ISSN 1061-9348, Journal of Analytical Chemistry, 2021, Vol. 76, No. 6, pp. 779–784. © Pleiades Publishing, Ltd., 2021.
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ARTICLES

Detection and Assessment of Natural Bitumen Sources in Ancient Mummy Resins

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Received March 29, 2019; revised November 16, 2020; accepted November 21, 2020

Abstract—The composition of resins of seven ancient Egyptian mummies from the collection of the Pushkin State Museum of Fine Arts was studied. *n*-Alkanes were found in the resins by gas chromatography–mass spectrometry, which suggests the presence of natural bitumen in these resins. By comparing the hydrocarbon profiles of the studied mummies with the profiles of *n*-alkanes from mummy resins, reported in publications, the bitumen of the Dead Sea basin was identified. Concentrations of some trace elements were determined by inductively coupled plasma atomic emission spectrometry; vanadium, nickel, and molybdenum were found in the resins of five mummies. The identification of bitumen (its origin) by the relative concentrations of these elements was proposed.

Keywords: ancient Egyptian mummies, natural bitumen, gas chromatography, mass spectrometry, atomic emission spectrometry, trace elements

DOI: 10.1134/S1061934821040122

Mummification is a natural or an artificial preservation of a body after death; it is an integral feature of the culture of Ancient Egypt [1]. In different periods of the history of Ancient Egypt, various substances of organic nature, for example, beeswax, vegetable wax, natural bitumen, tar, softwood resins, animal fats, vegetable oils, and aromatic resins of some plants, were used for embalming compositions during mummification [2–8]. One of the key points in the study of resin coatings of ancient Egyptian mummies is the identification of bitumen in mummification compositions and the determination of its geographical origin. Benson et al. published one of the first works on the identification of bitumen [9], in which the resin of an Egyptian mummy from the Historical Museum of Manchester was studied by gas chromatography. The authors compared the profiles of *n*-alkanes in the resin of the mummy and the bitumen of the Dead Sea and showed their similarity.

Natural bitumen contains marker compounds with chemical structures associated with their biological precursors: plants, bacteria, and algae. Steranes and triterpanes, that is, aromatic steroidal hydrocarbons used in geochemical studies [10], were recognized as such markers. The distributions of these hydrocarbons were different for bitumen from different deposits and can serve as a means of assessing their geographic origin. Rullkötter et al. [11] described one of the first studies of the distribution of steranes and triterpanes in Dead Sea asphalt by gas chromatography–mass spectrometry (GC–MS) with ion monitoring of characteristic fragments (*m/z* 217 and 191). This approach has been repeatedly applied to identify bitumen in the resins of ancient Egyptian mummies [12–14]. *n*-Alkanes C_{19}–C_{35} and hopane and terpane derivatives can serve as markers of the presence and origin of bitumen in embalming resins of mummies. The main disadvantage of this method is that, in many cases, these markers were either not detected, or were present in trace amounts, which did not guarantee their reliable determination in mummifying compounds [5, 14].

On the other hand, oil is known to contain over 60 trace elements. The concentration of vanadium and nickel reaches 0.1%; the concentration of Fe, Mo, As, Co, Cu, Mn, Sr, Se, and Rb is ~0.003% [15, 16]. Spielmann was one of the first to discover the presence of vanadium and nickel in the resins of Egyptian mummies [17]. Other researchers also found these elements in the resins of mummies [9, 14]. In the resins

Table 1. Description of exhibits from the collection of the Pushkin State Museum of Fine Arts, provided for research

Sample no.	Name, inventory number
1	I-1a 7150 Head of a human mummy in a tarnished shroud; length 20 cm
2	I-1a 6932 Head of a mummy; height 22 cm, circumference 53 cm
3	I-1a 6505 Head of a male mummy; height 28 cm, circumference 54 cm
4	I-1a 6506 Head of a female mummy; height 25 cm, circumference 53.5 cm
5	I-1a 1241 Headless mummy swaddled in a large amount of bandages
6	I-1a 5934 Head of a female mummy; height 24 cm, circumference 52 cm
7	I-1a 1239 Mummy Ipanhi in a cardboard case

of many mummies, molybdenum was also found in addition to vanadium and nickel [5, 9, 18].

The goal of this study was to determine the presence and origin of bitumen in the resins of seven ancient Egyptian mummies from the collection of the Pushkin State Museum of Fine Arts using GC–MS and inductively coupled plasma–atomic emission spectrometry (ICP–AES).

EXPERIMENTAL

Test samples. The description of the studied exhibits is presented in Table 1. The approximate dating of mummies is 1000 years BC. Samples of the resinous substance were collected from the surface of the mummies in the form of naturally separated fragments of resinous material of almost black color, odorless.

Reagents. We used *n*-hexane, chloroform, and *o*-xylene of cp grade as solvents.

Apparatus and auxiliary equipment. An HP 6890 gas chromatograph with an MSD 5975 mass spectrometric detector (Agilent Technologies, United States) was used. The chromatographic conditions were as follows: a DB-5ms capillary column (30 m in length and 0.25 mm in inner diameter; the thickness of the stationary phase was 0.25 μm). The initial temperature of the column thermostat was 100°C; programmable temperature raise from 100 to 280°C at a rate of 15°C/min. The column was maintained at the final temperature for 10 min. The carrier gas (helium) flow rate was 1 mL/min with a split ratio of 1 : 10. The evaporator temperature was 280°C; the detector interface temperature was 280°C. The injected sample volume was 1 μL. The detection was carried out in a total ion current mode.

The preparation of the test solution was performed according to the recommendations [19]. Approximately 100 mg of a resin was crushed, and 1 mL of chloroform was added. Extraction was carried out in an ultrasonic bath (60°C, 60 min). Forty milliliters of *n*-hexane was added to the resulting suspension, shaken vigorously for 5 min, and centrifuged (5000 rpm, 10 min). The liquid phase was separated; the solvent was removed until a dry residue was formed. The residue was dissolved in 50 μL of *n*-hexane.

The concentration of elements in the resins of mummies was determined using a Thermo Scientific iCAP 6300 Duo inductively coupled plasma–atomic emission spectrometer (United States) with an ISOMIST attachment. The maximum plasma power was 1150 W. The following flow rates were maintained in the system: 11 L/min for plasma-forming argon flow, 0.7 L/min for auxiliary argon flow, and 2 mL/min for nebulizing argon flow (Meinhard cyclone spray chamber). An additional (auxiliary) argon flow was used to decrease the effect of the solution viscosity on the amount of aerosol entering the plasma. The spray chamber temperature was –10°C. The analytical signals of the elements were recorded at wavelengths listed in Table 2.

To construct the calibration curves, we used solutions that were prepared by diluting the CONOSTAN S-21 900 ppm multielement calibration standard (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, and Zn) in blank oil (cat. no. 150-021-015, Conostan, Canada).

The test solution was prepared according to a modified procedure [20]. A 100 mg sample of a resin was crushed; 20 mL of *o*-xylene was added, and the mixture was treated in an ultrasonic bath (60°C, 60 min). The resulting solution was centrifuged (5000 rpm, 10 min). The liquid above the sediment was transferred into a 10 mL volumetric flask, and the volume of the solution was brought to the mark with *o*-xylene.

RESULTS AND DISCUSSION

To determine the composition of hydrocarbons present in the test resin, the sample was extracted with chloroform, and asphaltenes were precipitated with an excess of *n*-hexane [19]. Compounds in the resin extracts were identified by GC–MS. Chromatograms of the resin extracts of two mummies in *n*-hexane are shown in Fig. 1.

n-Alkanes with a chain length of 16 to 35 carbon atoms were identified in the extracts. The predominance of hydrocarbons with odd numbers of carbon atoms C_{25}–C_{33} in the chromatograms, typical of bees-

Table 2. Results (μg/g) of determination of trace elements in the resins of mummies ($n = 3$, $P = 0.95$)

Element	λ, nm	Mummy						
		1	2	3	4	5	6	7
Cd	228.8	0.60 ± 0.02	0.30 ± 0.01	0.40 ± 0.03	1.0 ± 0.1	0.30 ± 0.02	0.30 ± 0.01	0.50 ± 0.02
Cr	267.7	9.1 ± 1.3	6.1 ± 0.4	2.1 ± 0.1	7.0 ± 0.3	2.0 ± 0.9	3.0 ± 0.2	5.0 ± 0.3
Cu	324.7	17 ± 2	14 ± 1	15 ± 2	12 ± 1	7.0 ± 1.1	24 ± 1	28 ± 2
Mn	257.6	24 ± 2	11 ± 1	21 ± 3	13 ± 1	2.0 ± 0.8	7.0 ± 0.5	5.0 ± 0.6
Mo	202.0	6.0 ± 1.0	<0.2	6.0 ± 0.4	6.0 ± 0.5	<0.2	6.0 ± 0.7	11 ± 1
Ni	231.6	45 ± 4	0.30 ± 0.06	17 ± 2	17 ± 1	0.20 ± 0.01	18 ± 1	40 ± 4
Pb	220.3	17 ± 2	0.50 ± 0.07	2.0 ± 0.3	42 ± 2	0.50 ± 0.02	33 ± 2	0.50 ± 0.01
Ti	336.1	16 ± 2	<0.2	37 ± 2	31 ± 2	<0.2	26 ± 2	19 ± 1
V	292.4	63 ± 5	<0.2	31 ± 2	42 ± 3	<0.2	29 ± 2	51 ± 4
Zn	213.8	21 ± 2	38 ± 3	7.0 ± 0.5	35 ± 3	25 ± 2	18 ± 1	22 ± 2
$\Sigma_{(Mo,Ni,V)}$		114	–	54	65	–	53	102
V, %		55.3	–	57.4	64.6	–	54.7	50.0
Mo, %		5.3	–	11.1	9.2	–	11.3	10.8
Ni, %		39.4	–	31.5	26.2	–	34.0	39.2

wax, suggested its presence in the resins of mummies. In the composition of beeswax, there are neither *n*-alkanes with an even number of carbon atoms nor carbon chains shorter than 23 carbon atoms. Such hydrocarbons were found in the resin extracts of five mummies. This suggested the presence of natural bitumen in them.

To determine the origin of bitumen, histograms of the distribution of *n*-alkanes in the profile of mummy resins were built using hydrocarbons with an even number of carbon atoms to exclude the effect of beeswax hydrocarbons. The obtained histograms (Fig. 2) allowed a conclusion that the distribution of bitumen hydrocarbons in the resins of the studied mummies was approximately the same. The maximum content of hydrocarbons falls on alkanes with the number of carbon atoms 22–26.

Jones et al. [8] reported similar distributions of *n*-alkanes for mummy resins, in the composition of which the bitumen of the Dead Sea basin was identified. The distribution maximum was noted for hydrocarbons containing 20–25 carbon atoms. A comparison of the profiles obtained in this work with the data of [8] enabled us to assume that the resins of the mummies studied in this work contained bitumen from a deposit in the Dead Sea basin.

The methods of elemental analysis of oil and its various fractions are well developed and widely used [15, 20, 21]. The results of the determination of trace elements in the resins of the studied mummies by ICP–AES (Table 2) show that vanadium and nickel were present in the resins of five of the seven studied mummies (except for mummies 2 and 5). This confirms the absence of bitumen in the resins of mummies 2 and 5. The resins of these mummies also contained no lead and titanium. The presence of these elements is also a characteristic of natural bitumen, but there are no such data in the literature.

In the resins of mummies 1, 3, 4, 6, and 7, we found molybdenum in addition to vanadium and nickel. According to research results [3, 9, 17], molybdenum was found in the bitumen of the Dead Sea. According to [9], the proportion of V and Mo in the total content of V + Mo + Ni in the natural bitumen of the Dead Sea was approximately 50 and 24%, respectively. The proportion of these elements in the resin of the mummy based on the Dead Sea bitumen, found in the Fayum oasis of Egypt [3], was 56 and 15%, respectively. The proportion of vanadium in the resins of the studied mummies was 50–65%, and the proportion of molybdenum was 5–11%. The results correlate well with the data [3] on the concentration of V, Ni, and Mo in the bitumen of the Dead Sea and the resin of the Fayum mummy based on this bitumen. This enables a conclusion that the resins of these mummies contain bitumen from the deposits of the Dead Sea basin.

CONCLUSIONS

Thus, the determination of V, Ni, and Mo in mummy resins is a convenient and simple way to identify bitumen in mummification compositions and to determine its geographical origin. The identification of bitumen in mummy resins by the concentrations of V, Ni, and Mo has many advantages: minimal sample preparation is required; the detection limit of elements is 0.2 μg/g; these elements can be determined in the presence of accompanying organic compounds; the determined elements are not subjected to physical,

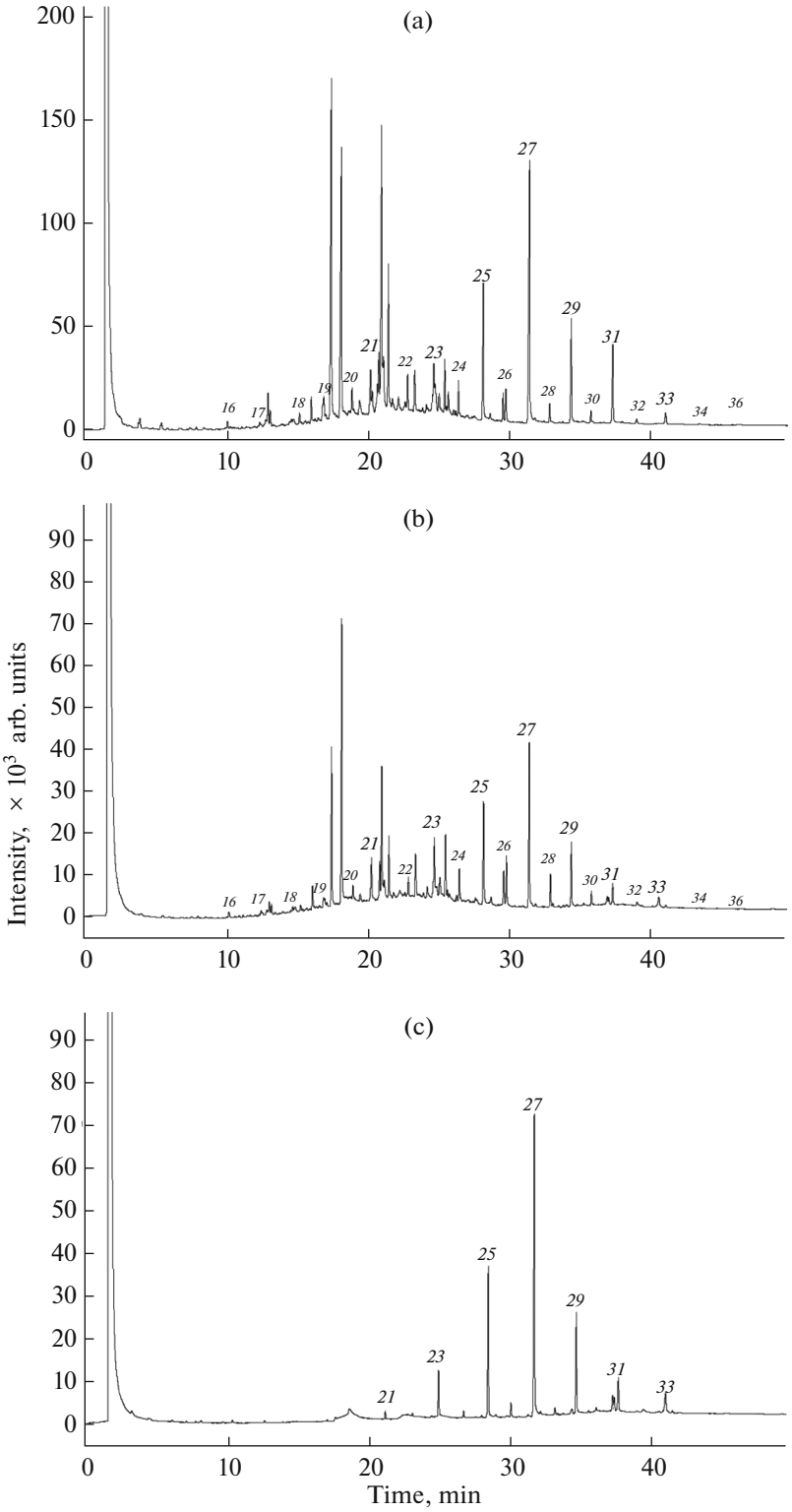

Fig. 1. Chromatograms of hydrocarbons in (a, b) the resins of mummies and (c) beeswax. The number above the peak indicates the number of carbon atoms in the *n*-alkane.

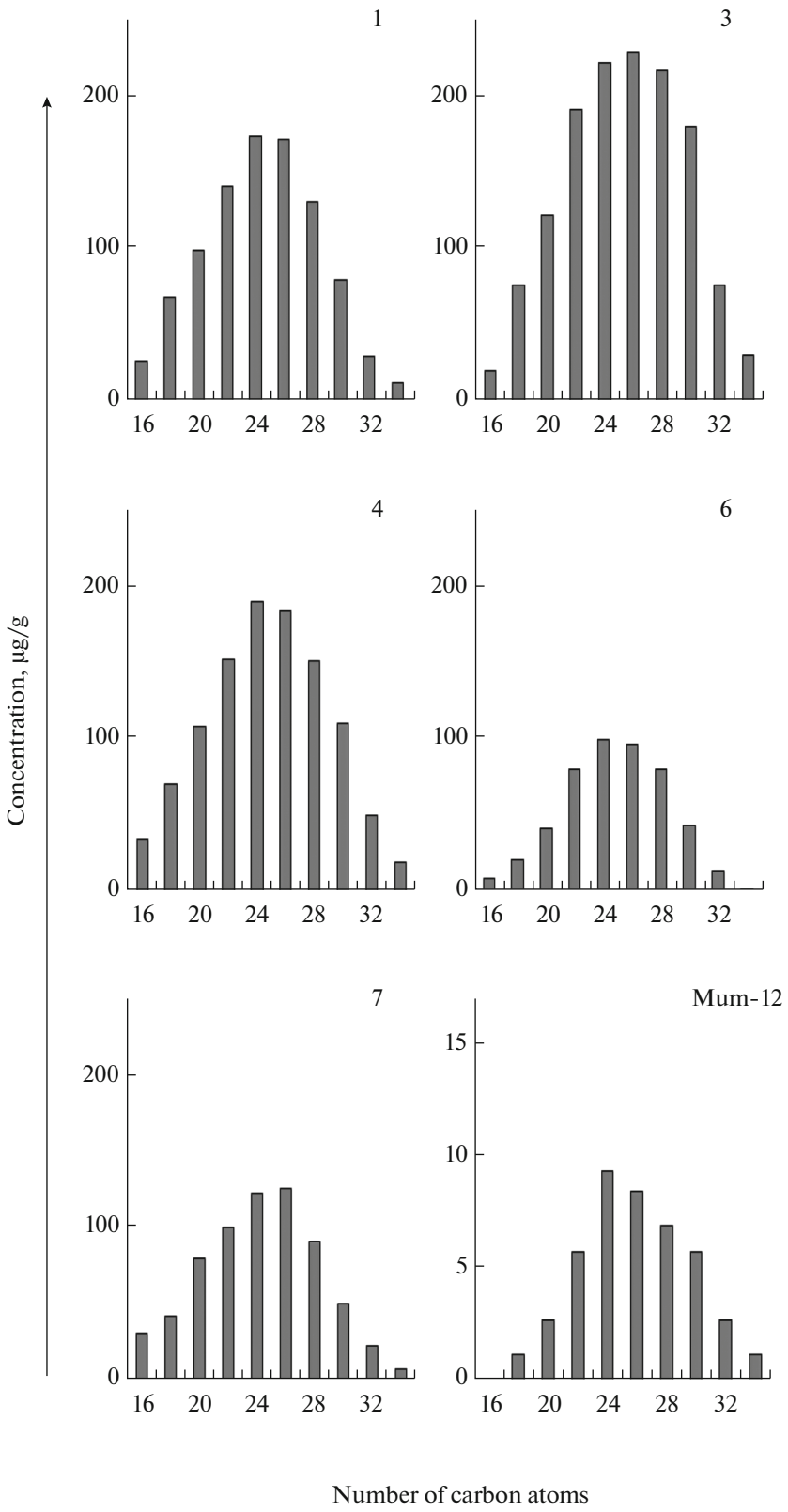

Fig. 2. Distribution of *n*-alkanes in the hydrocarbon profile of the resins of the studied mummies (1, 3, 4, 6, and 7) and the resin of the Mum-12 mummy from the Dakhla Oasis [4].

chemical, or biological effects in the process of long-term burial.

FUNDING

This work was supported by the Russian Foundation for Basic Research, project nos. 17-29-04144 and 17-29-04100.

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Translated by O. Zhukova