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Archaeometric Identification of a Perfume from Roman Times

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Abstract: Although archaeological excavations have recovered a large number of vessels used to hold perfumes or ointments in ancient Rome, little is known about the chemical composition or origin of the substances they contained. Most available information pertains to ointment and/or cosmetic bases rather than to essences. The discovery in 2019 of an ointment jar (*unguentarium*) made of rock crystal (quartz) that was sealed with a stopper and contained a solid mass in a Roman tomb in Carmona (Seville, Spain) was a rather unusual finding. This paper reports the results of an archaeometric study of the *unguentarium* stopper and its contents. Based on them, and on comparisons with commercially available patchouli and nard oil standards, the perfume held in the *unguentarium* was probably patchouli. To our knowledge, this may be the first time a perfume from Roman times has been identified, which is a major advance in this field. The *unguentarium* stopper consisted of dolomite, a material also unknown in this type of use, and bitumen was used to seal the *unguentarium* with the stopper.

Keywords: *unguentarium*; perfume; patchouli; bitumen; dolomite

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1. Introduction

Carmona was one of the major cities in *Baetica*, a Roman province in the south of *Hispania*, in the first and second century A.D. The city retains a number of buildings and remains from Roman times especially prominent among which is the largest funeral ensemble in the Iberian peninsula; also, ancient funeral structures continue to be frequently unearthed during building work at the necropolis site. In August 2019, rehabilitation work in progress at 52 Seville St. in this city unearthed an underground passageway that was subsequently identified as a collective Roman mausoleum (Figure 1a). Based on the type of tomb and the objects it housed—which were mainly associated with offerings and burial furnishings for the deceased—the mausoleum must have belonged to a high-standing family. The chamber had been used to bury three male and three female adults who were cremated and their bones stored in stone or glass urns [1]. Careful inspection of the inside revealed a vaulted chamber decorated with paintings and eight niches in very good condition suggesting that the site had been neither looted nor pillaged (Figure 1b). Six of the niches held urns in various shapes and made of different materials. The site was a collective underground funeral ensemble—possibly a family burial place—of the shaft tomb type. As we just said, there were eight niches (*loculi*) in the side walls. The two in the left wall (*loculi* 1 and 2) were empty and showed no sign of ever being occupied. The other six contained ash urns and various other objects associated with burial rituals and offerings, all in very good condition. *Loculus* 7 contained an egg-shaped lead case closed with an also egg-shaped lid and containing a glass urn (*olla ossuaria*) with two omega-shaped handles (Figure 1c,d).

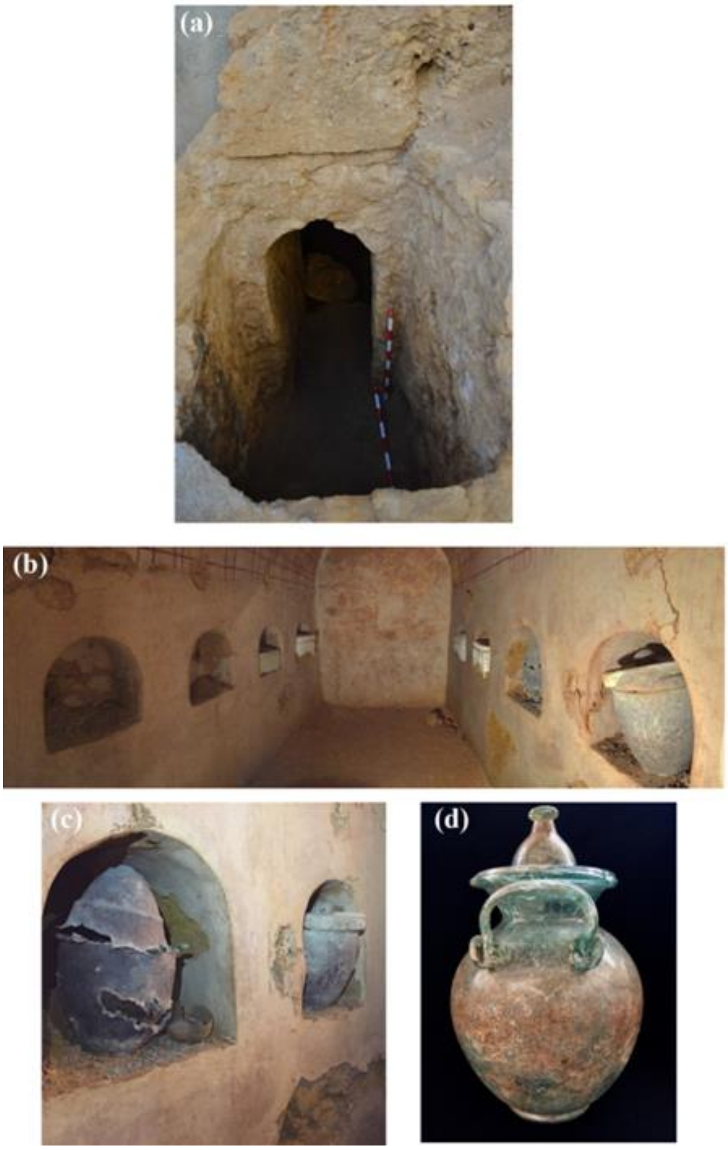

Figure 1. (**a**) Access to the funeral chamber; (**b**) funeral chamber; (**c**) *loculi* 7 and 8; (**d**) glass urn containing remains and *unguentarium*.

The urn was closed by a lid with a glass handle positioned upside down for easier closing of the lead case and contained the cremated bones, organic remains of a cloth bag, three round amber beads, and a stopped amphora-shaped ointment jar (*unguentarium*) made from rock crystal (quartz) that contained a solid mass (Figure 2a,b). In Roman times, quartz vessels were very rare luxury objects several of which have been found near Carmona [2]. The *unguentarium* was thus a rather unusual finding for an archaeological site, and even more unusual is that it was tightly stopped and contained a solid mass. This provided a unique opportunity to establish the chemical composition of the substances once held in the *unguentarium*—most probably, a high-quality perfume or cosmetic judging by the nature of the vessel. While unusual, there have been relatively similar findings such as a small metal bottle containing cream made from animal fat that was found in London [3], organic residues analysis in different container types [4], or glass *unguentaria* containing fat-based extracts unearthed in Naples (the former *Oplontis*) [5]. Similar objects, albeit from the Greek [6] or Egyptian [7] civilization, have been found and characterized.

Figure 2. (**a**) *Unguentarium* found in the mausoleum; (**b**) Precise location of the *unguentarium* inside the urn.

Humans have used perfumes for more than 5000 years and the Egyptian civilization is believed to have been the first. The Egyptians thought perfume came from Ra, the sun's god. From ancient Egypt, perfumes expanded to other places such as Greece and, subsequently, Rome. Perfumes were also highly appreciated by Eastern cultures such as the Chinese and Persian. Archaeologists have found evidence of the use of perfume throughout history. In most cases, perfumes had been held in variably shaped vessels. The oldest perfume was found on the island where Aphrodite is believed to have been born [8]. The Roman civilization only started to appreciate perfumes after the conquest of the eastern Mediterranean strip and the war against Antioch III. Roman perfumes were produced on a large scale during the Empire. Dioscorides compiled several recipes for aromatic oils that were used as perfumes and medicines [9], and Pliny [10] described how to make perfume. According to Pliny, perfumes or ointments should contain two essential ingredients, namely a liquid portion and a solid one. Occasionally, a colouring agent was added to make perfumes coloured. The oils most frequently used to make perfumes were extracted from sesame, hot radish, almonds—or, especially, oil, which was easily obtained in large amounts. Olive oil from unripe olives resisted oxidation better than oil from ripe olives [10]. Therefore, the perfumes made by Roman craftsmen contained an oily foundation rather than alcohol and required holding in a vessel as a result. In any case, the actual recipes compiled by classical authors were very vague or confusing as regards the amounts of ingredients and procedures to be used.

Romans used perfumes not only in daily life but also on special occasions such as funerals, where incense was mandatory. In addition, perfumes were applied as ointments or used to embalm the deceased. When a corpse was cremated, bones and ash were kept in an urn together with more or less costly perfumes held in metal, glass, ceramic or rock crystal containers [11] depending on the fortune of the deceased or the gratefulness of their heirs. The rich had funerary chambers made to keep the urns of all family members [12].

The primary aims of this work were to identify the substance or substances the *unguentarium* may have held, to characterize the solid mass it contained in chemical terms, and to identify the stopper material. For this purpose, we conducted a multi-analytical archaeometric study using different instrumental techniques such as X-ray diffraction (XRD), scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), micro-Raman (μ-Raman) and Fourier transform-infrared (FT-IR) spectroscopies, and gas chromatography–mass spectrometry (GC–MS).

2. Materials and Methods

2.1. XRD Analysis

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer equipped with a goniometer and a DACO-MP automated recording system. Samples were irradiated with Kα line for copper ($\lambda = 1.54$ Å). The instrument was furnished with a nickel filter and a graphite monochromator, and operated at a goniometer speed of 2°/min. This technique was employed to assess in a qualitative manner the mineral composition of the stopper.

2.2. Scanning Electron Microscopy—Energy Dispersive Spectroscopy

Scanning electron micrographs and energy-dispersive spectra (SEM-EDS) were obtained with a JEOL JSM 6300 microscope. The instrument comprised a secondary electron (SE) detector for acquisition of topographic images of sample surfaces and a back-scattered electron (BSE) microscope to identify elements present on the surface from differences in electron absorption—which depends on atomic number. Such differences resulted in different shades of grey that were analysed qualitatively and quantitatively with an EDS detector. The combination of scanning electron microscopy and energy-dispersive spectroscopy provides morphological information and semi-quantitative data for chemical elements and allows their spatial distribution to be established by mapping. We have used this technique to establish the chemical nature of the stopper.

2.3. Micro-Raman Spectroscopy

Micro-Raman (μ-Raman) spectra were obtained with a Renishaw InVia Raman instrument equipped with a Leica microscope that was furnished with various lenses, monochromators and filters, and a charge-coupled device (CCD) detector. Samples were excited with green laser light ($\lambda = 532$ nm) and spectra were acquired over the wavenumber range 150–1700 cm^{-1} by using the different microscope lenses. The laser power, number of acquisitions and exposure time used with each sample were those needed for an optimal signal-to-noise ratio. Spectra were processed with the software Wire v. 3.4 from Renishaw (Wotton-under-Edge, UK). All spectral treatments (baseline correction, smoothing, etc.) were done with the software Peakfit v. 4.12 (Inpixon HQ, Palo Alto, CA, USA). This technique has allowed us to confirm the chemical composition of the stopper, study the substance used as sealant and advance in the study of the content of the *unguentarium*.

2.4. Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectra were acquired over the wavenumber range 4000 to 400 cm^{-1} by using an FT-IR Nicolet Magna IR 500 instrument. Spectra were recorded on pellets made from ca. 5 mg of sample and 150 mg of KBr. Measurements were made in the transmission mode and a total of 32 scans were used for optimal signal-to-noise ratio and spectral reproducibility. We have used this technique to confirm the presence of a sealing substance in the plug of the ointment and to characterize its content.

2.5. Gas Chromatography–Mass Spectrometry

Gas chromatography–mass spectrometry (GC/MS) analysis was carried out on a Bruker Mod Scion Triple Quadrupole mass spectrometer. Sample extraction (100 mg) was carried out with 2 mL of ethyl acetate under sonication for 30 min, after which the solvent was evaporated under a stream of nitrogen to 100 µL and injected (2 µL) by splitless injection on the GC. 5%phenylsilicone, 30 m, 0.25 mm i.d., 0.25 µm film thickness column was used (DB′5MS from Agilent, PN122-5532). Chromatographic conditions were as follows: injector, 250 °C; oven column: 55 °C (1 min), then 5 °C/min to 235 °C, then 8 °C/min to 310 °C (5 min); MS conditions were as follows: EI ionization, source temperature 250 °C, mass scanning 40–450 umas (0.6 s/scan). MS electronic ionization energy was 70 eV, the standard energy for the use of mass libraries. Compounds were identified by comparing mass spectra both with the NIST library and the internal library.

The oily matter held in the unguentarium was transesterified for analysis by GC–MS, which is the typical procedure for archaeological material and works of art [13,14]. All samples were pretreated by hydrolysis, and fatty acids were derivatized for conversion into methyl esters (FAMEs) with increased volatility as a result. This was accomplished by using the method of Manzano et al. [15]. Thus, an amount of 15 mg of the dark solid, which contained the organic compounds, was placed in a microvial and treated with 15 µL of a methanol solution of *m*-(trifluoromethylphenyl)trimethylammonium hydroxide (TMTFAH) and 200 µL of toluene to transesterify triglycerides. The mixture was sonicated for 30 min and then centrifuged at 3000 rpm for a further 5 min; the ensuing supernatant was analyzed by GC–MS. FAMEs identification was carried out by the NIST library and the FAME standard mix (Supelco 37 component FAME Mix, PN CRM47885).

3. Results and Discussion

3.1. Analysis of the Unguentarium Stopper

Although *unguentaria* were fairly commonly found in *Baetic* Roman burial sites [12], stoppered specimens are rather exceptional findings. For this reason, the stopper was analysed before the *unguentarium* here in order to ascertain whether the vestiges contained in the latter came from the former. The high archaeological value of the stopper required using non-destructive techniques for this purpose (specifically, XRD, µ-Raman spectroscopy and SEM–EDS). The stopper was about 7 mm thick (Figure 3) and differed markedly inside and outside. Thus, the outer side (Figure 3b), which was in contact with the urn contents, showed yellowish ochre zones and darker, nearly black zones. On the other hand, the inner side (Figure 3c), which was in contact with the *unguentarium* contents, was largely white. Removing the stopper left more uniform, brown vestiges stuck on the *unguentarium* neck (Figure 3d,e).

As can be from Figure 4, the XRD patterns for the three stopper parts (viz., inner side, outer side and edge) were all similar and exhibited a strong diffraction peak at 31°. This peak, together with others at 37.4°, 41.2°, 45.0°, 50.6°, 51.1°, 59.0° and 59.9°, was clearly consistent with the presence of dolomite [16], an anhydrous carbonate mineral composed of calcium magnesium carbonate [JCPDS card number 36-0426, $CaMg(CO_3)_2$]. No information about the chemical composition of the materials used in ancient *unguentaria* stoppers has seemingly been reported to date. Usually, amphora and ampoule stoppers were made from perishable materials such as cork or wood [17–19] and frequently covered with ceramic discs for fitting. As noted by Mayer i Olivé [19], there are very few references to the use of other materials such as clay or mortar in pozzolana stoppers, which have been the subject of some largely speculative studies about their usage [20,21]. Ceramic stoppers in general, and the one examined here—which was made from dolomite—in particular, were used to seal containers; however, tight, waterproof sealing required using additional means [22]. Usually, amphorae were sealed with lime mortars, pozzolanic materials or resins [23]. Therefore, the next step here was to search for a sealing agent and, if found, determine its chemical nature. On removal from the *unguentarium*, the stopper zone in contact with its neck was found to contain a dark brown, almost black residue that was also present on the *unguentarium* neck (see Figure 3d,e). This led us to think that the stuck substance might have been used to seal the *unguentarium* and to confirm it by analysing the stopper with SEM−EDS and μ-Raman spectroscopy.

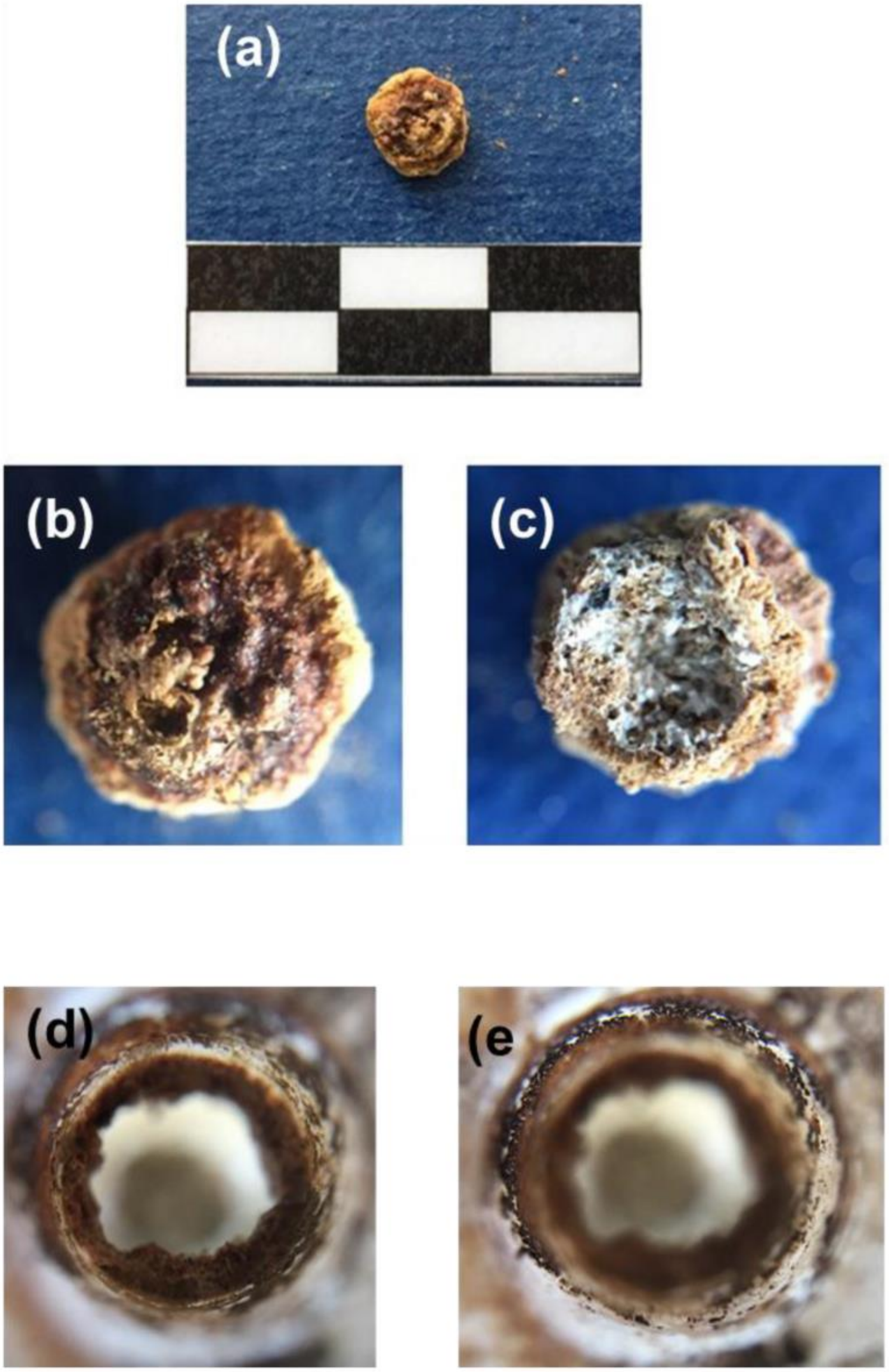

Figure 3. (**a**) Stopper after removal from the unguentarium. (**b**) Outer and (**c**) inner side of the stopper, respectively. (**d**,**e**) Unguentarium neck after removal of the stopper clearly showing traces of stuck matter.

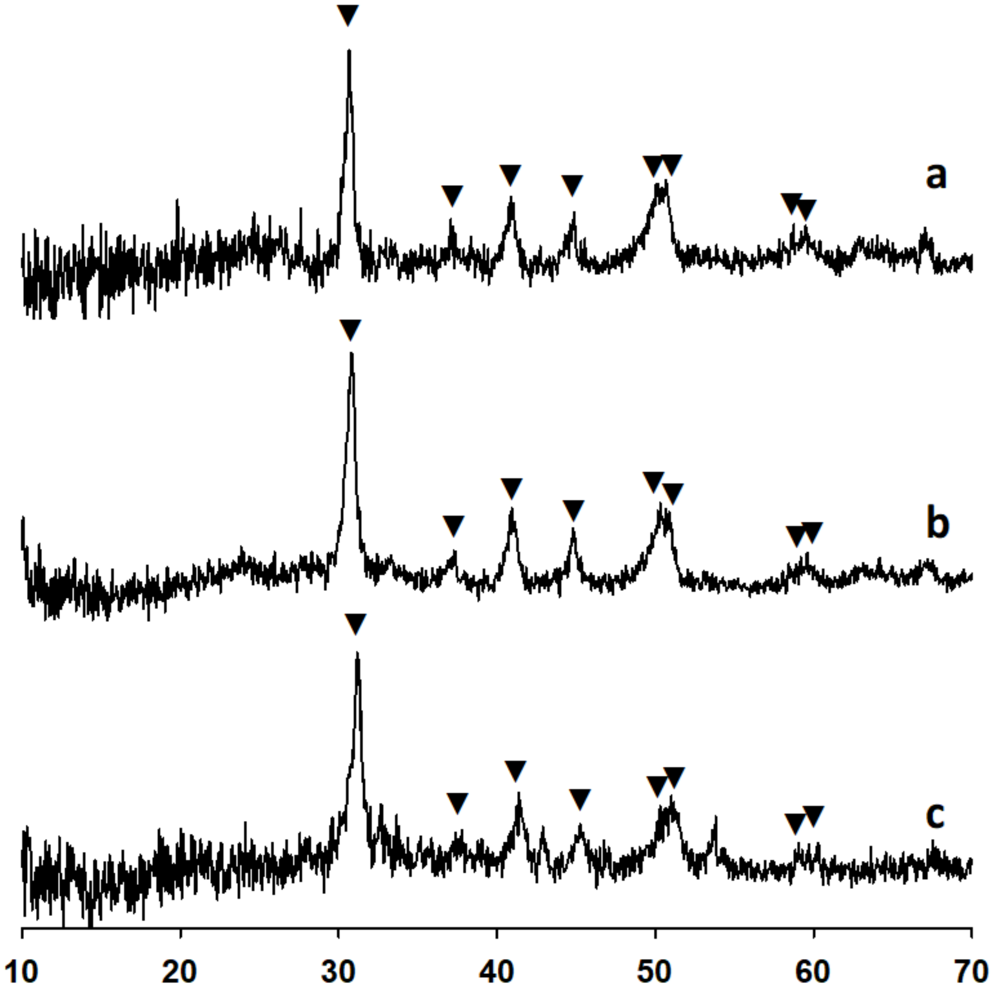

Figure 4. XRD patterns for the outer side of the stopper (**a**) the inner side (**b**) and edge of the stopper (**c**), respectively. The black triangles denote dolomite diffraction peaks.

Whether a material undetectable by XRD might have been used was ruled out with the SEM–EDS technique. Table 1 shows the results of the semiquantitative elemental analysis, and Figure 5 shows the micrographs of the studied zones and EDS maps.

Table 1. Semiquantitative SEM-EDS analysis of the *unguentarium* stopper. All values are weight percentages.

Element	Inner Side (%)	Outer Side (%)
C	21.7	40.8
O	52.9	48.7
Ca	10.8	3.7
Mg	13.8	4.4
Na	-	1.2
Si	-	0.1
P	-	0.9
S	-	0.2

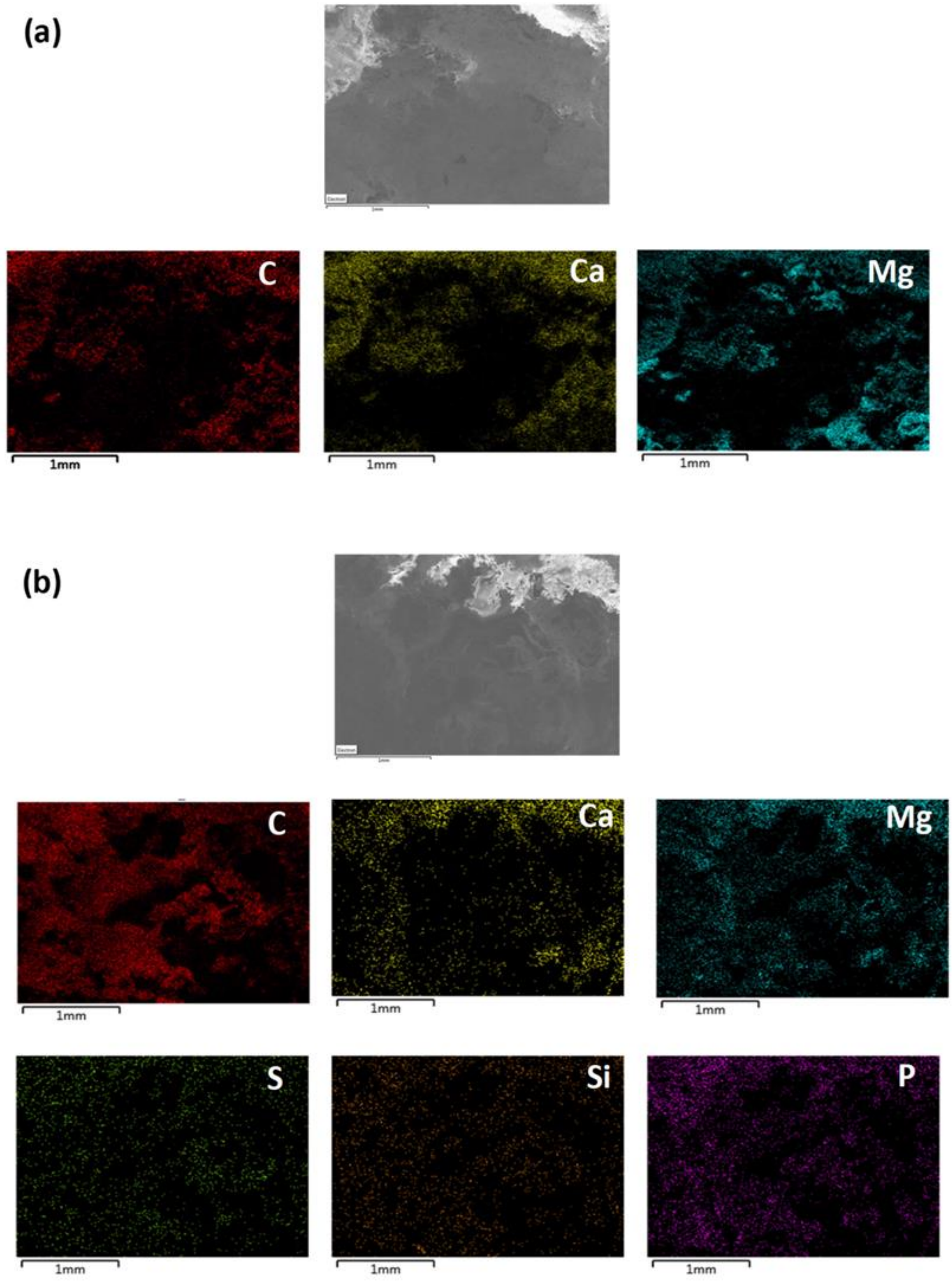

Figure 5. SEM-EDS micrographs and element maps for the *unguentarium* stopper: (**a**) inner and (**b**) outer sides.

The inner side of the stopper only contained carbon, oxygen, calcium and magnesium, whereas the outer side additionally contained silicon, phosphorus, sodium and sulfur, albeit in very small amounts. The fact that the carbon content of the outer side was almost twice higher than that of the inner side suggested the presence of some compound undetectable by XRD. As can be seen in Figure 5a, the C, Mg and Ca maps for the inner side of the stopper were superimposable; therefore, the only compound present was dolomite. By contrast, the element maps for the outer side of the stopper (Figure 5b) revealed that C was more widely distributed across the surface than were Mg and Ca, which was compatible with the presence of an additional carbon compound that required using a different technique for identification. The absence of additional diffraction peaks in the XRD spectrum for the outer side of the stopper (Figure 4a) relative to its inner side (Figure 4b) and edge (Figure 4c) suggested that the additional compound was not crystalline. The compound concerned was identified by µ-Raman spectroscopy, which allows spectra to be obtained from microscopic areas of a surface. Under the Raman microscope, the outer side of the stopper exhibited white, greyish and black zones consistent with those of the edge. On the other hand, the inner zone only exhibited white zones. Whichever the stopper side, the µ-Raman spectra obtained at different points in the white zone were all similar to that of Figure 6a, which is consistent with that for dolomite [24]. On the other hand, the spectrum for the dark zones exhibited two strong bands (Figure 6b) possibly due to carbon [25]. However, no graphite was detected from the XRD, so the carbon must be associated with noncrystalline phases. The µ-Raman spectrum for the less dark particles on the outer side of the stopper (Figure 6c,d) contained not only the previous bands, but also one at 1008 cm^{-1} and another at 960 cm^{-1} that were assigned to calcium sulfate [26] and calcium phosphate [27], respectively, and were consistent with the presence of sulfur and phosphorus, which were detected by SEM–EDS.

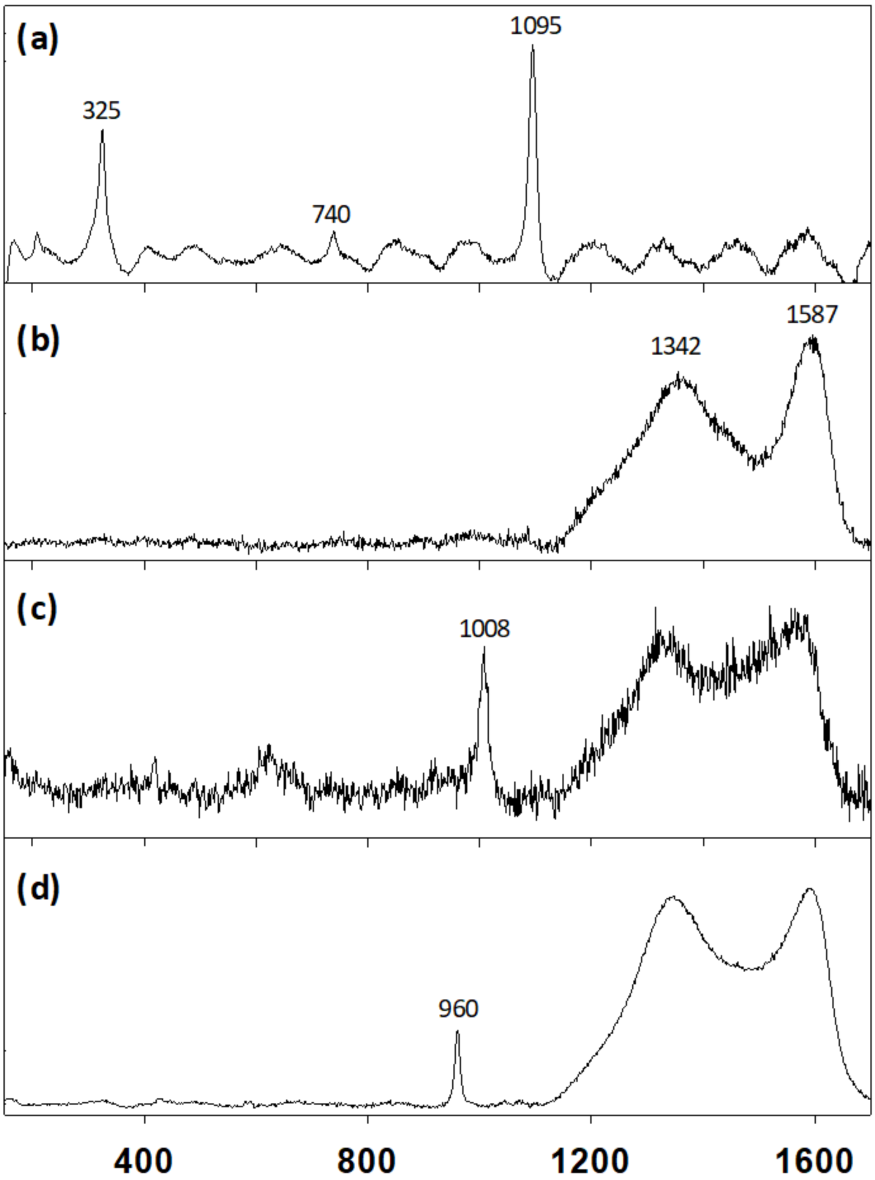

Figure 6. Raman spectra for the white zone in the inner side (**a**); the black zone in the outer of the stopper (**b**) and the grayish particles of solid material in the *unguentarium* (**c**,**d**).

Based on the previous results, the carbon compound detected by SEM−EDS and µ-Raman spectroscopy was probably used to seal the *unguentarium*. As stated above, Roman vessels were typically sealed with lime mortar, pozzolanic materials or resins [23]. No mortar or pozzolanic material was obviously present, so the sealing material used might be a resin. However, the absence of other bands in the Raman spectrum was suggestive of an essentially carbon-based material. A comprehensive literature search revealed that bitumen had also been used as a sealing and waterproofing agent for various types of vessels since ancient times [28]. Thus, bitumen was frequently used in Roman amphorae for storage and transport [29]. The Raman spectrum for bitumen exhibits two bands in the 1000−1800 cm^{-1} region that appeared at 1587 (band D) and 1342 cm^{-1} (band G) in our spectrum (Figure 4b) [30–32]. These results suggested the use of bitumen to seal the *unguentarium* stopper. The presence of this sealant was confirmed by FT-IR spectroscopy. Figure 7a shows the FT-IR spectrum for a sample of solid stuck to the inner side of the *unguentarium* neck. The strong FT-IR band at 1447 cm^{-1}, together with those at 882 and 732 cm^{-1}, confirmed the presence of dolomite previously suggested by the XRD and µ-Raman spectra [24]. However, the FT-IR spectrum included several other, much weaker bands that were assigned to bitumen [33,34]. In fact, the bands immediately below 3000 cm^{-1} were assigned to stretching vibrations of C−H bonds in the CH_3 and CH_2 groups of a hydrocarbon chain. The additional band at 1751 cm^{-1}, due to stretching vibrations in C=O bonds, together with those at 1030 and 1132 cm^{-1}, which are typical of C−O bond stretching, confirmed the presence of carboxylic acid or esters.

Based on the previous results, the stopper was made from dolomite and presumably sealed with bitumen. However, because some of the bands may be due to other organic substances present in the sample from the *unguentarium* contents, the use of bitumen to seal the vessel required confirmation with another technique: GC−MS.

3.2. Analysis of the Unguentarium Contents

The contents of the *unguentarium*, which were stuck to its walls, consisted of variably coloured particles ranging from whitish ochre to black (Figure 2a). The chemical composition of the particles was established by µ-Raman and FT-IR spectroscopies. The Raman spectra obtained were similar to those shown in Figure 6a,b. The white residue was dolomite and the black particles were a carbonaceous material. Therefore, the dolomite vestiges inside the *unguentarium* could have come off the stopper over time. These results were confirmed by using FT-IR spectroscopy. Figure 7b,c show the spectra for a sample of the white and black particles, respectively. The FT-IR spectrum for the white particles (Figure 7b) only exhibited the above-described bands for dolomite at 1447, 882 and 732 cm^{-1}. On the other hand, the spectrum for the black particles (Figure 7c) included some bands that were very weak in the spectrum for the *unguentarium* neck. Such bands were assigned to stretching vibrations of organic compounds consistent with those for bitumen [33,34]. In fact, the presence of strong bands for C=C, C−C and =C-H stretching vibrations at 1580−1700 cm^{-1}, 1400−1500 cm^{-1} and above 3000 cm^{-1}, respectively, suggested the presence of aromatic compounds and saturated hydrocarbons. These results seemingly confirm the presence of bitumen as a sealant and waterproofing agent for the *unguentarium* stopper. However, its presence required further confirmation by searching for specific molecular markers. Obtaining a marker profile for bitumen calls for laboratory work to separate the saturated hydrocarbon, aromatic hydrocarbon, resin and asphaltene fractions [35–37]. We extracted the *unguentarium* contents—both the lighter and the darker material—with ethyl acetate to remove compounds typically present in bitumen and others potentially present among the original content. The extract was subsequently analysed by GC−MS.

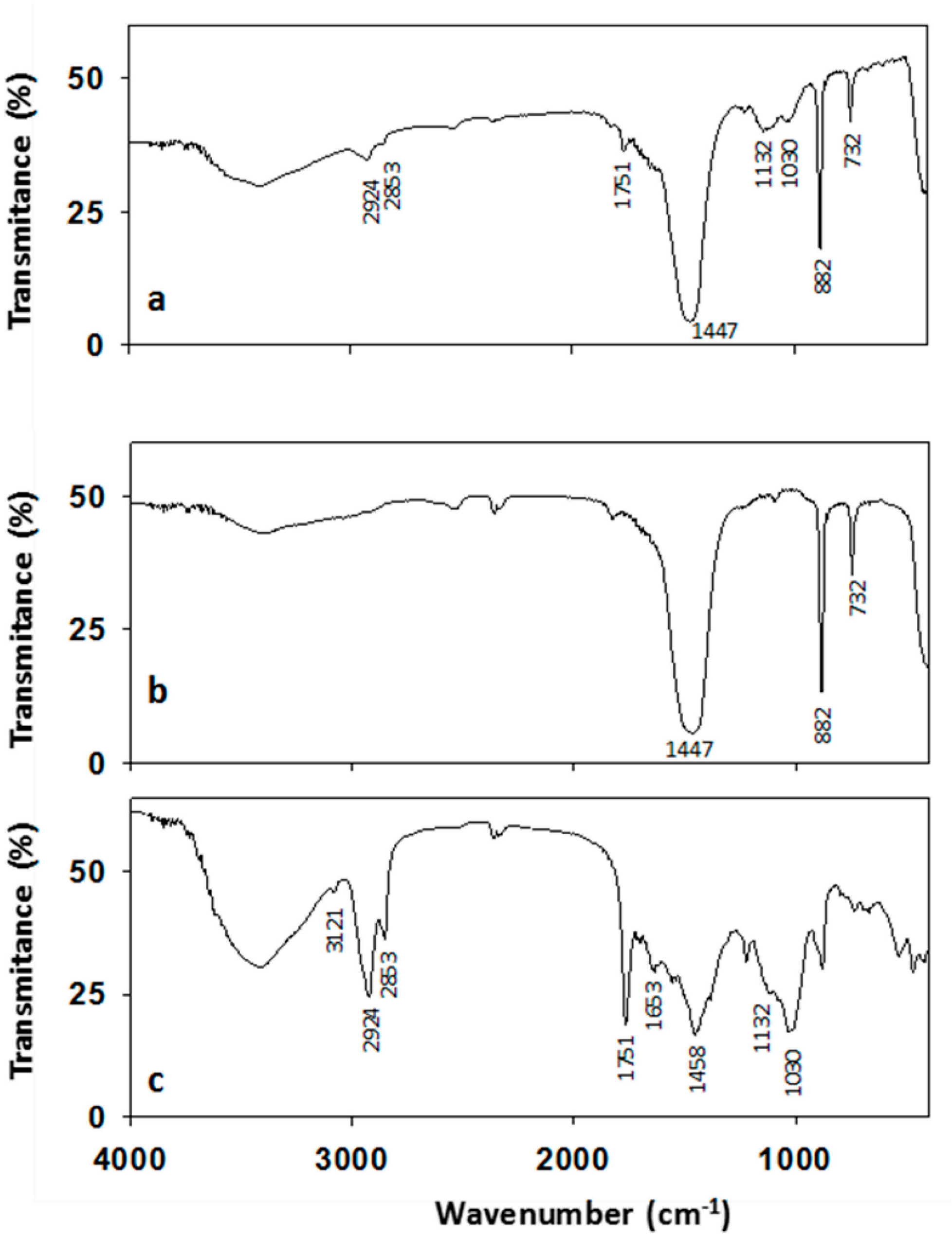

Figure 7. FT-IR spectra of (**a**) the material adhered to the neck of the *unguentarium*; (**b**) white particles from inside the *unguentarium*; and (**c**) black particles from inside the *unguentarium*.

The resulting chromatogram (Figure 8) was rather complex but the mass spectra allowed a number of compounds to be identified that were classified into three groups: hydrocarbons associated with bitumen (heavy alkanes, terpanes, steranes and some polyaromatic compounds) [38,39], sesquiterpenes associated with the presence of an essence and, finally, a third group of compounds associated with the presence of a lipid of vegetable origin. The presence of this fat was confirmed by transesterification with methanol and GC–MS analysis of the product (Figure 9). The chromatogram was consistent with the presence of oleic, stearic and linolenic methyl esters, among others.

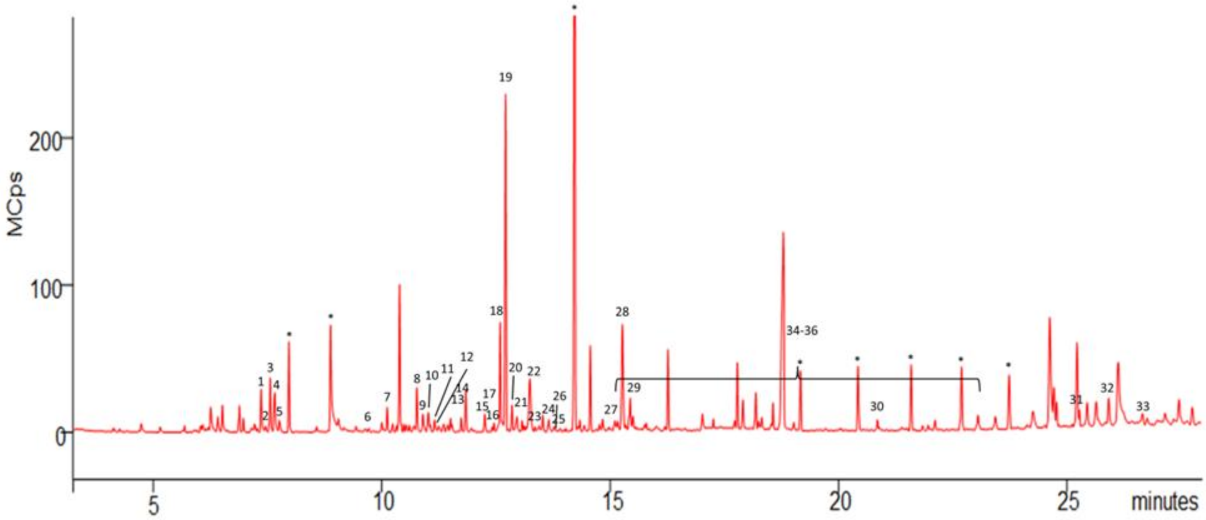

Figure 8. Chromatogram for the *unguentarium* contents. (*) Column blend bands.

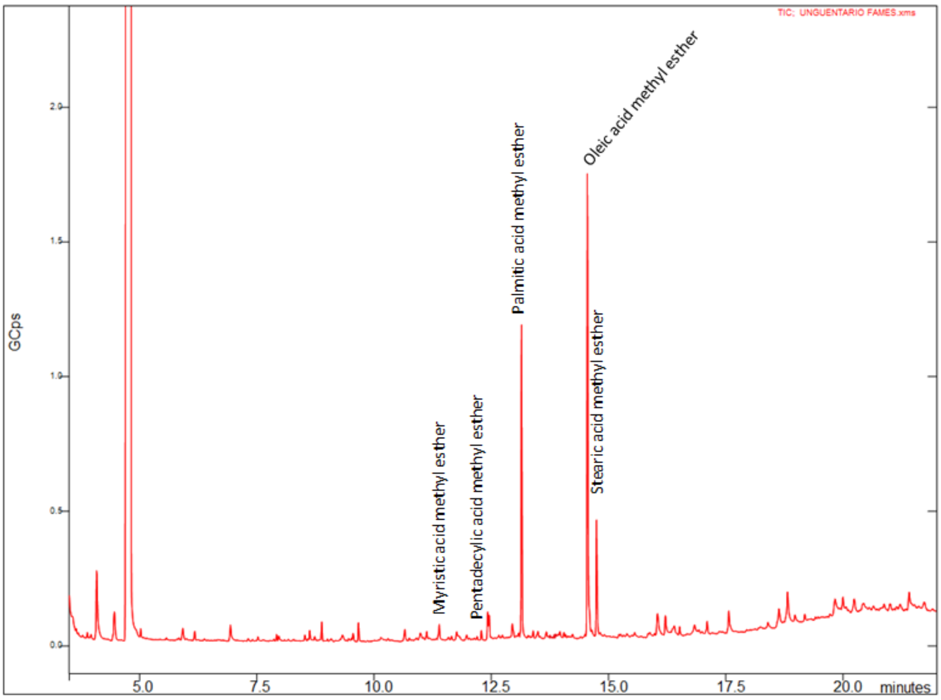

Figure 9. Chromatogram for the *unguentarium* contents after transesterification with methanol.

A chromatographic analysis of the bitumen-related compounds (Table 2) allowed long-chain linear alkanes to be identified. As previously found by other authors in archaeological bitumens [40,41], such alkanes were relatively regularly distributed. We additionally identified some branched alkanes and the hydrocarbon retene—a bitumen biomarker—in small amounts [42,43]. This compound is also a marker for pine resin and pitch [44–46]. However, the major terpenes are limonene, *trans*-carveol, carvone, (S)-*cis*-verbenol and caryophyllene oxide, none of which was found in our sample. Pine pitch contains other major components such as norabietatrienes and guaicols, which were also absent. Based on these results, we can rule out the use of pine pitch or pine resin as the *ungentarium* sealant. The right side of the chromatogram of Figure 8 contained some signals associated with the presence of polycyclic aromatic hydrocarbons that could not be unequivocally identified but are typical components of bitumen [47]. However, the definitive proof of the presence of bitumen has been the identification of some typical biomarkers of this material, such as terpanes and steranes, as well as other compounds related to retene that are also markers of bitumen (Figure S1). The identification of these compounds has been carried out in a similar way as described in the literature by Hauck et al. [48] and Connan and Nissenbaum [49]. Therefore, the combination of these results and the previous ones suggests that bitumen was used as a sealing and waterproofing agent for the *unguentarium*.

Table 2. Identified compounds from their mass spectra in the chromatogram of Figure 8.

Peak	Compound	tR (min)	Peak	Compound	tR (min)
	From bitumen			**From the essence**	
1	Decane	6.88	12	α-Copaen-8-ol	11.29
3	4,5-Dimethylnonane	7.55	13	β-Patchoulene	11.74
4	Undecane	7.65	15	Caryophyllene	12.19
5	6-Ethyl-2-methylnonane	7.76	16	Thujopsene	12.26
6	Dodecane	9.71	17	α-Guaiene	12.35
7	Tridecane	10.11	18	Alloaromadendrene	12.42
8	Tetradecane	10.65	19	Seychellene	12.63
9	Pentadecane	10.79	20	α-Bulnesene	12.78
10	Hexadecane	10.91	21	Aromadendrene	12.82
11	Methylpentadecane	11.02	22	α-Patchoulene	12.95
14	Heptadecane	11.82	23	Acyphyllene	13.13
25	Octadecane	13.54	24	Isoaromadendrene	13.22
28	Nonadecane	13.76	26	α-Cubenene	13.66
30	Retene	20.85	27	Azulol	15.34
34	Dimethylretenes	15–20	29	Patchoulenol	15.43
35	Methylretenes	18–23		**From the fat**	
36	Staranes	17–19	31	Squalene	25.42
37	Terpanes	15–20	32	β-Sitosterol	26.22
			33	Stigmasterol	26.75

Chromatographic analyses also allowed some sesquiterpenes to be identified. These compounds are present in essential oils from a number of plants. In fact, they belong to their volatile fraction and are responsible for "high notes" in perfumes. They are so volatile that they are easily lost by evaporation [50]. That substances like these were preserved in an archaeological setting is rather unusual. Their permanence in the *unguentarium* can be ascribed to ready adsorption of terpenes by some carbonaceous material such as bitumen [51,52]. Thus, evaporated sesquiterpenes in the *unguentarium* must have been partially adsorbed in the bitumen used to seal it with the stopper. With time, this carbonaceous material, and the adsorbed compounds it contained, decomposed and deposited, together with dolomite particles from the stopper, on the inner walls of the *unguentarium*. Deposited bitumen must have continued to adsorb perfume components after it came into contact with them inside the *unguentarium*. The sesquiterpenes identified from their mass spectra included seychellene, patchoulenol (patchouli alcohol), β- and α-patchoulene, α-copaene-8-ol, alloaromadendrene, α-cubenene or cariophyllene, among other (see Table 2). In classical sources about perfume-making, Pliny the Elder used the words *folium nardi*, i.e., "nard leaves" [10], to refer to *Nardum indicum*, a plant of the family *Valerianaceae* known as "true nard" or "Indian nard" (*Nardostachys jatamansi*). The rhizome from this plant was combined with fibrous, aromatic rootlets to obtain a highly prized extract that was used as medicine and perfume. The Latin word *folium* literally meant "leaf" but was also used to designate an indefinite plant which, according to André [53], might have been patchouli—with which the cassia flower tree and, specifically, *Pogostemon patchouli Pell*, have also been associated. Although some authors distinguished them, this plant was occasionally confused with nard. Dioscorides himself (I 12) [54] noted that some believed cassia was Indian nard.

The sesquiterpene fraction of patchouli essential oil is rather complex and strongly influenced by the origin of the particular *Pogostemon* species used to extract the oil. *Pogostemon cablin* is widely at present used by the perfume and cosmetic industries. However, the lack of specific, reliable information precludes knowing which *Pogostemon* species was or was typically used to obtain patchouli essence in ancient times. There is sufficient evidence, however, that patchouli alcohol was the major component of the oil whichever the species. Van Beek and Joulain [55] reviewed more than 600 papers dealing with the composition of patchouli essential oil and found them to agree on their major component: patchouli alcohol, present in an average proportion of 39%. This component was accompanied by other major sesquiterpenes including α-bulnesene, α-guaiene, seychellene, and α- and β-patchoulene, all of which were present in the sample extracted from the unguentarium here. Obviously, the proportions found in our sample were not the same because, even if the perfume had been made from patchouli, the particular *Pogostemon* species was unknown; also, as shown below, the patchouli extraction method used in ancient times was rather different from those employed at present.

Based on the results, the unguentarium was highly likely to contain patchouli essential oil. However, confirming this assumption required excluding the presence of nard essential oil, which also contains sesquiterpenes [56–58]. This ambiguity was solved by conducting a GC/MS analysis of commercial essential oils from patchouli (Sigma−Aldrich (Darmstadt, Germany) Ref. 05591501) and nard (Esenciales, *Nardostachis jatamansi*).

Figure 10 shows the chromatograms for the commercial oil and the *unguentarium* contents. The chromatogram for the commercial oil (Figure 10a) allowed the sesquiterpenes listed in Table 2 to be unequivocally identified. The chromatographic profile is similar for the essential oil and the *unguentarium* contents and the major components of the latter are present in patchouli oil [55]. Our sample also contained one or more compounds of MW = 204 which could not be precisely identified since patchouli oil contains at least 23 compounds with that molecular weight [55]. Figure S2 shows selected mass spectra for the compounds. Comparing the chromatogram for the commercial oil with that for the *unguentarium* content revealed that most of the compounds identified in the former were also present in the latter. Additional compounds contained in patchouli oil were also identified (see Table 2). The 204 ion chromatogram has been extracted for β-patchoulene (t_R = 11.74 min) and α-patchoulene (t_R = 12.95 min) (Figure S3). The mass profile of this ion, which corresponds to the molecular mass of numerous terpenes present in patchouli oil, shows a high similarity between the commercial standard and *unguentarium* contents. This similarity shows that patchouli oil was probably originally contained in the *unguentarium*.

As can be seen from the chromatogram of Figure 11, the major components of nard oil are α-copaene, β-cubenene, caryophyllene, humulene, longipinene, β-cadinene and patchouli alcohol. As noted earlier, some sesquiterpenes in the nard oil standard were also present in patchouli oil and in the *unguentarium* extract; however, the overall sesquiterpene profile of the extract was more similar to that of patchouli oil than to that of nard oil. Aside from this terpene profile, the presence of patchouli alcohol helps us rule out nard oil. We have selected the extracted ion chromatogram for m/z = 222 (Figure S4). Both in the *unguentarium* and in the patchouli oil, as we have seen before, the content of this compound is relatively high, while in the nard oil, its intensity is very low (135 kCps vs. 92 MCps). Therefore, the *unguentarium* was likely to contain patchouli essential oil.

The *unguentarium* extract not only had a compound profile more similar to that of patchouli oil, but also contained certain compounds not present in the commercial oils, probably because the latter was obtained by steam distillation, a technique obviously unknown in Roman times. In fact, essences and essential oils contained in plant leaves or flowers were then obtained either by cold soaking or by dissolution in vegetable (almond, olive) oil. Aroma compounds were soaked in cloth that was subsequently pressed to recover them [59]. Cold soaking was one of the most simple yet effective methods for extracting essences from some flowers such as those of jasmine or roses. For extraction, the flowers were placed on alternately stacked cloth and fat-impregnated layers [60].

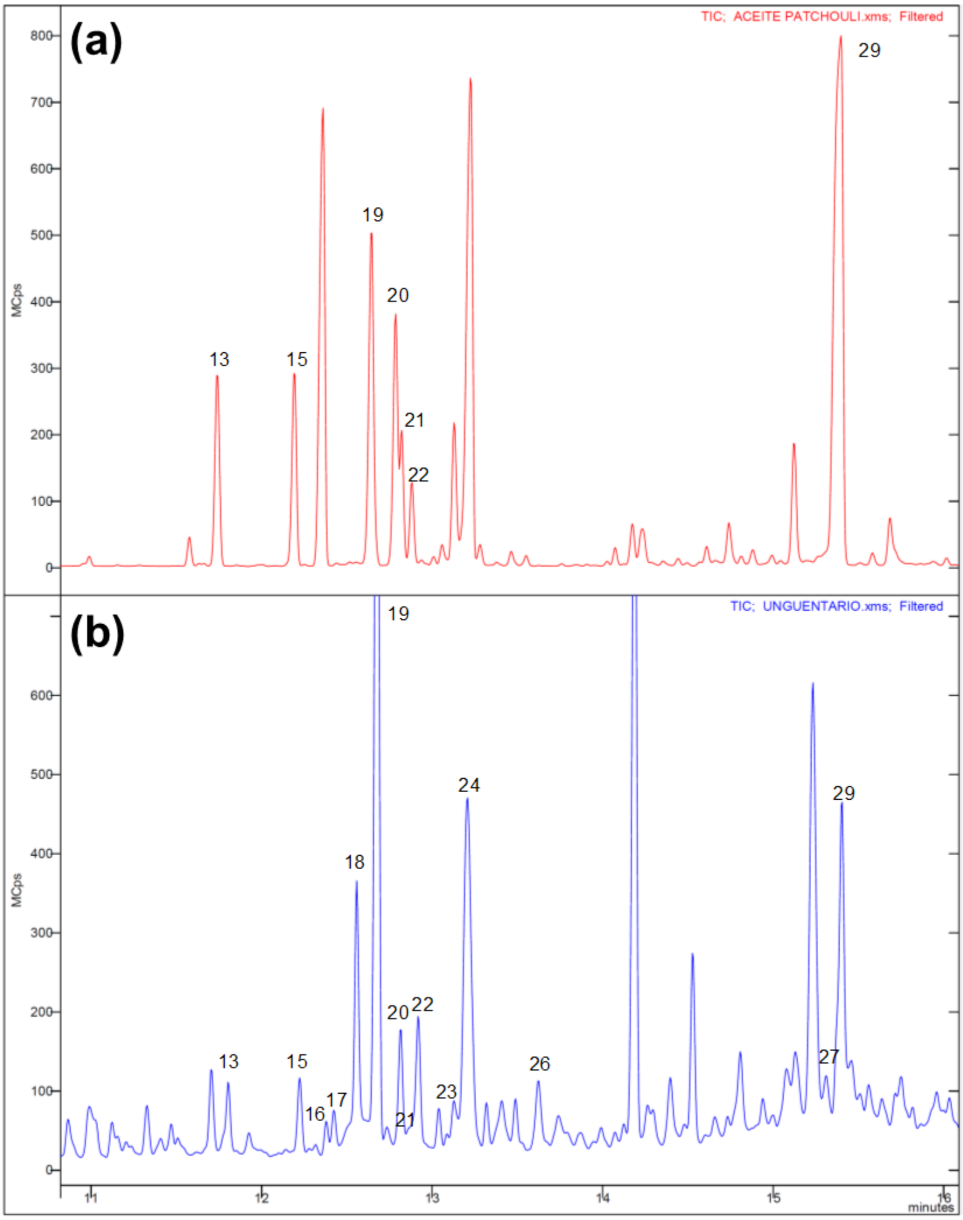

Figure 10. (**a**) Chromatogram for commercial patchouli oil and (**b**) Detail of the chromatogram for the *unguentarium* contents (some bands show coincidence with those of the commercial patchouli oil).

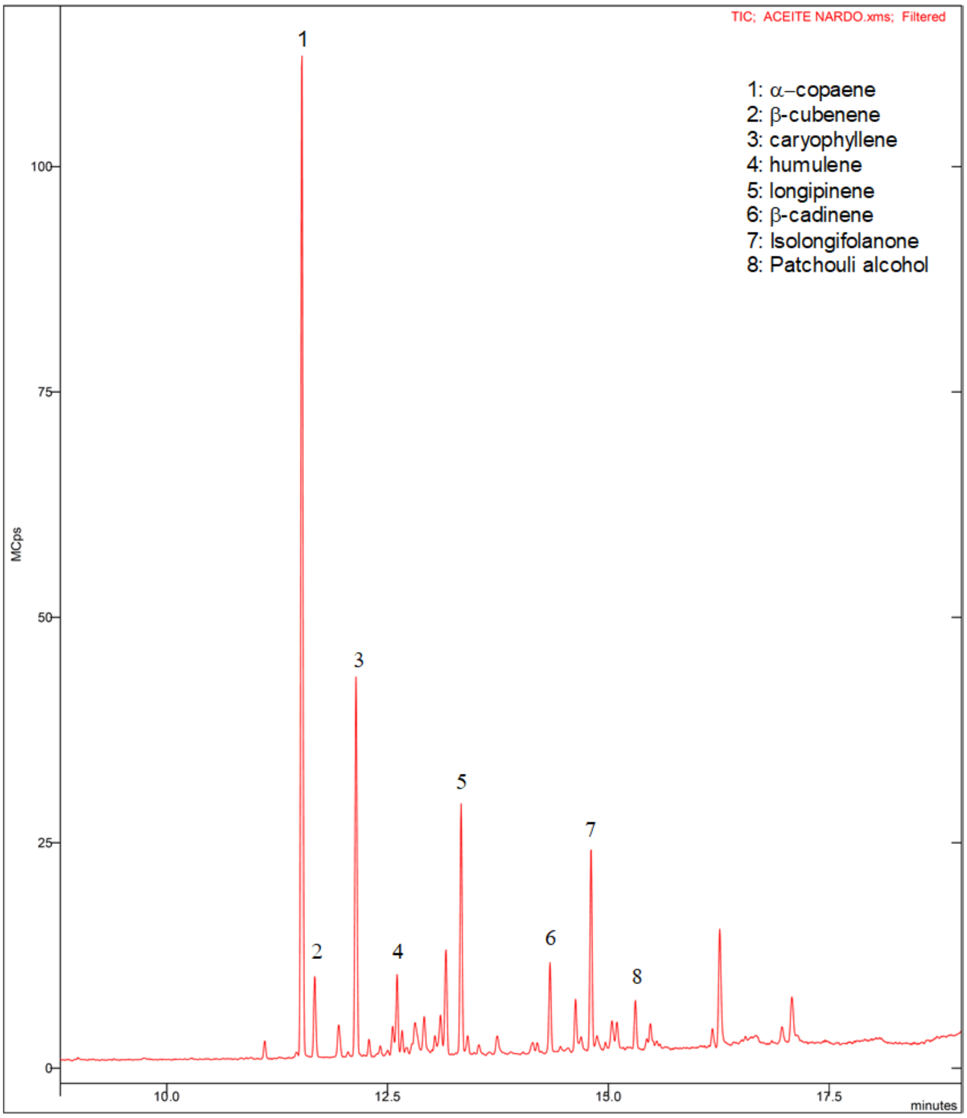

Figure 11. Chromatogram for commercial nard oil.

Finally, the fact that the chromatograms revealed the presence of compounds such as β-sitosterol, campesterol or squalene suggested that the *unguentarium* might have held vegetable fat. Because it contains a large number of C=C bonds, squalene is very easily degraded, so it is very rarely found in archaeological materials. Therefore, its presence is usually ascribed to contamination at a later stage [61]. In our case, however, the compound was found inside a closed, sealed vessel in the absence of oxygen and light, which, together with the relatively cool environment of the tomb, made squalene degradation highly unlikely. The samples used for analysis were obtained immediately after the *unguentarium* was opened and kept in tightly sealed vials. Therefore, squalene in the *unguentarium* was originally present in the fat held in it. The presence of the fat was confirmed by transesterifying with methanol a small portion of the dark-coloured solid found inside the *unguentarium*. This was followed by GC−MS, which allowed the methyl esters of oleic, palmitic, stearic, myristic and pentadodecanoic acid to be identified and quantified. In fact, the previous acids accounted for 53.7, 30.9, 12.8, 1.7 and 0.9%, respectively, of the analysed mass (see Figure 9). The presence of these methyl esters together with β-sitosterol, campesterol and squalene confirmed that the *unguentarium* contained some vegetable fat. There have been reports of fat residues in amphorae which once held olive oil from Roman times [62]. The residues contained most of the fatty acids of olive oil including some with an odd number of bonds, albeit at very low concentrations. Unsurprisingly thus, our sample contained pentadodecanoic acid, also known as "pentadecylic acid", as a result of acids with an odd number of C atoms being naturally present in fats.

Based on the foregoing and on classical works, the *unguentarium* once held a perfume which, based on the results, consisted of patchouli essential oil and some vegetable oil. In Roman times, perfumes were typically held in metal, ceramic or glass vessels [11] some of which included a reservoir [63,64]. However, those found in Pompeii [65] or the Rue Charcot necropolis [66], contained residual fat but no typical components of any perfume by the time they were examined.

As stated in the previous paragraph, the perfume held in the *unguentarium* was identified not only by chemical analysis but also with the aid of Pliny the Elder's writings [10]. According to this classical author, and as noted in the Introduction section, perfumes had two essential ingredients: a liquid oil and one or more solid or liquid scents. The perfumer was free to add a third, colouring element. Our analyses confirmed the presence of both essential ingredients. Thus, the presence of esters of various fatty acids, together with β-sitosterol, stigmasterol and squalene, confirm that a vegetable oil was used; also, that of sesquiterpenes suggests that the *unguentarium* contained an essential oil bearing the scent of the perfume. Identifying the vegetable oil was made rather difficult by its composition most probably changing with time. In fact, the chromatographic results only confirmed that some vegetable oil was used. However, the terpene and terpenoid composition as determined by GC–MS did allow us to identify with a high likelihood, though not unequivocally, the origin of the essential oil: patchouli. At present, this oil is extracted from dry leaves and young branches of *Pogostemon cabli*, a plant of the family *Lamiaceae* [67], and it is one of the most widely appreciated perfume ingredients. In addition to is characteristic odour (heavy, woody, earthy and camphor-like), patchouli oil has long fixing properties. Its main components include patchoulenol, α-cubenene, seychellene, β-caryophyllene, α-patchoulene, β-patchoulene and benzaldehyde [55], all of which were detected in our sample.

4. Conclusions

The compounds found in the *unguentarium*, which were adsorbed in bitumen (i.e., the components associated with patchouli and fat), support the assumption that the *unguentarium* once held a perfume. The perfume held in the unguentarium must have consisted of an essential oil containing a sesquiterpene fraction in addition to some fat containing the fatty acids identified here by transesterification. Based on classical works, perfumes contained essential oils made from various plant parts such as flowers (rose, jasmine), roots or even resins exudated by myrrh or incense. Use of these flowers, roots or resins to make the perfume can be discarded because the chemical composition of their essential oils differs markedly from those of patchouli and nard oil.

The novelties of this work are of special interest and constitute a great archaeological development. This is thus the first report on the use of bitumen as a sealing agent in an *unguentarium* with a dolomite stopper—another unique finding. Using bitumen to seal and waterproof the dolomite stopper was quite plausible since the *unguentarium* might have been made in a perfume workshop from another place in the Roman empire and subsequently purchased by the owners of the tomb. Therefore, ensuring that the *unguentarium* would hold its content intact for a long time required using a tightly sealed, waterproofed stopper To our knowledge, this is possibly the first time a perfume from Roman times has been identified. Based on the GC/MS analysis of the sample, the perfume in question was patchouli. The results are consistent with classical works according to which a perfume consisted of at least two different substances: an essential oil (or the plant leaves from which it was extracted) and a fatty material. The *unguentarium* contents' composition is consistent with that of an extract of patchouli mixed with vegetable fat as inferred from the presence of β-sitosterol, stigmasterol and squalene. Additionally, we succeeded in identifying the material of the *unguentarium* stopper, which was dolomite—a previously unreported choice for this type of object.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6060236/s1, Figure S1: Total ion chromatograms and extracted ion chromatograms of (a) m/z 247 and 262 ions (dimethylretenes); (b) m/z 233 and 248 ions (9-methylretene); (c) m/z 219 and 234 ions (retene); (d) m/z 217 ion (estearanes) and (e) m/z 191 ion (terpanes); Figure S2: Chromatograms and mass spectra for selected compounds present in the *unguentarium* contents and also in the commercial patchouli oil; Figure S3: Extracted ion chromatograms of m/z 204 for patchoulene (α- and β-) (a) commercial patchouli oil (b) *unguentarium* contents; (c) mass spectrum for b-patchoulene; Figure S4: Extracted ion chromatograms of *m*/*z* 222 for *unguentarium* contents (a) and nard oil (b).

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