes and hopanes (*m/z* 217) in the bitumen deposits of Gebel El Zeit (A); Abu Durba (B); Dead Sea (C) and in the resin of the mummy No. 7 (D):
1 – 13β,17α-diacholestane 20S (diasterane);
2 – 13β,17α-diacholestane 20R (diasterane);
3 – 5α,14β,17β-cholestane 20S;
4 – 5α,14α,17α-stigmastane 20S;
5a – 5α,14β,17β-stigmastane 20R;
5b – 5α,14β,17β-stigmastane 20S;
6 – 5α,14α,17α-stigmastane 20R.

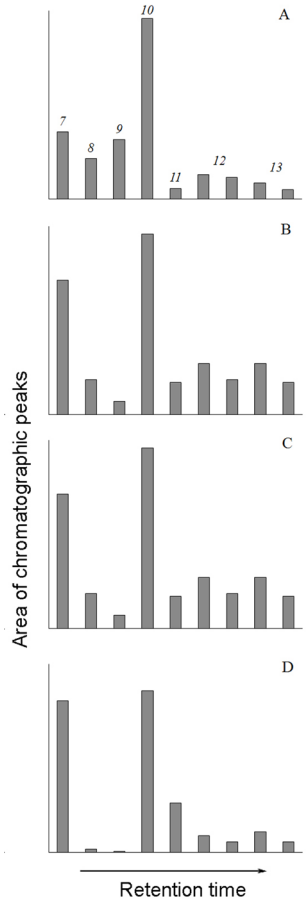

Fig. 5. Histograms of the content of steranes and hopanes (*m/z*191) in the bitumen deposits of Gebel El Zeit (A); Abu Durba (B); Dead Sea (C) and in the resin of the mummy No. 7 (D):
7 – 17α,1β(H)-30-norhopane;
8 – 18α(H)-30-neonorhopane; 9 – oleanane;
10 – 17α,21β(H)-30-hopane; 11 – gammacerane;
12a – 17α,21β(H)-29-tris-homohopane 22S;
12b – 17α,21β (H)-29-tris-homohopane 22R;
13a – 17α,21β(H)-29-pentakis-homohopane 22S;
13b – 17α,21β(H)-29-pentakis-homohopane 22R.

The obtained data were compared with the experimental data on the distributions of steranes and pentacyclic terpenes in the modern bitumens of three deposits in the basins of the Suez Canal and the Dead Sea, published in [41]. The phytane and prystane were not detected in the resins of the studied mummies. In resins of mummies No. 2 and No. 5, steranes and terpenes were also absent. In the resins of these two mummies, there were no *n*-alkanes with an even number of carbon atoms and a chain length of less than 23 atoms. The obtained results led to the assumption that there is no bitumen in the embalming compositions for mummies Nos. 2, 5.

There were practically no neonorhopane (18α(H)-30-neonorhopane) and oleanane on the chromatograms of chloroform extracts of the resins of mummies Nos. 1, 3, 4, 6, 7 under ion monitoring conditions at *m/z* 191. According to [41], these compounds are present in the bitumen of the Suez Canal deposits. In the bitumen of the Gebel El Zeit deposit, hydrocarbons are contained in rather large quantities, and in somewhat smaller quantities in the bitumen of the Abu Durba deposit. In the composition of the Dead Sea bitumen, only trace amounts of neonorhopane and oleanane are present [41].

The chromatograms of the resins of the studied mummies under ion monitoring at *m/z* 191 show a peak of gammacerane, which is typical for Dead Sea bitumen. In the bitumen deposits of the Suez Canal, only trace amounts of gammacerane are present [41].

The GC–MS analysis of chloroform extracts of the resins of mummies Nos. 1, 3, 4, 6, 7 at *m/z* 217 showed an almost complete absence of diasteranes, which is typical

for the Dead Sea bitumen. Diasteranes are present in the bitumen deposits of the Suez Canal basin [41].

Thus, the results of the study of the resins via the GC–MS method in the monitoring mode of the specified ions (*m/z* 217 and 191) confirmed the hypothesis about the use of natural bitumen from the Dead Sea basin deposits in the compositions of the resins of mummies Nos. 1, 3, 4, 6, 7.

As noted above, the ratio of the content of vanadium and nickel in the mummy resin may serve as a biomarker of their geographical origin [42]. For this purpose, the content of certain trace elements in the resins of the studied mummies was determined with the method of an atomic emission spectroscopy with inductively coupled plasma. The results of elemental analysis are given in Table 2.

Table 2. Quantitative content of the elements in the mummy resins

Element/ λ, Å	Content of elements, *ppm*						
	Mummy No.						
	1	2	3	4	5	6	7
Al_{3961}	6925.6	118.9	307.8	5382.6	≤0.1	183.4	706.6
Ba_{4554}	19.6	1.6	24.9	32.2	≤0.1	5.307	12.427
Cd_{2288}	0.6	0.3	0.1	1.0	0.2	0.2	0.4
Co_{2286}	5.5	0.6	0.7	7.1	0.7	0.3	1.4
Cr_{2677}	9.3	6.3	0.8	7.0	≤0.1	2.6	4.5
Cu_{3247}	174.1	13.5	14.6	103.7	3.1	43.7	80.1
Fe_{2599}	6462.4	571.9	485.3	7387.0	85.8	299.5	1051.1
K_{7664}	2070.5	10310.4	1617.2	5943.4	5180.6	551.3	412.4
Li_{6707}	3.9	0.3	0.1	2.0	0.2	0.1	0.7
Mg_{2795}	2105.8	644.6	835.3	2448.1	1485.4	111.5	876.4
Mn_{2576}	74.1	10.7	20.8	132.9	0.2	7.1	34.5
Mo_{2020}	26.2	0.6	6.2	6.0	0.2	6.2	20.7
Na_{5895}	1176.9	21237.1	3399.6	4611.1	20401.1	1095.1	624.4
Nb_{3094}	8.8	0.3	2.2	6.0	0.2	2.6	8.3
Ni_{2316}	44.7	0.3	6.6	17.1	≤0.1	11.7	39.6
P_{2136}	229.2	8881.4	284.3	1281.9	3814.7	58.2	91.1
Pb_{2203}	16.7	≤0.1	1.5	424.9	≤0.1	33.4	≤0.1
Sb_{2068}	0.6	4.4	0.2	7.0	0.4	1.1	1.7
Se_{1960}	1.1	5.7	2.5	7.1	2.2	3.6	≤0.1
Si_{2516}	703.8	≤0.1	532.2	1027.2	338.6	523.9	103.9
Sr_{4215}	46.5	5.0	43.2	64.4	6.7	3.4	35.5
Ti_{3361}	665.9	≤0.1	36.7	610.3	≤0.1	25.6	59.3
V_{2924}	87.3	≤0.1	20.6	42.3	≤0.1	22.9	77.6
Zn_{2138}	21.3	78.2	7.4	35.2	25.0	8.4	2.1
Σ(Mo, Ni, V), *ppm*	**158.4**	**-**	**33.6**	**65.5**	**-**	**41.0**	**138.1**
V, %	**55.1**	**-**	**61.3**	**64.6**	**-**	**55.9**	**56.2**
Mo, %	**16.5**	**-**	**18.4**	**17.3**	**-**	**15.4**	**15.0**

It should be noted from the data in Table 2 that vanadium and nickel are found in all the examined resins, with the exception of mummies Nos. 2 and 5. This confirms the conclusion about the absence of natural bitumen in the resins of these mummies. It is also interesting to note the absence of lead, niobium, and titanium in the resin compositions of mummies Nos. 2 and 5. It is possible that the presence of these elements is also a feature of natural bitumen, but data on this are not yet available in publications.

Molybdenum was found in the resins of mummies Nos. 1, 3, 4, 6, 7, in addition to vanadium and nickel. According to the results of the research of a number of authors [10, 21, 47, 48], molybdenum was found only in the bitumen of the Dead Sea. According to [21], the shares of vanadium and molybdenum in the natural Dead Sea bitumen from the sum of the three elements were about 50 and 24%, respectively. The shares of these elements in the embalming composition of the mummy based on the Dead Sea bitumen found in the Fayoum Oasis of Egypt [10] amounted to 56.3 and 15.1%, respectively.

The share of vanadium in the resins of the studied mummies was 55.1–64.6%; molybdenum was

at 15.0–18.4%. The results correlate with the published data on the content of vanadium, nickel and molybdenum in the bitumen of the Dead Sea and in the resin of the Fayoum mummy based on this bitumen. Consequently, natural bitumen from deposits of the Dead Sea basin was used in the resins of mummies Nos. 1, 3, 4, 6, 7.

Using the method of identification of the bitumen in mummy resins for determining the contents of vanadium, nickel and molybdenum has several significant advantages:

– instruments used for this method allow for the detection of these elements at the level of 0.05 *ppm*;

– the method has high selectivity, which allows one to determine the elements in the presence of any organic compounds, regardless of their quantity;

– the analyzed elements were not subjected to physical, chemical or biological influences in the process of a long-term immurement;

– vanadium, nickel and molybdenum are concentrated as a result of natural bitumen formation, and their relative content remains constant.

Thus, the detection of the relative content of vanadium, nickel and molybdenum in mummy resins can provide a reliable identification for the geographic origin of natural bitumen in mummification balms.

Conclusions

A GC–MS study of the resins of seven Ancient Egyptian mummies from the collection of the Pushkin State Museum of Fine Arts was carried out, its objective being of determining the presence and origin of natural bitumen. *n*-Alkanes with a chain length of 16 to 35 carbon atoms have been identified in the resins. The dominance of C_{25}–C_{33} hydrocarbons, typical of beeswax, led to the assumption of its use in mummies' resins, which was confirmed by the GC analysis of FAME. In the resins of five mummies, *n*-alkanes with the number of carbon atoms less than 23 atoms were found, which points to the presence of natural bitumen. The bitumen from the Dead Sea basin was identified by comparing the distributions of hydrocarbons with the profiles of *n*-alkanes of mummy resins from the published sources. Evidence of the geographical origin of the bitumen was obtained by studying the mummy resins with the GC–MS method in the mode of ion monitoring (*m/z* 217 and 191).

The content of trace elements in the samples taken for the study was determined using the method of atomic emission spectroscopy with inductively coupled plasma. Vanadium, nickel and molybdenum were found in the resins of five mummies. The absence of these elements in two of the seven studied mummies confirmed the conclusion about the absence of natural bitumen in the composition of their resins. The results of determining the relative quantities of vanadium, nickel and molybdenum in the resins of the studied mummies showed a good correlation with the published data on the content of elements in the Dead Sea bitumen and in the resin of the Fayum mummy.

The advantages of identifying bitumen in mummy resins by the relative contents of vanadium, nickel and molybdenum are shown.

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